Cotton as Precursor for the Preparation of Porous Cellulose Adsorbers

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Natural biopolymer-based porous spherical adsorbers from cellulose have good efficiency for removal of metal ion pollutants from aqueous media. However, high purity cellulosics, most commonly used as precursors for preparation of the adsorber spheres, require complex synthesis processes, which consume energy and chemicals, and may thus lead to other types of pollution. In this work, the possibility to prepare cellulose-based porous spherical adsorbers directly from cotton, using an ionic liquid-based platform is analyzed in detail. The dissolution of microcrystalline cellulose (MCC), as reference, and of cotton in ionic liquid-based solvents and the properties of the obtained polymer solutions are investigated in order to evaluate their processability toward porous macrospheres using the drop shaping cum nonsolvent induced phase separation process. The properties of the prepared spheres are assessed. The dissolution of cotton is more difficult than the dissolution of MCC and the formed cotton-based solutions are considerably more viscous, which makes their processability possible only after careful adjustment of the cotton solution concentration. The maximum adsorption capacities toward Cu²⁺ are ≈110 and ≈72 mg/g for the porous cotton-based spheres prepared from 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]):dimethylsulfoxide (DMSO) = 2:1 and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]):DMSO = 2:1 solutions, respectively.

1. Introduction

Chemicals and the corresponding chemical processes and technologies are very important components of the modern societies, bringing incontestable benefits. However, chemicals may be released during their lifecycle and have a negative impact to the environment and human health. Their number is continuously increasing and although most of them are registered for production and use, many chemicals and their impact to the environment remain unknown to public due to confidentiality issues and/or incomplete description/testing.¹ The industrial development in general, combined with the population growth and the increase of aridity due to the climate change have led to an increased demand for clean water in certain regions of the globe.² A major share of the aquatic pollution, ≈31%, is a consequence of the discharge of heavy metal ions into the environment by different kinds of industrial processing like mining, metallurgy, electroplating, tanning, dyeing, or the use of fertilizers.³ The mean heavy metal concentration in global river and lake water strongly increased after the 1990s, and for many ions the World Health Organization recommended limits are exceeded, especially in parts of Africa, Asia, and South America.⁴ Most of the heavy metals like As, Cd, Cr, and Ni are dangerous to the human life being classified as group 1 carcinogens by the International Agency for Research on Cancer.⁵ Other heavy metals as Cu and Zn, which in small concentrations are vital minerals for different intracellular processes, in higher concentration may lead to toxicity, like the liver toxicity for copper oral exposure.⁶ Aside from the direct exposure, the non-essential heavy metal can be taken up by humans through the food chain, for example by consumption of contaminated fish. A comprehensive analysis of the heavy metal ions and metalloids bioaccumulation in freshwater fish in connection with the risks to the human health was done by Ali and Khan.⁷ Apart from the negative impact to the human health, the presence of heavy metal ions in water and soil has also a negative impact on the germination and growth of different plants.⁸ Gautam and co-authors provided a summary of the most widespread negative effects of the heavy metal contamination, along with an overview on the most common remediation technologies for the removal of the heavy metals from water and wastewater.⁹ Those include coagulation and precipitation, adsorption, ion-exchange, bioremediation, chemical oxidation, electrochemical precipitation and membrane separation.¹² From the above-mentioned remediation routes, adsorption stands out as one of the most effective methods for...
the removal of heavy metal ions from water by combining high efficiency with flexibility of design. The mostly used adsorbers for wastewater treatment are carbon-based materials (activated carbon, carbon nanotubes, and graphene oxide), natural and synthetic zeolites as well as metal oxides.\cite{2} The search for cheaper adsorbers which exhibit good biocompatibility, biodegradability and availability of renewable sources led the scientists in the field to several natural biopolymers like chitin, chitosan, cyclodextrin, and cellulose; and a wide range of adsorbers based on polysaccharides were developed.\cite{10}

Cellulose which is the main component in plants being found in a proportion up to 60% in dry wool and even higher than 90% in raw cotton, is the most abundant occurring biopolymer and an almost inexhaustible raw material.\cite{11,12} The structure of cellulose consists in a linear chain whose repeating unit contains two anhydroglucose rings linked together through an ether linkage between the C1 position of one ring and C4 position of the other ring. The linear configuration of chains is a consequence of the intrachain hydrogen bonding between hydroxyl groups and oxygen in the neighboring rings while the parallel organization of the cellulose chains is due to van der Waals and intermolecular hydrogen bonds between hydroxyl groups and oxygen of neighboring molecules. The strong inter- and intramolecular hydrogen bonding in cellulose is responsible for its insolubility in water and most of the common solvents.\cite{11}

