

Preparation of water insoluble carboxymethylated bacterial cellulose with maximum lead retention capacity

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Abstract

Chemical modification of bacterial cellulose (BC) through carboxymethylation was carried out to prepare a low-cost highly stable lead adsorbent material (CMBC). Aiming to maximize its adsorption capacity, the effect of the carboxymethylation extent conferred to BC on the lead retention ability of the insoluble CMBC products obtained was studied. Results evidenced a strong linear correlation between the lead retention capacity of CMBC samples and their degree of substitution, highlighting a key role on the biobased adsorbents performance of the amount of negatively charged carboxylate groups available for an ion-exchange-governed lead adsorption process. Proper tuning of the carboxymethylation extent conferred to BC thus allowed maximizing its lead adsorption capacity, reaching values (*i.e.* 127.2 mg g⁻¹) that doubled those previously reported.

Keywords Bacterial cellulose · Carboxymethylation · Chemical modification extent · Insoluble products · Lead retention capacity

Introduction

Human health risks associated with the consumption of water contaminated with heavy metals are well known [1]. For instance, lead (Pb) is a toxic metal that affects multiple body systems, being children the most vulnerable ones to its neurotoxic effects [2, 3]. From this perspective, and considering that lead can be found in aqueous systems due to the lixiviation of mining areas and industrial effluents, the WHO has limited the lead concentration for drinking

water in 0.01 mg L⁻¹ [1]. To fulfill this requirement, methods to remove lead from contaminated water are needed, *e.g.* coagulation-flocculation, reverse osmosis, ion exchange, precipitation, membrane filtration, solvent extraction, and adsorption. Among them, and based on its low cost, simplicity, flexibility and versatility, adsorption is recognized as a particularly attractive lead removal method [4–6].

Heavy metals adsorbents can be derived from both synthetic and natural polymers, being the latter especially attractive due to their abundance and renewable origin, as it is the case of alginates, starch, chitosan and cellulose [7–29]. Among cellulose sources, bacterial cellulose (BC) has the advantage of being produced with high purity, thus avoiding the use of the chemical reagents needed to isolate cellulose from plant sources [30, 31]. Chemical modification of cellulose hydroxyl groups may result in numerous derivatives with different properties and a variety of applications, but for the purpose of heavy metal adsorption cellulose water insolubility needs to be guaranteed.

In this context, we recently demonstrated the suitability of water insoluble carboxymethylated bacterial cellulose (CMBC) with a DS of 0.17 (DS = average number of substituted hydroxyl groups per anhydroglucose unit (AGU)) for effectively removing lead from water [7]. Results also showed that: i) the adsorption of lead onto CMBC was fast, reaching the equilibrium in less than one hour, ii) it followed

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the pseudo-second-order kinetic model and the Langmuir isotherm model, iii) the maximum lead retention capacity at room temperature was close to 60 mg g^{-1} , and iv) adsorption was governed by ionic interactions between lead cations and the carboxylate anions of CMBC. Besides, it was demonstrated that CMBC could be efficiently regenerated and reused for more than 50 cycles [7], highlighting its potential as a low-cost biobased lead adsorbent, and triggering further studies devoted to enhancing its retention capacity.

In this framework, the aim of this contribution was to maximize the lead retention ability of CMBC. With this purpose, and bearing in mind that the water insolubility of carboxymethylated cellulose strongly depends on its DS (with DS values higher than 0.40 resulting in water soluble derivatives [32–34]); CMBC samples with varying DS values within the 0.11–0.40 interval were prepared, tested for their insolubility, and assayed for their maximum lead adsorption capacity under previously established conditions.

Materials and methods

Materials

Sodium monochloroacetate (NaMCA, Sigma-Aldrich), isopropanol, sodium hydroxide, methanol (Cicarelli, San Lorenzo, Argentina) and glacial acetic acid (Merck) were used as received in the carboxymethylation of BC. All reagents used were of analytical grade.

