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ORIGINAL ARTICLE

Sorption onto crosslinked cyclodextrin polymers for industrial pollutants removal: an interesting environmental approach

B. Sancey · G. Trunfio · J. Charles · P.-M. Badot · G. Crini

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Abstract An insoluble polymeric network containing cyclodextrins (CDs) and amino, hydroxyl and carboxylic groups, was used for the detoxification of multicontaminated wastewaters. The comparison of its sorption capacity with that of a similarly prepared starch material showed superior efficiency towards organic compounds, though maintaining the same efficiency towards inorganic species. The incorporation of cyclodextrin cavity into a solid network provides an easy separation of pollutants from water, after their uptake onto the sorbent surface. In fact, the presence of CDs ensures the formation of inclusion complexes enhancing the sorption properties. The proposed sorbent also shows good sorption capacity for cations and other inorganic compounds, which is mandatory for the treatment of multicontaminated wastewaters.

Keywords Cyclodextrin · Insoluble network · Sorption · Wastewater treatment · Cations · Anions · Organic compounds · Inclusion complexes

Introduction

The discharge of toxic heavy metals into the environment is a serious environmental problem affecting water and soil quality, hence presenting a direct danger to human health [1]. Among them, mainly Cr(VI), Cd(II), Cu(II), Zn(II) and Ni(II), often present in industrial wastewaters, cause serious dysfunctions to living beings as well as many anions (i.e., F^-, CN^-) [2–7]. Nowadays, the surface-treatment enterprises are considered to be one of the largest water consumers and polluters. In fact, their process waters contain both organic and metallic pollutants, coming from rinsing and washing baths (e.g., Cu, Zn, Ni, Sn, Ag, Cr, CN^-, mineral oils, organic acids or aromatics), which are quite difficult to remove. Unfortunately, the release of organic and inorganic pollutants is not uniform (neither in quality nor in quantity), but always have a unique result: toxicity for aquatic ecosystems creating worries for the population [8–10]. The literature reports a multitude of processes for the decontamination of polluted waters from surface-treatment industries (e.g., precipitation, adsorption, membrane filtration, etc.), but many of them cannot be used at on industrial scale because of technological and economic reasons [11–15]. With its inexpensive and easily controlled procedures, chemical precipitation is still the most widely used technique among wastewater treatment plants, even if its peculiar limitations, such as stable complexes formation and relatively poor solubility constants of some hydroxides, lead to the release of waters containing amounts of pollutants sometimes overwhelming the regulation limits [16–19].

The removal of the remaining contaminants, both organic and metallic, requires further treatments, and sorption on various materials represents a feasible option [1, 9, 11, 15, 20]. With respect to the particular release of a surface treatment, the composition is highly complex and its detoxification requires proper actions for each category of substances, at least. On this context, derived organic materials represent an intriguing class of substances to be employed in the finishing treatment by sorption [1]. In fact, they can be derived from agricultural byproducts needing proper disposal, so being quite inexpensive, and can be modeled to insert functional groups specifically designed for

B. Sancey · G. Trunfio · J. Charles · P.-M. Badot ·
G. Crini (✉)
CNRS-Université de Franche-Comté, UMR 6249
Chrono-Environnement usc INRA, Place Leclerc,
25030 Besançon Cedex, France
e-mail: gregorio.crini@univ-fcomte.fr

particular uses. Cyclodextrins (CDs), with their ring-shape formed of 6–12 glucose monomers, represent a typical class of such materials, with an inner hydrophobic surface able to accept organic molecules and an outer hydrophilic sphere, given the presence of hydroxyl, making them be water soluble. Then, CDs and their derivatives provide a very broad interesting platform for various applications [21–24], such as controlled drug release [25], removal of ionic organic dyes from wastewater [26–28], and removal of heavy metals from wastewater [29]. Moreover, they are well-known to complex a huge number of guest molecules by hydrophobic and van der Waals interactions [30].

Thereafter, this work is intended to present a practical application of CD-based cross-linked polymer for the treatment of real wastewater streams and to provide a comparison with a similarly prepared starch-based material. This work, then, provides an interesting proof of another possible application of CDs as active sites of a complex modified polymeric network for the wastewater treatment, thanks to their cavities with inner hydrophobicity able to include organic compounds.