Shaping of cellulose into beads can be realized by various methods and the obtained porous functional spheres can find applications in many fields like chromatography, metal ion exchange, and as support for solid-phase synthesis or drugs loading and release.\cite{14} For example, cellulose aerogel spheres with controlled diameter have been prepared by atomization from cellulose solutions prepared from high purity cellulose powders. The prepared spheres were successfully used as carriers for energetic materials.\cite{15} Wang et al. proposed biodegradable collagen/cellulose adsorber beads which proved to act efficient in removal of Cu^{2+} ions.\cite{16} Wang and collaborators reported acrylic acid grafted porous spheres as efficient adsorbers for Cu^{2+} and Mn^{2+} ions.\cite{17} Effective and recyclable magnetic adsorbent microspheres from chitosan/cellulose blend have been tested for the removal of Cu^{2+}, Cd^{2+}, and Pb^{2+} ions.\cite{18} Porous cellulose beads with encapsulated CoFe_{2}O_{4} magnetic nanoparticles have been reported to be efficient adsorbers for metal ions removal.\cite{19} Amino functionalized magnetic cellulose composite beads were prepared by grafting on cellulose glycidyl methacrylate followed by epoxy ring opening with ethylene diamine.\cite{20} Magnetic cellulose beads with bentonite as reusable adsorbers for Pb^{2+} removal from drinking water were prepared by Luo.\cite{21} Porous cellulose spheres modified with trisodium trimethaphosphate were obtained by regeneration of cellulose from ionic liquid (IL) solution and have shown high adsorption capacity toward Pb^{2+} of ≈150 mg/g.\cite{22} In our previous works we were able to prepare porous cellulose-based beads and demonstrated that the blend cellulose/chitosan lead to much higher Cu^{2+} adsorption capacities compared to pure cellulose.\cite{23,24}

The preparation of the adsorbers in most of the above given examples involves chemical processes that are not always environmentally friendly and, in most of the cases, microcrystalline cellulose (MCC) is used as precursor. The preparation of the MCC itself usually involves chemical processes which have an impact to the environment. In a conventional process, in the first step, wood chips are pre-hydrolyzed under acidic conditions, then they are pulped under alkaline conditions, and the resulting pulps are then purified. In the next step, the purified pulps are undergoing a second pulping process where the material is hydrolyzed with a mineral acid (HCl or H_{2}SO_{4}) in order to dissolve the amorphous cellulose. After a final washing process the resulting material is dried and milled.\cite{25} In order to reduce the number of chemical steps required for the preparation of the porous cellulose adsorbers spheres, in this work we investigate the possibility to prepare porous spherical adsorbers directly using cotton as precursor, in combination with low volatile organic compounds emissions ILs and relatively low toxicity solvent DMSO. The used commercial cotton was pre-bleached. The most common bleaching process involves the treatment of the fibers with an aqueous solution of hydrogen peroxide, caustic soda, and surfactants in a steamer at temperatures close to 100 °C.\cite{26} The technical challenges implied by the direct use of cotton were analyzed and the properties of the resulting spheres were evaluated in comparison with the properties of spheres prepared by similar processes from Avicel PH 101 MCC.

### 2. Results and Discussion

The polymerization degree (DP) of Avicel PH 101 cellulose was estimated to be around 250,\cite{27} while cotton fibers contain cellulose with DP =5940 in the primary wall and DP =10650 in the secondary wall.\cite{28} Cotton fibers were found to have 73.6% cellulose in the primary wall and 95.1% cellulose in the secondary wall.\cite{28} The cotton used in this work was, however, previously bleached (with oxygen obtained by disproportionation of peroxy compounds) and should have a DP of ≈2180.\cite{29} We have chosen to use in this work bleached cotton instead of native cotton due to two potential advantages: first, the bleached material has a smaller DP and is therefore more adequate for the preparation of the solutions for shaping; and, second, by bleaching the functionality of the cellulose may be changed improving the adsorber properties (e.g., by the introduction of carboxylic acid groups).