Preparation of BC culture medium

BC culture medium was prepared as previously reported using anhydrous dextrose, disodium phosphate.12 H₂O (Biopack, Zarate, Argentina), yeast extract, meat peptone (Britania, Laboratorios Britania S.A., CABA, Argentina), citric acid (Merck, Carlos Spegazzini, Argentina), and glycerol (Sintorgan, Villa Martelli, Argentina) [30].

Preparation of lead solutions

Aqueous solutions of Pb (II) were prepared using ultrapure water (18M Ω quality) and solid Pb(NO₃)₂ p.a. (Merck). Lead concentration was measured by use of an air-acetylene flame type atomic absorption spectrometer (Thermo Scientific, Model iCE 3000). Pb (II) standard solutions were prepared from 1000 mg L⁻¹ Pb standard solution (Merck).

Production of BC

BC production was carried out using a strain from *Gluconacetobacter xylinus* NRRL B-42. Inocula were cultured in Erlenmeyer flasks containing Hestrin and Schramm medium

(volume "medium/flask" = 1/5) [35] and statically incubated at 28 °C during 72 h. Afterwards, the Erlenmeyers were vortexed and aliquots of the broths were transferred (10% v/v) to 250 mL fermenters with 50 mL of Hestrin and Schramm medium containing glycerol instead of glucose.

Fermenters were kept in static conditions at 28 °C for 15 days. After that time, the BC pellicles produced were harvested, exhaustively washed out with distilled water, homogenized in a blender with KOH solution (5% w/v) during 5 min and finally left unattended in the alkali solution during 14 h. After this period, the BC suspension was repeatedly rinsed with distilled water till neutralization.

Carboxymethylation of BC

Carboxymethylation of BC was performed as previously described [36]. Briefly, a BC isopropanol suspension (6.2 mmol AGU, 100 mL) was prepared by proper solvent-exchange from water, and then 35% w/v NaOH solution was added dropwise while stirring (300 rpm) at a NaOH:AGU molar ratio of 3:1. The system was then kept at 30 °C during 1 h with stirring (300 rpm), followed by the addition of varying amounts of sodium monochloroacetate that guaranteed predefined NaMCA:AGU molar ratios in the 0.1:1–0.4:1 interval. The reaction system was then kept at 55 °C during 2 h with stirring. After this period, the crude product was filtered off, resuspended in 75 mL of methanol, and neutralized with glacial acetic acid using phenolphthalein as end-point indicator (pH 8). The CMBC produced was then washed with 70% v/v ethanol, dried in an oven (60 °C, overnight), and ground to powder.

Characterization of CMBC samples

Determination of DS values

The DS values of the CMBC samples were determined by conductometric titration [37] after drying (110 °C, 3 h). Samples (0.6 g) were suspended in 15 mL of 70:30 v/v methanol/water at room temperature and allowed to soak during 10 min. After this interval, 200 mL of cold CO₂-free distilled water and 5 mL of 0.3 M NaOH were added, followed by titration with 0.1 M HCl.

Fourier transform infrared spectroscopy (FT-IR)

Fourier Transform Infrared spectra of properly dried (110 °C, overnight) BC and CMBC samples (sample:KBr weight ratio: 1:20) were acquired in an IR Affinity-1 Shimadzu FT-IR Spectrophotometer in absorbance mode with a spectral resolution of 4 cm⁻¹. Measurements were conducted in the 650–4000 cm⁻¹ interval, and data was normalized against the 1168 cm⁻¹ band as described previously [7, 38].

Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed in a TGA-50 Shimadzu instrument. Properly dried (110 °C, 1 h) BC and CMBC samples (5 mg) were heated from 25 °C to 600 °C at 10 °C min⁻¹ under a nitrogen atmosphere (30 mL min⁻¹, 2 kg cm⁻²). T_{onset} (5 wt.% weight loss after moisture removal) and T_{max} values (greatest rate of change on the weight loss curve) were calculated and compared among samples.

