Development of synthetic and natural mineral based adsorptive and filter media containing cyclodextrin moieties

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Abstract. Adsorptive filter media were developed based on UHMWPE (ultra high molecular weight polyethylene), perlite mineral and sol-gel synthesized silica gel as support and various cyclodextrin oligomers and polymers as active adsorbents. Adsorptive capacity was characterized by dye adsorption before and after Soxhlet extraction in water to check the hydrolytic stability of the structures obtained. Morphological and in some cases spectroscopic studies were made to understand the differences in behaviour. At the present stage the development of such structures hardly exceeds the trial and error approach, nevertheless some promising formulations were found.

1. Introduction

Environmental risks are complex: in addition to toxicity in general subtler dangers, such as reprotoxicity, hormone disrupting effect, mutagenicity, ecotoxicity are also posed by a series of compounds, such as drug residues and their metabolites, pesticide residues etc. which are inevitably present in our environment, among others in the potable water or in the wastewater [1]. Presently used physical (adsorptive), chemical (oxidative) and biological methods of wastewater treatment and potable water purification exhibit widely varying effectiveness in removing these potentially dangerous substances being present in very low concentration [2].

It is well known that cyclodextrins (CDs), the cyclic fermentation products of starch [3], capable of specific interactions with several organic molecules, together with other polysaccharide derivatives play an important role in wastewater treatment [4]. As cyclodextrins are partly soluble in water, in order to use them as filtering media, they should be immobilized by polymerization, crosslinking or by grafting onto organic or inorganic supports. One obvious way of polymerization and/or grafting is the use of ionizing radiation [5], or alternatively use of water soluble peroxides, which also generate radicals. Cyclodextrins can also be polymerized by several divalent reagents as diacid anhydrides, epichlorohydrin, acyl or alkyl-dihalogenides etc. [6]. Diisocyanates [7,8] cyclic polymetaphosphates [9,10], polysilicates [11] are also useful in the immobilization of soluble polysaccharides.

In 2008 a consortium including the mother institutes of the authors set out to develop complex risk evaluation methodology together with analytical methods to assess the relative risk attached to various potentially dangerous substances and to develop multiple-use active filtering media based on selective adsorption caused by cyclodextrin moieties [12]. The items to be developed included adsorptive
sampler and sensor for micro-pollutants, filter systems for potable water – for industrial and household use, secondary wastewater treatment technology and filter cartridge. This publication describes some results related to the development of filter media. In addition to the description of the synthetic methods results are presented on the hydrolytic stability of the attachments of the cyclodextrin moieties to the filter media by physical and/or chemical methods. The stability of the attachment is characterized by the changes of dye adsorbing capacity of the “decorated” medium before and after aqueous Soxhlet extraction.

2. Experimental

Due to size limitations the experimental procedures used in preparing the samples and the adsorptive evaluation method used to characterize the “active CD content” of the immobilized systems are given by references wherever such was available.

2.1. Materials

Two groups of materials will be distinguished: CD containing (“active”) substances and support materials.

The following substances (all commercial products of CycloLab Ltd., details available from the website) were used as “active” sites to be immobilized or attached to supports: β cyclodextrin (hereinafter BCD, a macrocycle with 7 glucopyranose rings, solubility at room temperature < 2 g/100 ml), which can be regarded as “monomer”, soluble β cyclodextrin polymer (sBCDP) and bead β cyclodextrin polymer (bBCDP). The latter two polymeric forms are both prepared by epichlorohydrin reaction, only the reaction conditions and the degree of polymerization are different. The sBCDP grade remains below the gel point, thus remains soluble in water (for molecular weight distribution see [13], solubility at room temperature >20 g/100 ml water), while bBCDP is a fine granular material (average particle size in dry state is in the range of 0.1-0.3 mm) that is not soluble, only swells in water. A further active agent tried was the so-called “conversion mixture” (hereinafter CM) obtained during the fermentation process [3] which is a mixture of α, β and γ cyclodextrins which also contains a certain amount of linear oligomers before the separation of the individual components. The reason for including this “impure” material is its cheapness (about 1/3 of BCD) which is offset by the lower BDC content (about 30% of the mixture). We have also tried polymerization induced by water soluble peroxides (K2S2O8) and by trisodium trimetaphosphate (Na3P3O9) but the reaction products remained water soluble, so we stopped further experiments with these materials.