Materials and methods

Sorbent materials

The starch-based cross-linked polymer (SM) has been prepared in two steps, reticulating a starch-enriched flour, a gift from Sauvin SA (Patornay, France) using 1,4-butanediol diglycidylether as cross-linking agent in the presence of NH_4OH and 2,3-epoxy-propyltrimethylammonium chloride, and then carboxymethylating it by means of a chloroacetic acid solution. The cross-linked polymer containing both hydroxyl, quaternary ammonium and carboxylic groups was dried overnight at 100 °C, and then crushed and sieved into different particles sizes. The synthetic procedure and characterization have already been described in detail elsewhere [31, 32] and current studies were carried out, following previous evidences, using the size fraction of 150–250 μm, with a surface area value (SA_{BET}), evaluated with the BET method, of 70 $m^2\ g^{-1}$. The CD-based material employed (CDM) has been prepared following the same procedure adopted for SM sample. The principal characteristics of the two sorbents are summarized on Table 1. In particular, DS_{COOH} and N represent the degree of substitution (in terms of carboxylic groups) and the amount of nitrogen present in the molecule, respectively.

Table 1 Sorbent materials and their principal physicochemical characteristics

Starting material	Code	Particle size (μm)	Surface area ($m^2\ g^{-1}$)	DS_{COOH}	N (%)
Starch	SM	150–250	70	0.20	4
Cyclodextrin	CDM	150–250	2.4	0.22	4

Industrial effluents

Experiments were carried out on discharged waters from Silac Industry, located in Champlitte (Haute-Saône, France), and the chemical parameters were studied in consideration of the regulation limits allowed by the public authorities. In particular, the standards of discharge are fixed to 150 $mg_{O_2}\ L^{-1}$ for the chemical oxygen demand (COD), 5 mg L^{-1} for aluminum and 15 mg L^{-1} for fluoride.

Batch experiments

The experiments were conducted on industrial treated wastewaters using the batch method without changing the effluent pH in order to simulate the industrial process. 100 mg of sorbent were mixed with 100 mL of treated industrial discharge in a tightly closed flask, and the solution was stirred on a thermostatic mechanical shaker operating at a constant agitation speed (300 rpm), for 1 h at room temperature (22 ± 1 °C). The solution was then filtered, centrifuged, and analysed. The sorption performance, representing the ratio between the amount of sorbed pollutant and the starting amount of pollutant, is expressed in percentage uptake.

Physicochemical properties

The pH of each sample was measured using a portable pH meter (3110 model, WTW, Alès, France). COD was determined by the dichromate COD method based on the use of colorimetric measurement for high-range COD (0–1500 mg L^{-1} range, model COD Vaxio, Aqualytic PCCompact, Dortmund, Germany). Al was measured in triplicate by a furnace atomic absorption spectrometer (Zeeman Correction, Varian models 240Z, Les Ulis, France). On the other hand, fluoride and boron concentrations were measured by a portable photometer (Spectroflex 6100 model, WTW, Alès, France) using rapid test kits (cuvette test and/or reagents test) and results were directly expressed in mg L^{-1}.

Germination test

Germination rates for both the discharged and treated samples were evaluated using the French normalized method AFNOR NF X 31-201. The germination rate of lettuce (*Lactuca sativa*) seeds (from Sélection Laitue, Aramon, Gard, France), expressed as the number of germinated seeds with respect to the planted ones (average of three replications), was evaluated for each solution after 7 days.

Results and discussion

Wastewaters used for our sorption tests were collected at the treatment plant outlet of a small enterprise concerned with the final treatment of large aluminum slabs, mainly for architectural purposes, by cleaning, passivating and painting their surfaces (Silac Industry, Champlitte, France).