Solubility of CMBC

Quantitative water solubility assays of CMBC samples were performed by immersion of properly dried (110 °C, 2 h between disks) and weighted films in 50 mL of distilled water during 24 h at 25 °C; followed by samples recovery, drying and weighting (110 °C, 2 h).

Lead adsorption studies

The maximum lead adsorption capacity of CMBC samples was determined in triplicate at the experimental conditions adjusted in our previous work [7]. Briefly, each sample (25 mg) was suspended in lead aqueous solutions (150 mg L⁻¹, 50 mL) at pH 7 and 25 °C, and stirred at 400 rpm during 2 h. After this time, suspensions were filtrated and the Pb concentration in the supernatant was determined by flame type atomic absorption.

Results and discussion

Synthesis and characterization of CMBC

As already described, carboxymethyl celluloses with DS values higher than 0.40 have proved to be water soluble [32–34]. Thus, aiming to tailor the extent of carboxymethylation of BC within the water insoluble interval, the NaMCA:AGU molar ratio used to prepare the CMBC samples was herein varied within the 0.10–0.40 interval, while all other conditions were kept at predefined values (Sect. Carboxymethylation of BC). CMBC samples with DS values of 0.11, 0.13, 0.20, 0.28, 0.35 and 0.40 were thus obtained.

Carboxymethylation of BC was confirmed by *FT-IR* spectroscopy (Fig. 1). All spectra showed absorbances typical of cellulose I [39, 40]; whereas in the *FT-IR* spectra of CMBC samples the stretching vibration of the carbonyl (C=O) present in the carboxylate groups (COO⁻) was also observed at 1606 cm⁻¹ [41]. Besides, a progressive increase of this absorbance was observed in accordance with the evolution of the DS determined by conductometric titration.

Thermal decomposition curves of BC and CMBC samples with varying DS are shown in Fig. 2. In all samples a first weight loss associated to samples dehydration was observed between room temperature and 135 °C. The following weight loss event exhibited in the thermograms corresponds to cellulose decomposition. As evidenced from Fig. 2, a progressive reduction in the thermal stability of cellulose took place upon carboxymethylation, as inferred from T_{onset} and T_{max} values up to 65 °C lower than those measured for pristine BC