The support materials included ultra high molecular weight polyethylene (UHMWPE, GUR 4022-6, product of Ticona), expanded filter perlite (a volcanic silicate, product code PD, ANZO Ltd. Hungary) and polysilicates made in situ from tetraethyl orthosilicate (Sigma Aldrich) or from an ethyl silicate prepolymer (TES 40 WN, product of Wacker). Other materials used in the synthesis (ethanol, citric acid, glutaric aldehyde, disodium hydrogenphosphat dihydrate, dichloroethane, sulfuric acid etc.) were all commercially available fine chemicals or solvents obtained from Aldrich, Fluka, or Reanal. Triallyl isocyanurate (TAIC) used as crosslinking co-agent in the irradiation crosslinking experiments was the product of Evonik. Polyvinyl alcohol (Mowiol 4-88 with a molecular weight of 31000, Aldrich) was used in one of the immobilization experiments.

2.2. Sample preparation

First we tried to immobilize the active agents in UHMWPE matrix. UHMWPE decomposes before melting, thus it can be processed by a combination of compression molding and sintering. In this case we tried BCD and sBCDP as soluble active agents and bBCDP as insoluble active agent. In the case of the soluble active agents we used TAIC crosslinking co-agent and gamma irradiation (200 kGy dose, the irradiation was done at room temperature in air at the facility of the Centre for Energy Research of the Hungarian Academy of Science), while in the case of bBCDP neither co-agent nor radiation crosslinking was used. 6 g UHMWPE powder was thoroughly mixed by hand with 2 g cyclodextrin (BCD, sBCDP or bBCDP) and the powder mixture was poured into the preheated (50 °C, 15 min)
mold (60 mm diameter disk, 2 mm thickness), which was pre-compressed at 190 °C for 15 min using 1 kg weight followed by compression using 4.7 kg weight at 190 °C. The piece was cooled rapidly in the mold using water cooling. In the case of the BCD and sBCDP samples 5 ml 5 w/w% TAIC solutions in ethanol were admixed to the cyclodextrin/UHMWPE powder mixture before the compression molding experiment and air dried at room temperature for 1 hour, followed by remixing the dried powder mixture. The combination of TAIC and ionizing radiation was used in the hope that the formed free radicals may initiate the following reactions: a.) crosslinking of UHMWPE, b.) polymerization/ crosslinking of the cyclodextrin component, c.) grafting of cyclodextrin to UHMWPE. All these effects are expected to stabilize the cyclodextrin component in the matrix.

The next group of samples was based on perlite support. We tried to bind the cyclodextrin component to the perlite surface by two methods: first by using citric acid (CA) and disodium hydrogenephosphate (Na$_2$HPO$_4$) treatment, second by using a combination of polyvinylalcohol (PVA) and glutaric aldehyde (GA). The perlite was first sieved with a sieve of about 1 mm distance between the wires to remove the fine fraction which tended to settle fast in aqueous suspension. In the case of the CA fixation experiment we tried only two water-soluble cyclodextins: sBCDP and the conversion mixture (CM). First the sieved perlite was treated by NaOH to activate the Si-OH groups on its surface (10 g perlite sample stirred in 3 wt% NaOH solution for 80 min at 40 °C and washed to neutral by distilled water), then it was dried at 100 °C for 10 minutes. 2.5 g sBCDP or 7.5 g CM (this latter was used in triple amount to compensate for the lower BCD content of CM) was dissolved in 250 ml distilled water containing 2.75 g citric acid monohydrate and 1.3 g Na$_2$HPO$_4$.2H$_2$O and the previously treated perlite was added to it and stirred at 40 °C for 30 minutes. Afterwards the system was fixed at 180 °C for 30 minutes to promote the reactions between the surface bound citric acid and the carbohydrate component. Finally the samples were washed 3 times for 30 minutes with 40 °C distilled water. The NaOH activated perlite was used in the other fixation experiment using the glutaraldehyde induced crosslinking of PVA (and possibly the BCD monomer and polymer grades) too. Here we tried to use both soluble (BCD, sBCDP, CM) and insoluble (bBCDP) cyclodextrin grades. 1.5 g PVA was dissolved in 20 ml water at 70 °C, 0.5 g cyclodextrin and 2 ml 2% H$_2$SO$_4$ were added and the mixture was stirred at 50 °C for 60 min. Separately we mixed 1 g (pretreated) perlite, 10 g dichloroethane, 1 ml 2 w/w% H$_2$SO$_4$ and stirred them for 15 min at 50 °C. Finally this and the previous solution containing the cyclodextrin component were mixed together and 2 ml glutaric aldehyde was added and the mixture was allowed to gel for 1 hour. The gel formed was dried in a Petri dish in a vacuum chamber at 80 °C to constant weight.