The rheology of the cellulose solutions in ILs and in IL-based solvents has already amply been discussed in the specialized literature.\cite{30–32} Both the IL used and the concentration of the biopolymer in solution have a strong influence on the rheological behavior of the solution. Advanced rheological studies can offer valuable information about the thermodynamic quality of the IL as solvent for cellulose.\cite{10} Polar aprotic solvents like DMSO can dissociate the ILs and the anion can more easily break the hydrogen bond in cellulose.\cite{13} The presence of the DMSO in the IL-based cellulose solution was found to decrease the monomer unit friction coefficient without changing the entanglement state of cellulose but reducing the viscosity of the solution.\cite{13} The use of DMSO as co-solvent was also found to decrease the activation energy of the solution, making it more easily spinnable.\cite{32} For the present work we have chosen well-known solvent combinations which allow good dissolution of...
cellulose. The in-depth study of the rheological properties of the formed cellulose solutions serves understanding the differences between the cotton-based and MCC-based solutions in relation with the solution’s processability and the porous structure formation during the cellulose regeneration by non-solvent induced phase separation (NIPS).

After good homogenization of the cellulose source with the solvent mixtures in the mortar, homogenous solutions could be easily obtained. However, their viscosity was strongly dependent on the cellulose concentration in solution and on the DP of the cellulose source (Figures 1 and 2). The complex viscosities of both Avicel and cotton solutions increase with the increase of the biopolymer concentration in solution, this increase is though much more pronounced for the cotton solutions due to a much higher DP of cellulose in this precursor. For 5 wt% biopolymer solutions, cotton solution is ≈10 000 times more viscous than the corresponding Avicel one when [Emim][OAc]-based solvent was used, and ≈2000 times more viscous when [Bmim][OAc]-based solvent was used (Figures 1b and 2b). Most of the solutions, and especially at higher cellulose concentrations, exhibit a shear-thinning effect indicating an aligning of the swollen biopolymer coils at high shear rates.[34] In a good solvent the interactions between the polymer chains and solvent molecules are favorable and the polymer coils expand, in poor solvents, however, the polymer–polymer interactions are preferred and the polymer coils contract. The swelling of the polymer coils in good solvents has usually as consequence a strong increase in the viscosity. As recently summarized by El Seoud,[34] a requirement for the effective dissolution of cellulose is the disruption of the inter- and intramolecular hydrogen bonds and of the van der Waals interactions in the biopolymer. The charge density, hardness, and volume of the anion as well as volume, hydrophobic character and Lewis acidity of the cation affect the dissolution of cellulose. It was found that for a series of ILs with the same anion the ILs with less voluminous cations are able to dissolve cellulose at higher concentration.[15]

Based on the rheological results we may assume that [Bmim][OAc]:DMSO = 2:1 is a better solvent system for Avicel while the system [Emim][OAc]:DMSO = 2:1 is a better solvent for cotton. For the deeper evaluation of the Newtonian or non-Newtonian character of the biopolymer solutions in the studied solvent systems, the rheological experimental data recorded for the 5 wt% polymer solutions, presented in Figure 3, were fitted with the power law model[36] and the calculated model parameters are presented in Table 1.

The consistency coefficients K for the cotton-based solutions are 3 to 4 orders of magnitude higher than the coefficients of the corresponding Avicel solutions. The values of the liquidity indexes of the Avicel solutions are close to 1 suggesting an almost Newtonian character of the polymer solutions while...
the n values of 0.43 and 0.45 for the cotton solutions clearly indicate a strongly non-Newtonian character of the solutions. The consistency coefficient K of the cotton solutions in [Emim][OAc]:DMSO = 2:1 is much higher and the liquidity index n is slightly lower than for the cotton solutions in [Bmim][OAc]:DMSO = 2:1, suggesting that the biopolymer coils are more entangled in the [Emim][OAc]-based solvent even though their swelling degree is higher.

For the cotton samples dissolved in [Emim][OAc]:DMSO = 2:1 it can be observed that the values of the storage modulus (G') of a 1 wt% solution are mostly below the values of the loss modulus (G''), suggesting that the polymer solution is in the liquid state (Figure 4a). On the other hand, for the 3 wt% cotton solution the storage moduli are higher than the loss moduli for the whole shear rate interval confirming the presence of a gel. Similar results have been obtained also for the samples dissolved in [Bmim][OAc]:DMSO = 2:1 (Figure 4b). Based on these results we may assume that at cotton concentrations ≥ 2 wt% the biopolymer solutions will be in a gel state, and therefore inadequate for sphere shaping by dropping. As a consequence, we have chosen 1.5 wt% cotton in solution as the most adequate concentration for the sphere's preparation.

The stability of the biopolymer solutions against the precipitation with water was followed by turbidity tests that were evaluated photometrically (Figure 5a). It can be clearly observed that cotton solutions in both solvent systems have a poorer stability against precipitation with water than the studied Avicel solutions. The poorest stability against precipitation with water was exhibited by the cotton solution in [Bmim][OAc]:DMSO = 2:1.