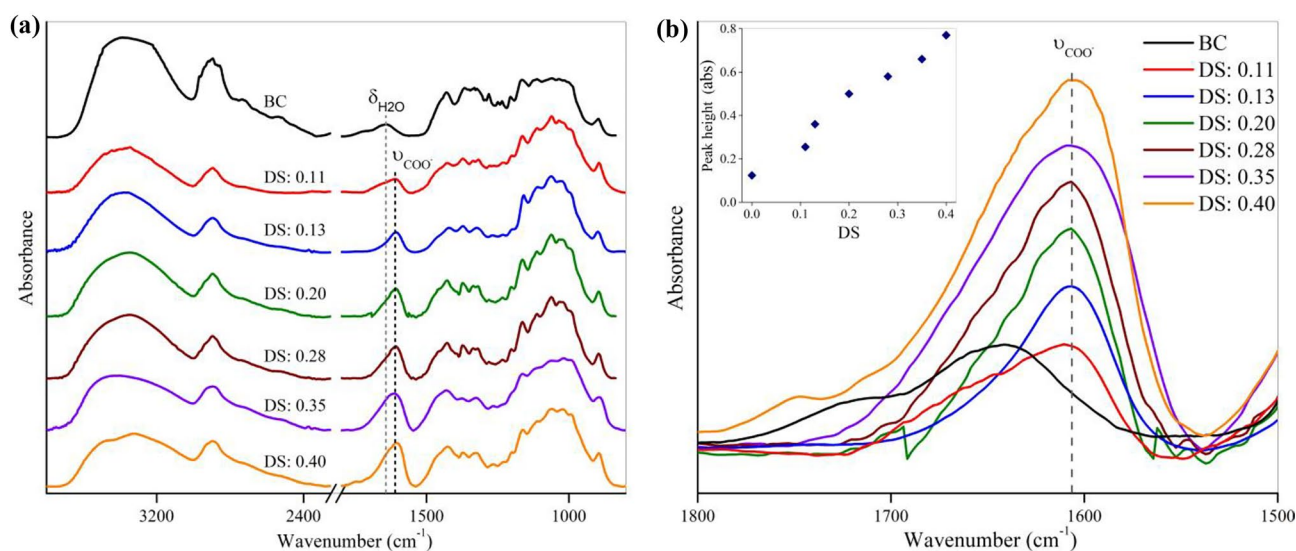


Fig. 1 (a) *FT-IR* spectra of BC and CMBC samples with varying DS; (b) Evolution of the intensity of the stretching vibration band of the carboxylate groups (COO⁻)

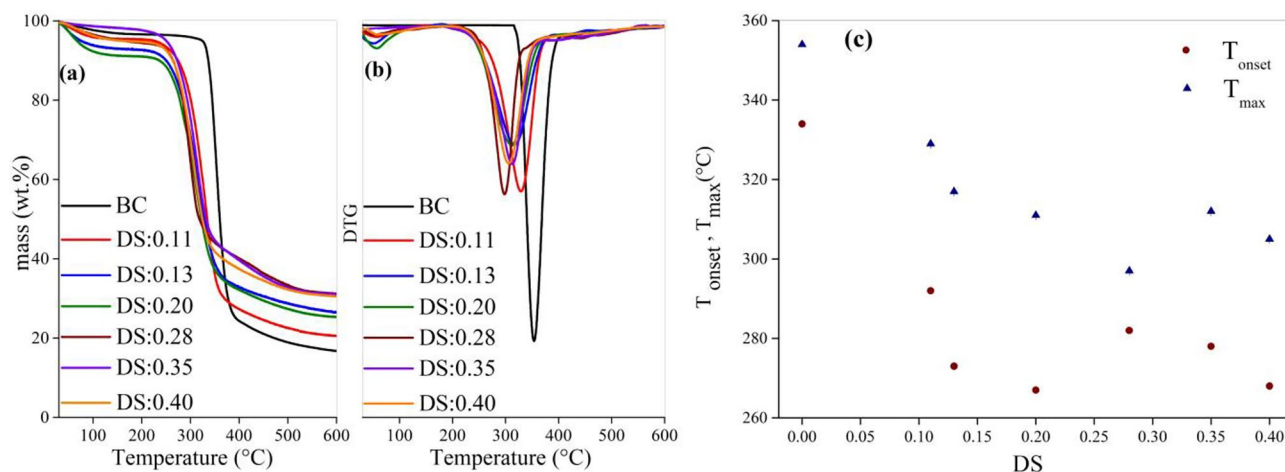


Fig. 2 (a) TG curves, (b) DTG curves, and (c) T_{onset} and T_{max} values determined for BC and CMBC samples with varying DS

depending on the DS of the sample (Table 1). The reduction of the thermal stability of cellulose and other polysaccharides as a consequence of carboxymethylation has been previously reported [33, 41–44]; and sometimes associated with the breaking of hydrogen bonds due to carboxymethylation which accelerates the degradation of the modified polymer. In any case, the thermal stability reduction extent of CMBC herein measured is not at all expected to affect the materials properties within the operation/regeneration temperature interval involved in the proposed application (usually not higher than 40 °C).

Lead adsorption studies

All CMBC samples were assayed for water solubility at room temperature and only the sample with a DS of 0.40 exhibited partial solubilization (*i.e.* 6%, 24 h, 25 °C). Insoluble water samples with DS values within the 0.11–0.35 interval were tested as lead adsorbents from aqueous solutions under conditions defined on the base of previous results of our group [7]. As it is shown in Fig. 3, the maximum lead adsorption capacities of the CMBC

samples increased linearly with the samples' DS. A maximum value of 127.2 mg g⁻¹ was obtained for the adsorbent with the highest level of substitution that still guaranteed its water insolubility. This value doubled that previously reported for this material [7], and it was actually higher than those of many lead biobased adsorbents described in the literature (Table 2).