The last group of immobilized samples was based on the co-precipitation (possibly reaction) of ethyl silicate prepolymers (TES 40) and various soluble (sBCDP, and CM) and insoluble (bDCDP) cyclodextrin polymers. 12 g cyclodextrin polymer was dissolved in 22.5 g absolute ethanol, 2.8 g glacial acetic acid and 45 g TES 40 were added. The mixture was stirred at 60 °C for 120 min, then 45 g water was added and the stirring was continued for another 12 min at 70 °C. The sample gelled. The gel was first washed 3 times with distilled water then dried: 20 hours in vacuo at 70 °C and 4 hour at 80 °C. The dried gels were crushed.

In each case a blank sample was also prepared, which contained the same ingredients and were exposed to the same treatment, but without any cyclodextrin component. These blank samples were utilized in the further evaluation for comparison purposes.

The hydrolytic stability of samples was checked by Soxhlet extraction with water as solvent. In order to reduce weight changes due to the fragmentation of the samples we have put the samples into small sacks cut from nylon pantyhose. (Of course the sacks were previously exposed to the same extraction treatment to avoid weight changes due to extraction from the nylon fibers). The extraction losses were measured after thorough drying in vacuo after 6, 12 and 24 hours extraction. (It was observed that wherever a large weight change was observed, it was present already after the first 6 hours, therefore hereinafter we quote only the 24 hours extraction loss and will not deal with the extraction kinetics).
Where the extraction loss data were significantly lower than those measured for the corresponding blanks, we tried to estimate the active (available) β cyclodextrin ring content of the immobilized samples using an empirical colorimetric method [15]. The change in the absorbance of dye molecules (phenolphthalein and methyl orange) after contacting a cyclodextrin-containing solid or solution can be correlated with the cyclodextrin content using an empirical curve. Of course, the change observed in the blanks should be subtracted from the observed value. 5 ml phenolphthalein (3x10^{-4} M) or methyl orange (2.4x10^{-5} M) solution was pipetted into the test tube, in which the solid samples were added, too. The discoloration of the solutions was determined by spectrometry at 552 nm and 506 nm, respectively. SEM micrographs were taken of the fracture surfaces after gold sputtering using a JEOL JSM-5600LV type SEM + EDS equipment. In two cases transmission FTIR measurements were made on ATI MATTSON Research Series 1 FTIR instrument using powdered samples in KBr tablets.

3. Results and discussion

The results of the tests are very briefly summarized in Table 1.

Table 1. Weight losses measured after 24 hours Soxhlet extraction, estimated available BCD-content measured by methyl orange adsorption (after extraction), SEM and IR measurements