The variation of the complex viscosity of the polymer solutions at 3 s\(^{-1}\) as a function of the water content (Figure 5b) has also revealed that the increase in the viscosity of the solutions starts for cotton sooner than for Avicel (12 wt% vs 18 wt% water), confirming once again a poorer stability against precipitation with water of the cotton-based solutions.

For the studied four types of biopolymer spheres both Brunauer, Emmet and Teller/Barlett, Joyner and Halenda (BET /BJH) and scanning electron microscopy (SEM) analysis methods offer only a limited description of the real bead’s porosity, because the drying method is expected to have influence on the porous structure of the dried spheres. Additionally, by BJH we can only assess the pores in the micro- and meso ranges. Complementary information can theoretically be obtained from Hg-intrusion experiments (method was unfortunately not available).\(^{[37]}\) On the other hand, the porosity evaluation from SEM micrographs on freeze-dried samples is also imprecise because the water expansion during freezing may also have an impact on the pore size of the dried material.\(^{[14]}\) However, even after taking into consideration the above-mentioned limitations of the BET/BJH and SEM methods, we still consider that both methods may yield important information which allows the direct comparison of the spheres.

Figure 6 presents the cross-section images of the biopolymer spheres at two different magnifications and Table 2 presents

![Figure 3](image3.png)  
**Figure 3.** Viscosity versus shear rate for 5 wt% biopolymer (cellulose and cotton) solutions in [Emim][OAc]:DMSO = 2:1 and [Bmim][OAc]:DMSO = 2:1 with different compositions.

![Figure 4](image4.png)  
**Figure 4.** Storage and loss modulus for cotton solutions with different compositions in a) [Emim][OAc]:DMSO = 2:1 and b) [Bmim][OAc]:DMSO = 2:1.

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### Table 1. Power law equations for 5 wt% cellulose solutions in [Emim][OAc] and [Bmim][OAc].

| Solvent [wt%] | K [Pa s\(^n\)] | n | Power law equation |
|--------------|----------------|---|-------------------|
| Avicel in [Emim][OAc] | 0.5 | 0.97 | μ = 0.5 \(\gamma^{0.97}\) |
| Cotton in [Emim][OAc] | 1446 | 0.43 | μ = 1446 \(\gamma^{0.43}\) |
| Avicel in [Bmim][OAc] | 1.1 | 0.98 | μ = 1.1 \(\gamma^{0.98}\) |
| Cotton in [Bmim][OAc] | 786 | 0.45 | μ = 786 \(\gamma^{0.45}\) |
the BET specific surface area and BJH pore volume results for the four types of spheres. Both the cellulose source and the IL used have an impact on the porous structure formation during the water induced phase separation. The spheres prepared from Avicel solution in [Emim][OAc]:DMSO = 2:1 exhibit a lamellar-like structure (Figure 6) with the walls of the lamella consisting mainly of macro- and mesopores. All other types of spheres exhibit sponge-like structure, also with most of the pores situated in the macro- and meso range. The spheres prepared from cotton-based solutions in both solvents are denser and have a higher number of pores than the spheres prepared from Avicel solutions, a fact reflected also by a higher specific surface area (Table 2). The spheres prepared from [Emim][OAc]-based solutions have, regardless of the used cellulose precursor, a denser porous structure compared to the ones prepared from [Bmim][OAc]-based solutions, as it can be seen from the SEM pictures with higher magnification (Figure 6) bottom). Also, the viscosity of the precursor solutions influences the non-solvent phase separation: the higher is the viscosity of the solution the slower is the solvent-non-solvent exchange and the denser are the formed spheres. This also translates in much higher values of the specific surface area. The obtained results are in good agreement with the results presented in one of our previous works discussing the factors affecting the NIPS of cellulose from IL-based solutions.[38]

Figure 7 presents the Cu$^{2+}$ adsorption isotherms of the Avicel- and cotton-based spheres prepared from solutions in the two studied solvent systems. When evaluating the Cu$^{2+}$ adsorption results and the BET specific surface area of the studied materials it can be concluded that the type of precursor used had the most important influence on the adsorption capacity of the spheres: the amount of Cu$^{2+}$ ions adsorbed at equilibrium is much higher when cotton spheres are used, the best adsorber properties being recorded for the cotton-based spheres prepared from [Emim][OAc]:DMSO = 2:1. One hypothesis could be that bleaching of the cotton precursors may be responsible.

**Figure 5.** a) Turbidity and b) complex viscosity @ 3 s$^{-1}$ dependence on the water content for 1 wt% cellulose and 0.5 wt% cotton solutions in [Emim][OAc]:DMSO = 2:1 and [Bmim][OAc]:DMSO = 2:1.

