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Polysaccharide Ecocomposite Materials: Synthesis, Characterization and Application for Removal of Pollutants and Bacteria

Simon Duri, Bilal El-Zahab, and Chieu D. Tran

Department of Chemistry, Marquette University Milwaukee, WI 53201-1881

Abstract

A novel, simple and totally recyclable method has been developed for the synthesis of nontoxic, biocompatible and biodegradable composite materials from cellulose and chitosan. In this method, [BMIm⁺Cl⁻], an ionic liquid (IL), was used as a solvent to dissolve and synthesize the [CEL+CS] composite materials. Since the IL can be removed from the materials by washing them with water, and recovered from the washed solution, the method is totally recyclable. XRD, FTIR, NIR and SEM were used to characterize the materials and to confirm that CEL and CS were successfully regenerated by the method without any chemical transformation. More importantly, we have successfully demonstrated that [CEL+CS] material can serve as an effective adsorbent for removal of various endocrine disruptors including polychlorophenols and bisphenol A. This is because the composites have combined advantages of their components, namely superior chemical stability and mechanical stability (from CEL) and excellent adsorption capability for pollutants (from CS).

Introduction

Sustainability, industrial ecology, eco-efficiency, and green chemistry are directing the development of the next generation of materials, products, and processes. Biodegradable and biocompatible composite materials generated from renewable biomass feedstock are regarded as promising materials that could replace synthetic polymers and reduce global dependence on fossil fuel sources. As a consequence, chitosan has been a subject of intense studies for many years. The popularity stems from the fact that in addition to being derived from chitin, the second most abundant naturally occurring polysaccharide found in the exoskeletons of crustaceans such as crabs and shrimp and cell walls of fungi, chitosan (CS) is biodegradable, biocompatible, and possesses unique structure and properties which has been successfully exploited in many applications including hemostasis, wound healing, bactericide and fungicide, drug delivery and very good adsorbent for various organic and inorganic pollutants (1 – 7). For examples, CS has been found to effectively remove organic pollutants and/or endocrine disruptors such as bisphenol A, PCB, chlorophenols as well as a variety of heavy metal ions including mercury, arsenic, copper, hexavalent chromium, lead.

Unfortunately, in spite of its potentials, there are drawbacks which severely limit applications of CS. For example similar to cellulose (CEL), the most abundant substance on earth, in CS, an extensive network of intra- and inter-hydrogen bonds enables it to adopt a highly ordered structure. While such structure is responsible for CS to have desirable properties it also makes it insoluble in most solvents (1). As a consequence, an acid such as acetic acid is required to break hydrogen bonds to facilitate dissolution. Subsequent neutralization with a base solution is then needed. Such a procedure is not only costly and time consuming, but also may lead to acid induced changes in the structure of CS. Another drawback is that CS is known to swell in water which leads to structural weakening in wet environments. To increase the structural strength of CS-based products, attempts have been made to cross-link CS chains with a crosslinking agent or convert its functional group via a chemical reaction. Such chemical modification is not desirable because it may inadvertently alter CS properties, making it not biocompatible and toxic, as well as lessening or removing its unique properties. In fact, all reported CS-based products are based on the use of rather costly, complicated and multistep process used to dissolve CS which involves strong acid, base and other environmentally harmful chemicals, and covalently bind or grafting onto man-made polymers to strengthen structure of chitosan based materials (8 – 13). It is, therefore, *desirable* to improve the structural strength of CS products not by chemical modification with synthetic chemicals and/or polymers but rather by use of *naturally occurring* and *most abundant biopolymers such as CEL* which is structurally similar to CS.

Considerable efforts have been made in the last few years to find suitable solvents for polysaccharides, and several solvent systems have been reported (2 – 7). However, all of solvents used in the preparation of commercial products listed above, suffer from high environmental toxicity, insufficient solvation power and/or chemical complications (side reactions) and practically difficulties (high temperature requirement (1 – 13). New, inexpensive and “green” solvents which can readily and effectively dissolve CS and CEL are, therefore, particularly needed. One such solvent is the simple ionic liquid, 1-butyl-3-methylimidazolium chloride, which can effectively dissolve not only CS but also CEL (14 – 16).