Table 2 reports the variations of pH, organic load (COD), and the levels of the inorganic species present in the considered wastewater, such as aluminum, fluoride and boron, during our 10-day study period. It is clear that the physico-chemical treatment process used at Silac for their wastewaters detoxification ensures an efficient purification, lowering the pollutant load at satisfactory levels for the current regulation limits. In fact, the Al content is reduced to under or near the legally required limit, while COD still remains relatively high, in the range of 80–200 mg L^{-1}. Indeed, on occasions, Al and COD concentrations were higher than the tolerated limit, due to the variability of the industrial processes. As expected, boron, with its peculiar metal/non-metal characteristics, is really difficult to separate by means of simple precipitation methods but, at the moment, boron is not a source of legislative concern, given the absence of any regulation limits.

For fluoride, the treatment was seen to be less efficient, with final concentrations in the range 8–50 mg L^{-1}, often higher than the accepted limits. However, it is known that high concentrations of fluoride in industrial effluents are difficult to be removed and usually are brought down just to ~25–30 mg L^{-1} [32, 33]. On this account, Saha [33] interestingly reported that, by conventional chemical precipitation, the fluoride concentration in an industrial effluent cannot be reduced, working at the very optimal conditions, to less than 10–15 mg L^{-1}, without the help of dilution with fresh water. In fact, it is precipitated as CaF_2 by the addition of $Ca(OH)_2$, but the solubility product of the salt is relatively low (Ks = 3.5×10^{-11}) allowing the presence in the solution of at least 8 mg L^{-1} of F^- [34].

It is evident from these results the necessity to further treat the discharged water easily to respect the regulation limits and, eventually, to be ready for the stricter newer ones. On this context, the ten considered samples were subjected to sorption using starch and CD-based materials, designed for this purpose. The two materials differ by the presence of cyclodextrins cavities, which could entrap the organic matter, forming stable inclusion complexes. Results are reported in Figs. 1, 2, 3 and 4 in terms of

Table 2 pH and pollutant content of ten representative samples collected at Silac Industry

Sample	pH	Al (mg L^{-1})	F (mg L^{-1})	B (mg L^{-1})	COD (mg_{O_2} L^{-1})
1	7.7	4.5	36	24.2	99
2	7.6	2.1	33	20.1	105
3	7.6	1.8	65	4.0	154
4	7.5	3.0	21	22.0	112
5	8.0	3.4	49	19.8	123
6	7.3	5.9	54	15.6	169
7	7.7	7.9	52	13.7	205
8	7.4	2.1	27	31.2	177
9	7.3	1.4	42	25.9	189
10	7.2	2.8	25	22.1	154
Legal limit	6.5–9.0	5.0	15		150

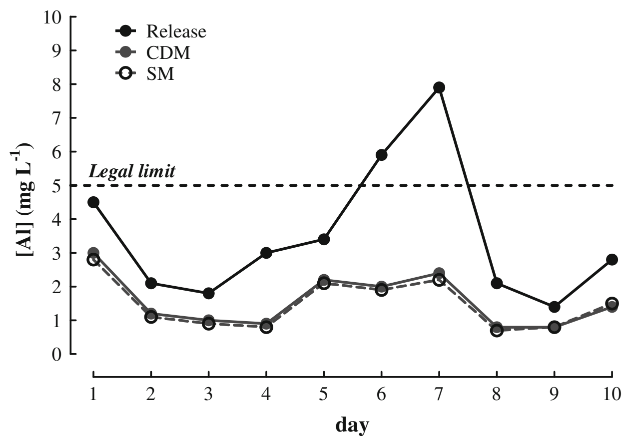

Fig. 1 Comparison of Al removal efficiency between CDM (*gray circle*) and SM (*white circle*) sorbents on wastewater releases coming from a surface treatment industry. *Full black symbols* and *lines* represent the released sample