**Figure 6.** Cross-section images of cellulose spheres prepared from a,c) Avicel and b,d) cotton solutions in [Emim][OAc]:DMSO = 2:1 (a and b) and [Bmim][OAc]:DMSO = 2:1 (c and d).
for the improvement of the adsorptive properties by generation of favorable functional (e.g., carboxylic acid) groups. However, this was not confirmed by the FT-IR results (see Figure S1, Supporting Information). For the spheres prepared from Avicel precursor the specific surface area of the spheres seems to have only a minimal influence on their adsorption capacities. In the case of the beads prepared from cotton the specific surface area seems, however, to have a higher impact on their adsorbent properties. With the help of the Langmuir model the maximal adsorption capacities of the spheres have been calculated and the results are presented in Table 3.

From the values of the Langmuir constants $K_L$ it can be observed that the affinity of the adsorber toward $\text{Cu}^{2+}$ is similar for almost all types of spheres and it is only slightly lower for the spheres made from cotton using $[\text{Emim}][\text{OAc}]:\text{DMSO} = 2:1$ solvent.

Recent studies proposed a modified form of the Langmuir model which can describe more precisely the adsorption phenomena in solution. The modified Langmuir model takes into account the influence of concentration of the solute in bulk solution on the desorption process.\[39\] For example, this model was successfully used at the evaluation of the adsorption properties against $\text{Pb}^{2+}$ of cellulose–boehmite films.\[40\] The modified Langmuir isotherms obtained with our experimental data are presented in Figure S2, Supporting Information. By comparing the values of the maximum adsorption capacity toward $\text{Cu}^{2+}$ calculated with both models we obtained similar values for most of the studied adsorbers (see Table S1, Supporting Information). Only for the spheres obtained from cotton from

### Table 2. Specific surface area and pore volumes from nitrogen adsorption of the spheres with different compositions.

| Samples                  | BET Surface Area $[\text{m}^2 \cdot \text{g}^{-1}]$ | Pore volume $[\text{mL} \cdot \text{g}^{-1}]$ |
|--------------------------|-----------------------------------------------|---------------------------------|
| Avicel in $[\text{Emim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈90                                           | 0.1660                          |
| Cotton in $[\text{Emim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈173                                          | 0.3264                          |
| Avicel in $[\text{Bmim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈13                                           | 0.0314                          |
| Cotton in $[\text{Bmim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈34                                           | 0.0848                          |

$^a$Fraction with pore size up to about ≈80 nm (upper limit of the method).

### Table 3. Langmuir isotherm parameter for the studied samples.

| Samples                  | $q_m$ [mg g$^{-1}$] | $K_L$ [L mg$^{-1}$] | $R^2$ |
|--------------------------|---------------------|---------------------|-------|
| Avicel in $[\text{Emim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈46                | $7.97 \times 10^{-4}$ | 0.99997 |
| Cotton in $[\text{Emim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈110               | $6.12 \times 10^{-4}$ | 0.99990 |
| Avicel in $[\text{Bmim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈42                | $7.07 \times 10^{-4}$ | 0.99999 |
| Cotton in $[\text{Bmim}][\text{OAc}]:\text{DMSO} = 2:1$ | ≈72                | $7.17 \times 10^{-4}$ | 0.99998 |

Figure 7. Adsorption isotherms of the a,c) Avicel- and b,d) cotton-based spheres prepared by precipitation from $[\text{Emim}][\text{OAc}]:\text{DMSO} = 2:1$ (a and b) and $[\text{Bmim}][\text{OAc}]:\text{DMSO} = 2:1$ solutions (c and d).
Table 4. Comparison of maximum adsorption capacity toward Cu$^{2+}$ for the adsorbers discussed in the present work and some reported in the specialized literature.