| Name                  | 24 h extr. loss% | %CD (MO sorption) | SEM      | IR |
|-----------------------|------------------|-------------------|----------|----|
| BDC-TAIC-UHMWPE       | -25%             |                   |          |    |
| CM-TAIC-UHMWPE        | -21%             |                   |          |    |
| bBCDP-UHMWPE          | -4%              | 7.7               |          |    |
| UHMWPE blank          | +0.6%            | 0.0               |          |    |
| sBCDP-CA-Perlite      | -12%             | 1.6               |          |    |
| CM-CA-Perlite         | -17%             |                   |          |    |
| CA-Perlite blank      | -9%              | 2.0               |          |    |
| sBCDP-PVA-GA-Perlite  | -12%             | 6.0               | 0 h, 24 h|    |
| bBCDP-PVA-GA-Perlite  | -9%              | 3.9               |          |    |
| CM-PVA-GA-Perlite     | -21%             |                   |          |    |
| BCD-PVA-GA-Perlite    | -17%             |                   | 0 h, 24 h|    |
| PVA-GA-Perlite blank  | -9%              | 2.0               | 24 h     |    |
| CM-Polysilicate (disint.) | -61%, -49%   |                   |          |    |
| sBCDP-Polysilicate    | -9%, -4%         | 0.9               | 0 h, 24 h| 0 h|
| bBCDP-Polysilicate    | -24%             | 13.5              | 0 h      |    |
| Polysilicate blank    | -22%             | 1.8               | 24 h     | 0 h|

A comparison of the weight losses observed in the blank samples and the CD-containing ones allows us to assess the hydrolytic stability. If the weight loss is much higher than that of the blank, there is good reason to believe that the cyclodextrin component is (also) extracted. It cannot be expressed by %CD loss as the preparation steps (e.g. washing) may also involve CD loss, so only the absolute numbers can be compared. In the case of the UHMWPE based systems it is clear that only the bBCDP containing samples retained the CD moieties, the grafting of the soluble cyclodextrins did not prove to be effective. The CD content of the bBCDP system proved to be acceptable (7.7 w/w% in the UHMWPE based system). In the case of the perlite based systems the citric acid immobilization proved to be relatively ineffective, the weight loss exceeded that of the blank, the sBCDP containing system was somewhat better, but even here the detected apparent CD content did not exceed that observed in the blank. The glutaraldehyde/PVA immobilization system was effective, at least with the sBCDP and bBCDP cyclodextrin components but ineffective with CM and BCD. The polysilicate based systems behaved in an unexpected manner. CM-polysilicate exhibited much larger, sBCDP-polysilicate much smaller weight loss than the blank (both tests were repeated to see the reproducibility). The CM-polysilicate sample disintegrated so much during the extraction experiment.
that much of the powder formed could not be retained by the nylon sack used, therefore the weight loss measurement is useless. The low weight loss of the sBCDP-polysilicate sample is puzzling, the IR study did not reveal any particular difference in terms of new bands from the other CD containing samples. One may only guess the occurrence of interpenetrating network formation. Interestingly, however the improved hydrolytic resistance was not accompanied by high CD retention according to the colorimetric method (or the CD ring became unavailable to the dye molecules). The bBCDP-silica combination exhibited a hydrolytic resistance similar to the blank, and a fair amount of available CD remained after extraction.

Figs. 1-4 show SEM electron micrographs of some samples.

![Fig. 1. sBCDP-PVA-GA-Perlite 35x magnification](image1)

![Fig. 2. sBCDP-PVA-GA-Perlite 250x magnification](image2)

![Fig. 3. sBCDP-PVA-GA-Perlite 1000x magnification](image3)

![Fig. 4. sBCDP-polysilicate 35x magnification](image4)

These figures show that the distribution of the immobilized phase is uneven on the inorganic surface, and the shapes of the perlite and polysilicate particles are quite different. The lamellar structures observed in Fig. 3 are due to the PVA component, as they can be seen even after the extraction of the respective CD component.

4. **Conclusion**

A wide range of cyclodextrins (monomeric, soluble and crosslinked polymeric and conversion mixture) were tried to be immobilized on various supports (UHMWPE, perlite and in situ formed silica gel). In general the crosslinked bBCDP component could be best immobilized on the support, but there were successful combinations with sBCDP too. Glutaric aldehyde/ PVA/perlite and the polysilicate formation immobilization processes seemed to be more effective than radical grafting onto UHMWPE or citric acid immobilization on perlite. In general it can be said that the development of cyclodextrin based filter media is still based on experience, trial and error, with several surprises regarding immobilization efficiency, hydrolytic and mechanical stability – nevertheless promising laboratory results have been achieved.
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