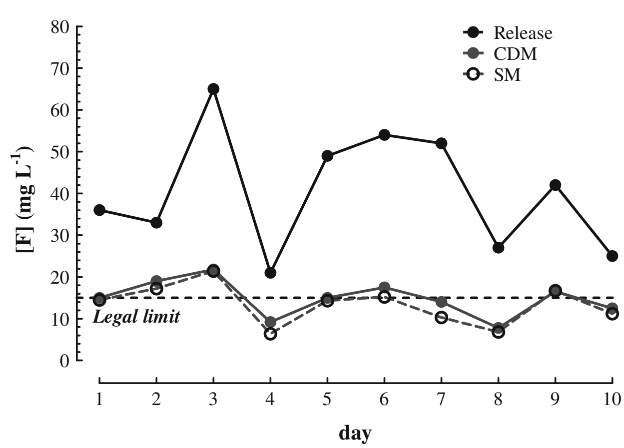

Fig. 2 Comparison of F removal efficiency between CDM (*gray circle*) and SM (*white circle*) sorbents on wastewater releases coming from a surface treatment industry. *Full black symbols* and *lines* represent the released sample

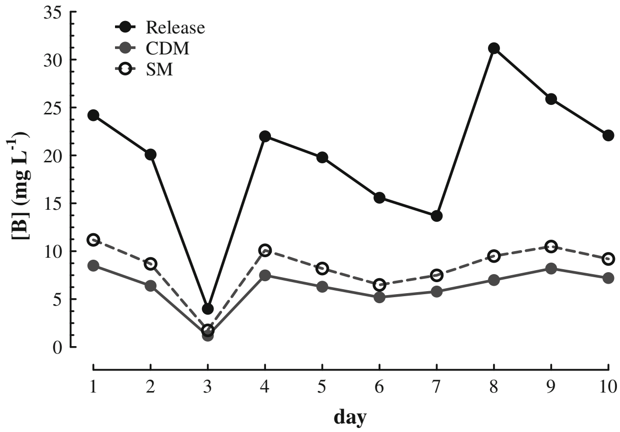

Fig. 3 Comparison of B removal efficiency between CDM (*gray circle*) and SM (*white circle*) sorbents on wastewater releases coming from a surface treatment industry. *Full black symbols* and *lines* represent the released sample

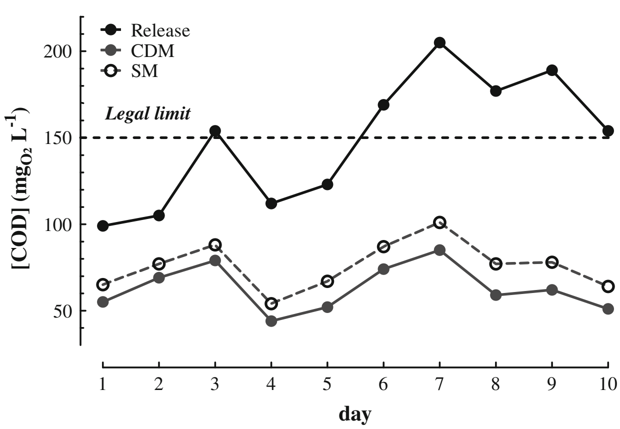

Fig. 4 Comparison of COD removal efficiency between CDM (*gray circle*) and SM (*white circle*) sorbents on wastewater releases coming from a surface treatment industry. *Full black symbols* and *lines* represent the released sample

pollutant concentration before and after sorption treatment on both SM and CDM for each studied sample. With regard to Al, both the sorbents showed very similar features (Fig. 1), lowering in the same order its content at concentrations constantly under 3 mg L^{-1}, well under the actual limit of 5 mg L^{-1}. Similar trends are reported in Fig. 2 for fluoride. In this case, the very high level present in the released water was lowered just to the regulation limit, which is, however, a very important goal, given the recalcitrance of this element to separation and the constant high concentrations in the so-released waters, overwhelming the permitted levels.

Even if boron does not create particular worries, due to the absence of regulation limitations, we also surveyed its concentration and the sorption efficiency of the two considered materials. In fact, boron can form stable soluble complexes with both aluminum and fluoride [35] and, as a consequence, reduce their removal. Figure 3 shows that both SM and CDM sorbents well abate it, with the first a bit less efficient than the second.