| Adsorber                                    | $q_m$ [mg g$^{-1}$] | $S_{BET}$ [m$^2$ g$^{-1}$] | Cu$^{2+}$ conc. interval [mg L$^{-1}$] | Ref.       |
|---------------------------------------------|---------------------|-----------------------------|----------------------------------------|------------|
| Avicel in [Emim][OAc]:DMSO = 2:1           | =46                 | =90                         | 50–500                                 | this work  |
| Cotton in [Emim][OAc]:DMSO = 2:1           | =110                | =173                        | 50–500                                 | this work  |
| Avicel in [Bmim][OAc]:DMSO = 2:1           | =43                 | =13                         | 50–500                                 | this work  |
| Cotton in [Bmim][OAc]:DMSO = 2:1           | =72                 | =34                         | 50–500                                 | this work  |
| Cellulose                                   | =9                  | =1.4                        | 0–700                                  | [23]       |
| Cellulose/chitosan 80/20                    | =52                 | ≈0.6                        | 0–700                                  | [23]       |
| Collagen/cellulose beads                    | ≈76                 | ≈43                         | 63.5–635                               | [16]       |
| Cellulose/ acrylic acid                     | =201                | -                           | 100–600                                | [17]       |
| Magnetic chitosan/cellulose                 | ≈88                 | ≈18                         | not given                              | [18]       |
| Carboxymethylated cellulose                 | =115                | -                           | 1–1000                                 | [41]       |
| Carboxylated cellulose                      | ≈124                | -                           | 120–540                                | [42]       |
| Aminoguanidine modified cellulose beads     | ≈95                 | ≈19                         | 0–500                                  | [43]       |
| Amino modified cellulose beads              | =163                | -                           | 2–400                                  | [44]       |
| Magnetic active carbon doped cellulose beads| ≈48                 | ≈90                         | 500–750                                | [45]       |
| Glycine modified cellulose beads            | ≈92                 | ≈59                         | 20–200                                 | [46]       |

[Emim][OAc]:DMSO = 2:1 the value of the maximum adsorption capacity calculated with the modified Langmuir model for the adsorbers prepared in the present work and some reported in the specialized literature. The unmodified cellulose spheres prepared from cotton solution in [Emim] [OAc]:DMSO exhibit a much higher adsorption capacity for Cu$^{2+}$ than the spheres prepared from Avicel solutions. However, the Avicel-based spheres reported here show considerably better adsorption capacities than some other Avicel-based spheres described in one of our previous works.[24] The reason for the improved adsorber properties of the new Avicel-based spheres is most probably connected with their higher specific surface area (90 m$^2$ g$^{-1}$ compared with 1.4 m$^2$ g$^{-1}$). On the other hand, the adsorption capacity of the present cotton-based spheres is higher even than the adsorption capacities of other cellulose adsorbers that had been modified with amino- or glycine groups or of cellulose beads doped with activated carbon (Table 4). Carboxylated and carboxymethylated cellulose adsorbers exhibit adsorption capacities that are comparable with the data for our best cotton-based spheres and only amino-modified or acrylic acid modified cellulose adsorbers exhibit considerably better adsorption capacities. Besides the presence/absence of some functional groups, also other parameters like the porosity and specific surface area have an influence. Theoretically, also the pH and concentration conditions at which the adsorption experiments were performed have an important impact on the adsorption capacities determined for the various samples, but, taking into account that the results presented in Table 4 have been all obtained at pH between 5 and 6 and in all studies similar maximal solute concentrations have been used, all data can be directly compared. It is, however, most remarkable, that unmodified porous cellulose adsorbers were able to achieve such high maximal adsorption capacities.

3. Conclusions

In the present work we were able to demonstrate that oxygen bleached cotton can be directly used for the preparation of porous spherical cellulose adsorbers for heavy metal ions removal from water. Even though bleaching of cotton still involves one chemical step, this is much easier and less aggressive than the processes required for the preparation of MCC from wood. The viscosity of the cotton solutions in both studied solvent systems was much higher than the viscosity of similar cellulose solutions obtained from commercial MCC, making biopolymer dissolution and solutions processability much more difficult. However, by the proper adjustment of the biopolymer concentration in solution these problems can be easily eliminated. The porous spheres prepared from cotton exhibited considerably higher adsorption capacities, which can be correlated with higher values for the specific surface area, than the Avicel-based porous spheres prepared by the same method. Their very good adsorption capacities, comparable with the ones of several chemically functionalized cellulose-based adsorbers, proved clearly that some production steps in between the raw renewable precursors and the final adsorber materials can be omitted and by this also some of the emissions with negative impact to the environment can be avoided. In a following work we also plan to extend the present studies by directly using unbleached cellulose; however, the processing conditions will have to be newly defined due to the even higher DP of the native material.
4. Experimental Section

**Materials:** For the preparation of the porous biopolymer spheres, 100% bleached cotton (natural fiber obtained from organic farming) which was purchased from a local drugstore (Ebelin Bio-Watte 100% Bio-Baumwolle, DM Drogerie Markt), and Avicel PH 101 (Sigma-Aldrich) were used as sources for cellulose. As solvents for the casting solutions the ILs 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]; assay ≥ 95%) and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]; assay ≥ 95%), both purchased from Sigma-Aldrich, in mixtures with DMSO (analytical reagent, ≥ 99.5%) obtained from VWR International, were used. The ILs used are hygroscopic, having water content below 1% according to supplier information. All materials were used as received. The IL:co-solvent ratio used was 2:1. The water used in all experiments was obtained from a Milli-Q Reference water purification system from Merck–Millipore and had a resistivity of ~18.2 MΩ cm @ 25 °C and a TOC value below 10 ppm.