1-Butyl-3-methylimidazolium chloride, ([BMIm⁺Cl⁻]), belongs to a group of compounds known as ionic liquids (ILs) (17 – 20). ILs are organic salts that are liquid at room temperature. They have unique chemical and physical properties, including being air and moisture stable, a high solubility power, and virtually no vapor pressure. Because of these properties, they can serve as a “*GREEN*,” recyclable alternative to the volatile organic compounds that are traditionally used as industrial solvents. Due to their advantages, ILs have been used for applications which are not possible with other chemicals. For example, the high solubilization power, and the fact that the solvation ability of ILs can readily be tuned and adjusted by appropriately modifying structure of either cation and/or anion (17 – 24). This feature makes it possible to use ILs to dissolve many different classes of inorganic and organic compounds and polymers such as CS and CEL. The fact that the same simple IL can effectively dissolve CEL and CS is of extreme importance as it offers possibility to synthesize novel, high performance and completely biocompatible CS-based composite materials. The composite materials may have combined advantages of their components,

namely physical and mechanical strength of CEL, and pollutant absorbency, bactericide and fungicide and drug delivery ability of CS.

The information presented is indeed provocative and clearly indicate that a major breakthrough in the polysaccharide-based smart ecocomposite materials may be possible. Such considerations prompted us to initiate this study which aims to hasten the breakthrough by systematically and revolutionarily addressing drawbacks which currently limit synthesis and applications of CS-based composite materials. The limitations are: (1) the rather costly and multistep process currently used to dissolve CEL and CS which involves strong acid, base and other environmentally harmful chemicals, and (2) the use of man-made polymers to strengthen structure of CS-based materials which are not desirable as they may inadvertently alter CS, making it less biocompatible and toxic, and lessening its unique properties, i.e., antimicrobial and pollutants removal. To accomplish this goal, we will (1) exploit advantages of IL, a green solvent, to develop a novel, simple, pollution-free and *totally recyclable method* to dissolve CS and CEL without using any harmful, volatile organic solvents and/or strong acid and base, (2) use only naturally occurring CEL as support materials to strengthen structure to expand utilities and to introduce selectivity while keeping the *biodegradable*, *biocompatible*, antimicrobial and pollutants and toxins adsorption properties of CS-based materials intact; and (3) to demonstrate that these CS based ecocomposite materials are not only fully biocompatible but also superior to currently available materials currently used in removal of endocrine disruptors (bisphenol A, PCB, chlorophenols) and bactericide.

Materials and Methods

Cellulose (microcrystalline powder) and chitosan (MW $\approx$ 310–375kDa, 75% degree of deacetylation, Sigma-Aldrich), microcystin-LR (Enzo Life Sciences) were used as received. 1-methylimidazole and 1-chlorobutane, obtained from Alfa Aesar, were further purified by vacuum and normal distillation, respectively. [BMIm⁺ Cl[−]] was synthesized from 1-chlorobutane and 1-methylimidazole using method previously reported (21, 22).

Preparation of CEL, CS and [CEL+CS] composite films

Homogeneous viscous solutions of CEL, CS or their composite mixtures were obtained by dissolving the polysaccharides in [BMIm⁺ Cl[−]] ionic liquid under magnetic stirring at 100 – 110 °C. Dissolution was performed in a 50mL 3-neck round bottomed flask under Ar or N₂ atmosphere. All polysaccharides were added in portions of approximately 1 wt% of the ionic liquid. Succeeding portions were only added after the previous addition had completely dissolved until the desired concentration has been reached. For composite films, the components were dissolved one after the other, with CEL being dissolved first. Using this procedure, solutions of CEL (containing up to 10% w/w (of IL)), CS (up to 4% w/w) and composite solutions containing CEL and CS in various proportions were prepared in about 6–8 hours.

Upon complete dissolution, the homogeneous solutions of the polysaccharides in [BMIm⁺ Cl[−]] were cast on glass slides or Mylar sheets using a RDS stainless steel coating rod with appropriate size (RDS Specialties, Webster, NY) to produce thin films with different

compositions and concentrations of CEL and CS. They were then kept at room temperature for 24 hours to allow the solutions to undergo gelation. The $[\text{BMIm}^+ \text{Cl}^-]$ remaining in the film was then removed by washing the films in deionized water for 3 days. During this period, the washing water was constantly replaced with deionized water to maximize the removal of the ionic liquid. The $[\text{BMIm}^+ \text{Cl}^-]$ used was recovered from the washed aqueous solution by distillation of the washed water. The regenerated [CEL+CS] composite materials were then dried at room temperature in a chamber with humidity controlled at 60%. Drying time was found to be dependent on thickness of the films but generally was in range of 2–3 days. It was found that humidity control is important to ensure that the films do not become brittle and cracked during drying.