The linear relationship observed in Fig. 3 is in accordance with an adsorption process governed by ionic interactions between lead cations and the carboxylate groups present in the modified BC, in line with the thermodynamic parameters calculated for the current adsorption process in a previous work [7]. As it is expected for an ion-exchange process, higher carboxymethylation extents conferred to BC (*i.e.* higher DS values) result in more carboxylate groups available to retain lead cations on the adsorbent's surface.

Table 1 T_{onset} and T_{max} values determined for BC and CMBC samples with varying DS

Samples	DS	T_{onset} (°C)	T_{max} (°C)
BC	0.00	334	354
CMBC	0.11	292	329
CMBC	0.13	273	317
CMBC	0.20	267	311
CMBC	0.28	282	297
CMBC	0.35	278	312
CMBC	0.40	267	305

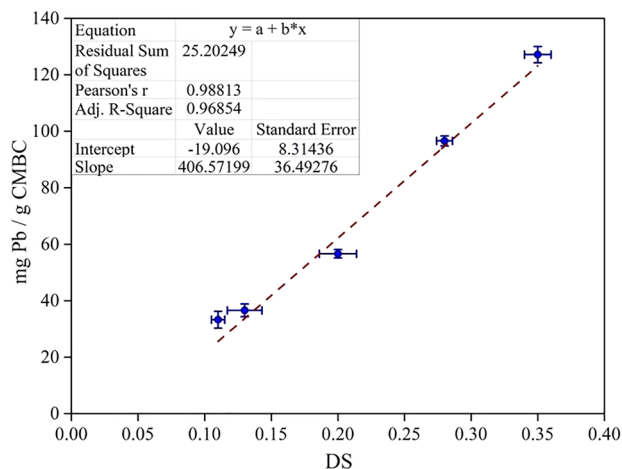


Fig. 3 Lead adsorption capacity of CMBC samples with varying DS. CMBC dosage: 25 mg per 50 mL; lead concentration: 150 mg L⁻¹; pH: 7; contact time: 2 h

Table 2 Lead adsorption capacity of some biobased materials (2018 onwards)

Adsorbent	Lead adsorption capacity (mg g ⁻¹)	Reference
CMBC DS 0.35	127	This study
CMBC DS 0.17	59	[7]
Chemically guanyl-modified cellulose	52	[17]
Thiol-functionalized cellulose nanofiber membrane	22	[29]
Carboxylated cellulose fabricated by TEMPO-mediated oxidation	81	[18]
Cellulose acetate modified first by polyethyleneimine grafting and then by ethylenediamine	2	[19]
Polyaniline grafted on natural cellulosic fiber	64	[20]
Carboxymethyl cellulose/polyacrylamide composite hydrogel	313	[21]
Arginine crosslinked chitosan–carboxymethyl cellulose beads	183	[22]
Mucic acid crosslinked chitosan	76	[13]
Adipic acid crosslinked chitosan	70	[13]
Thiosemicarbazide modified chitosan	57	[23]
Detonation nanodiamonds modified chitosan/PVA thin membrane	121	[24]
Electrospun chitosan/cellulose nanofibers	57	[25]
Starch phosphate	64	[26]
Starch graft poly (acrylic acid)	119	[27]
Starch graft poly(acrylonitrile)	116	[27]
Starch modified montmorillonite	22	[28]

Conclusions

In this work CMBC samples with DS values in the 0.11–0.40 interval were obtained and the materials that resulted insoluble in water (*i.e.* DS values between 0.11 and 0.35) were assayed for their lead removal capacity. Results demonstrated the existence of a linear relationship between the adsorption capacity of CMBC and its substitution level. In this way, the lead retention capacity of CMBC was maximized at a DS of 0.35 (*i.e.* 127.2 mg g⁻¹), with a value that doubled that previously reported for this material, and which was actually higher than those of many lead biobased adsorbents described in literature.

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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