**Polymer Solutions for Rheological Tests:** Biopolymer solutions with different concentrations (0.25, 0.5, 1, 2, 3, 4, and 5 wt%) in solvent mixtures (IL:DMSO = 2:1 wt:wt) were prepared as follows: the cellulose powder or the cotton wool and the solvent mixture were inserted in a mortar and grinded together for several minutes until the biopolymer was homogenously dispersed in the solvent. The homogenous lump free paste was transferred to a snap-cap vial and heated at 70 °C until the dissolution of the biopolymer and a partial degassing of the formed solution was achieved (~4 h). No further degassing under vacuum was performed in order to avoid the removal of the co-solvent.

**Spheres Preparation:** For the preparation of porous biopolymer spheres by dropping cum phase separation technique cellulose solutions (5 wt%) and cotton (7.5 wt%) solutions were used. The spheres were prepared using a procedure similar with the ones presented in our previous works.[12],[24] The detailed experimental procedure including a schematic description of the sphere’s preparation by “dropping cum phase separation method” can be found also in Scheme S1, Supporting Information.

**Characterization Methods:** The rheology of the polymer solutions was studied in rotation mode and oscillation mode using an Anton Paar Physica MCR 301 rheometer with a plate and plate geometry and Peltier temperature control system. All experiments were performed at room temperature. The rotational viscosity versus shear rate measurements were performed at shear rates between 0.1 and 1000 s⁻¹. The storage modulus (G’) and loss modulus (G’’) were measured as a function of the angular frequency between 0.05 and 500 rad s⁻¹.

The variation of the polymer solution’s turbidity as a function of the water content was followed with a Nanocolor 500 D photometer from Macherey–Nagel according to a previously reported procedure.[24] The detailed description of the used methods can be found in the Supporting Information file.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