Figure 4 presents the strong COD abatement obtained by the sorbents, with the same rate for both the materials. In this case, as expected, CDM was more efficient than SM, sorbing higher amount of organic matter, though presenting a sensible lower surface interaction. In fact, the COD abatement for CDM was in the range 35–67%, while for SM was in the range 27–58%. This means the CDM material sorb an average of 8–16 mg_{O_2} L^{-1} of COD more than SM, which is an significant result, given its poor SA_{BET}. This evidence would be in contrast with basic sorption principles suggesting high surface area for suitable sorbent materials to provide a greater number of active sites available for sorbate molecules. Cyclodextrins, with their hydrophobic cavities, can form inclusion complexes with many organic substances [21, 23, 36], and then removing, in our case, large amount of COD. The contemporaneous presence of carboxylic, hydroxyl and amino groups, coupled with the hydrophobic cavities ensures, then, CDM a particular "multifunction" feature, ideal for sorbent materials to be used in the treatment of multicontaminated waters, such is the case of surface-treatment industry releases. Crucial for our investigation is the possible employment of CDs for the concentration of organic matter. Cyclodextrins are, in fact, water soluble and they are generally used as solubilizers for hydrophobic compounds [24], while, in our case, they are used to entrap them. Then, their encapsulation in an insoluble network let them be separated easily from water once the inclusion complex is formed, so playing the role of water purifier.

The scarce surface area of the CDM material is, of course, the principal topic to be improved in our further studies, together with the optimal sorbent loading and contact time. Moreover, since it is evident the role of pH for ensuring the right surface charge to sorbent materials, this parameter is already under investigation to optimize the proper conditions for the higher sorption capacities for all the investigated pollutants.

Finally, the efficiency of the sorption treatment on the considered samples was proved by simple germination tests carried out on *L. sativa* seeds. In fact, contaminants present in the water can inhibit the germination of planted seeds, which can be taken as simple laboratory test for the evaluation of the water toxicity. All the ten samples showed a sensible increase of this parameter showing an average increase of 15%. As can be seen from Fig. 5, both SM and CDM exhibit a very good germination rate with the second more efficient in two cases and the first in one. In both cases the sorption treatment well decreases the water toxicity with respect to germination even if it is slightly affected in

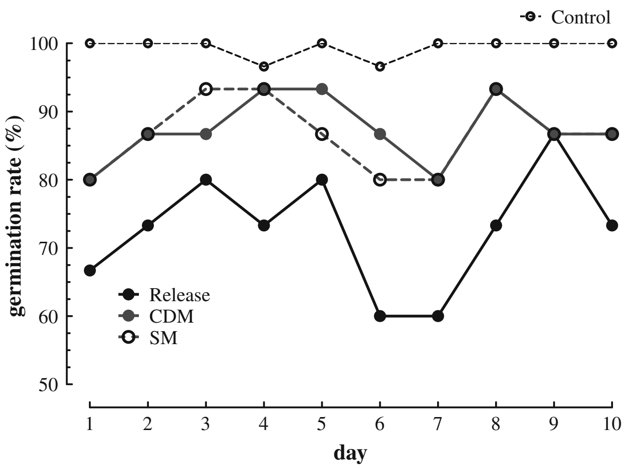

Fig. 5 Germination rate of lettuce seeds soaked by the so-released water (*black circle*), after sorption onto CDM (*gray circle*) and SM (*white circle*) sorbents

comparison with the control, carried out using distilled water to humidify the seeds. Evidently, other parameters must be taken into account in the future for a more detailed evaluation of the gravity of pollution for well treated waters.

The encouraging results emerging from this study make us pursue our research by synthesizing CD-based materials with higher specific surface area, and shedding light on the influence of the different functional groups on the pollutant removing efficiency.

Conclusions

Wastewaters coming from surface-treatment industries present a variegated contamination, due to the contemporaneous presence of organic and inorganic matters. This requires different sorbent materials for the final purification treatment. A novel network, presenting amino, hydroxyl and carboxylic groups coupled with the incorporation of cyclodextrins ensures the simultaneous sorption of different pollutants onto the surface material. The comparison with a similarly prepared starch-based material demonstrates the higher capacity for organic compounds sorption, due to the formation of inclusion complexes between cyclodextrins and pollutants. These findings prove that the sorption treatment using natural derived materials can be seriously considered as finishing treatment in wastewater treatment plants. The so treated waters present, in fact, better germination rates than the simply released ones.

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