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[1] Z. Wang, G. W. Walker, D. C. G. Muir, K. Nagatani-Yoshida, *Environ. Sci. Technol.* **2020**, *54*, 2575.
[2] S. Bolisetty, M. Peydayesh, R. Mezzenga, *Chem. Soc. Rev.* **2019**, *48*, 463.
[3] Q. Zhou, N. Yang, Y. Li, B. Ren, X. Ding, H. Bian, X. Yao, *Global Ecol. Conserv.* **2020**, *22*, e00925.
[4] H. S. Kim, Y. J. Kim, Y. R. Seo, *J. Cancer Prev.* **2015**, *20*, 232.
[5] A. A. Taylor, J. S. Tsuji, M. R. Garry, M. E. McArdle, W. L. Goodfellow, Jr., W. J. Adams, C. A. Menzlie, *Environ. Manage.* **2020**, *65*, 131.
[6] H. Ali, E. Khan, *Environ. Chem. Lett.* **2018**, *16*, 903.
[7] V. M. Brezoczki, G. M. Filip, *IOP Conf. Ser.: Mater. Sci. Eng.* **2017**, *200*, 012025.
[8] V. Kumar, S. Pandita, G. P. S. Sidhu, A. Sharma, K. Khanna, A. S. Bali, R. Setia, *Chemosphere* **2021**, *262*, 127810.
[9] R. K. Gautam, S. K. Sharma, S. Mahiya, M. C. Chattopadhyay, in *Heavy Metals in Water: Presence, Removal and Safety*, (Ed: S. Sharma), Royal Society of Chemistry, London **2015**, pp. 1–24.
[10] G. Crini, *Prog. Polym. Sci.* **2005**, *30*, 38.
[11] K. Kamide, *Cellulose and Cellulose Derivatives. Molecular Characterization and Its Applications*, Elsevier Science, New York **2005**.
[12] D. Klemm, B. Heublein, H. P. Fink, A. Bohn, *Angew. Chem., Int. Ed.* **2005**, *44*, 3358.
[13] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, *Chem. Soc. Rev.* **2011**, *40*, 3941.
[14] M. Gericke, J. Trygg, P. Fardim, *Chem. Rev.* **2013**, *113*, 4812.
[15] H. Bian, Z. Shao, L. Li, J. Liu, K. Chen, X. Zhang, *Macromol. Mater. Eng.* **2020**, *305*, 2000243.
[16] J. Wang, L. Wei, Y. Ma, K. Li, M. Li, Y. Yu, L. Wang, M. Qiu, *Carbohydr. Polym.* **2013**, *98*, 736.
[17] J. Wang, L. Dai, J. Cheng, L. H. Deng, J. He, *Desalin. Water Treat.* **2016**, *57*, 5821.
[18] X. Luo, J. Zeng, S. Liu, L. Zhang, *Bioresour. Technol.* **2015**, *194*, 403.
[19] X. Yu, D. Kang, Y. Hu, S. Tong, M. Ge, C. Cao, W. Song, *RSC Adv.* **2014**, *4*, 31362.
[20] X. Sun, L. Yong, Q. Li, J. Zhao, X. Li, X. Wang, H. Liu, *Chem. Eng. J.* **2014**, *241*, 175.
[21] X. Luo, X. Lei, X. Xie, B. Yu, N. Cai, F. Yu, Carbohydr. Polym. 2016, 151, 640.
[22] X. Ma, C. Liu, D. P. Anderson, P. R. Chang, Chemosphere 2016, 165, 399.
[23] A. S. M. Wittmar, H. Böhler, A. L. Kayali, M. Ulbricht, Cellulose 2020, 27, 5689.
[24] A. S. M. Wittmar, J. Klug, M. Ulbricht, Carbohydr. Polym. 2020, 237, 11635.
[25] X. T. Nguyen, US 7005514 2006.
[26] A. Reiche, J. Behnke, H. D. Brauer, US 5322647 1994.
[27] K. Vanhatalo, N. Maximova, A. M. Perander, L. S. Johansson, E. Haimi, O. Dahl, BioResources 2016, 11, 4037.
[28] L. E. Hessler, G. V. Merola, E. E. Berkley, Text. Res. J. 1948, 18, 628.
[29] T. Topalovic, V. A. B. L. Nierstrasz, D. Jocic, A. Navarro, M. M. C. G. Warmoeskerken, Cellulose 2007, 14, 385.
[30] R. Sescosse, K. A. Le, M. Ries, T. Budtova, J. Phys. Chem. B 2010, 114, 7222.
[31] Y. Lv, J. Wu, J. Zhang, Y. Niu, C. Y. Liu, H. He, J. Zhang, Polymer 2012, 53, 2524.
[32] X. Li, Y. Zhang, J. Tang, A. Lan, Y. Yeng, J. Polym. Res. 2016, 23, 32.
[33] Y. Zhao, X. Liu, J. Wang, S. Zhang, J. Phys. Chem. B 2013, 117, 9042.
[34] H. Song, J. Zhang, Y. Niu, Z. Wang, J. Phys. Chem. B 2010, 114, 6006.
[35] O. A. El Seoud, M. Kostag, K. Jedvert, N. I. Malik, Macromol. Mater. Eng. 2020, 305, 1900832.
[36] J. Zhang, L. Xu, J. Yu, J. Wu, X. Zhang, J. He, J. Zhang, Sci. China: Chem. 2016, 59, 1421.
[37] R. P. Chhabra, J. F. Richardson, Non-Newtonian Flow and Applied Rheology, Butterworth-Heinemann, Elsevier, New York 2008.
[38] M. Pinnow, F. K. Fink, C. Fanter, J. Kunze, Macromol. Symp. 2008, 262, 129.
[39] A. S. M. Wittmar, D. Koch, O. Prymak, M. Ulbricht, ACS Omega 2020, 5, 27314.
[40] S. Azizian, S. Eris, L. D. Wilson, Chem. Phys. 2018, 513, 99.
[41] Y. Chen, W. Cai, C. Deng, J. Fan, J. Zhou, Z. Liu, Chem. Eng. Des. 2020, 161, 332.
[42] F. Qin, Z. Fang, J. Zhou, C. Sun, K. Chen, Z. Ding, G. Li, X. Qiu, Biomacromolecules 2019, 20, 4466.
[43] L. V. A. Gurgel, O. K. Junior, R. P. F. Gil, F. L. Gil, Bioresour. Technol. 2008, 99, 3077.
[44] B. Li, Y. Pan, Q. Zhang, Z. Huang, J. Liu, H. Xiao, Cellulose 2019, 26, 9163.
[45] C. Tang, P. Brodie, Y. Li, N. J. Grishkewich, M. Brunsting, K. C. Tam, Chem. Eng. J. 2020, 392, 124821.
[46] X. Luo, X. Lei, N. Cai, X. Xie, Y. Xue, F. Yu, ACS Sustainable Chem. Eng. 2016, 4, 3960.
[47] K. Du, S. Li, L. Zhao, L. Qiao, H. Ai, X. Liu, ACS Sustainable Chem. Eng. 2018, 6, 17068.