Near-infrared (NIR) spectra were taken on a home-built NIR spectrometer (23, 24). FT-IR spectra were measured on a PerkinElmer 100 spectrometer. X-ray diffraction (XRD) measurements were taken on a Rigaku MiniFlex II Diffractometer (25). Tensile strength measurements were performed on an Instron 5500R Tensile Tester.

Adsorption Kinetics

Experimental Procedure—For all adsorption measurements, duplicate samples (about 0.02g) of dry film were used. One piece was used for the adsorption of the pollutant and the other piece was used as the blank in water. The samples were washed thoroughly in water prior to the adsorption experiments to further insure that $[\text{BMIm}^+ \text{Cl}^-]$ was completely removed because absorption of any residual IL may interfere with that of chlorophenol or BPA. To wash the samples, the weighed composite materials were placed in a thin cell fabricated from PTFE whose windows were covered by two PTFE meshes. The meshes ensured free circulation of water through the material during the washing process. The PTFE mould containing the samples was placed in a 2L beaker which was filled with de-ionized water and was stirred at room temperature for 24 hours. During this time, absorbance of washed water was monitored at 214 and 293nm to determine if there was any $[\text{BMIm}^+ \text{Cl}^-]$. The water in the beaker was replaced with fresh de-ionized water every 4 hours.

After 24 hours, the composite material was taken out of the water and placed into a 1cm×1cm square spectrophotometric cell. The materials were stirred using a small magnetic spin bar during the measurement. In order to prevent damage to the sample by the magnetic spin bar and to maximize the circulation of the solution during measurement, the samples were sandwiched between two PTFE meshes. Specifically, a piece of PTFE mesh was placed at the bottom of the spectrophotometric cell. The washed film sample was laid flat on top of the PTFE mesh. Another piece of PTFE mesh was placed on top of the sample and finally the small magnetic spin bar was placed on top of the second mesh. Exactly 2.70mL of $1.55 \times 10^{-4}\text{M}$ aqueous solution of chlorophenol or BPA was pipetted in to the cell. Measurements were carried out on a Perkin Elmer Lambda 35 UV/VIS spectrometer set to the appropriate wavelength for each pollutant. Care was taken to ensure that the cell contents are low enough to avoid blocking the analytical beam. For continuous stirring, the cells were returned to a magnetic stirrer after each measurement. Measurements were taken at 10 minute intervals during the first 2 hours and 20 minute intervals after 2 hours.

Analysis of Kinetic Data—The pseudo-first-order and pseudo-second-order kinetic models were used to evaluate the adsorption kinetics of different chlorophenols and BPA and to quantify the extent of uptake in the adsorption process.

Pseudo-first-order kinetic model: The linear form of Lagergren's pseudo-first-order equation is given as (26, 27):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad [1]$$

where q_t and q_e are the amount of pollutant adsorbed at time t and at equilibrium (mg g^{-1}) respectively and k_1 (min^{-1}) is the pseudo first order rate constant calculated from the slope of the linear plot of $\ln(q_e - q_t)$ versus t .

Pseudo-second-order kinetic model: According to the Ho model (28), the rate of pseudo second order reaction may be dependent on the amount of species on the surface of the sorbent and the amount of species sorbed at equilibrium. The equilibrium sorption capacity, q_e , is dependent on factors such as temperature, initial concentration and the nature of solute-sorbent interactions. The linear expression for the Ho model can be represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad [2]$$

where q_t is the amount of species sorbed at any time, t , q_e is the amount of species sorbed at equilibrium and k_2 is the pseudo second order rate constant. The constants can then be determined from the experimental data by plotting t/q_t against t .

Results and Discussion

Scheme 1 summarizes procedure used to dissolve and to regenerate films of CEL and/or CS by using $[\text{BMIm}^+\text{Cl}^-]$ ionic liquid as solvent. Specifically, $[\text{BMIm}^+\text{Cl}^-]$ solutions containing one (CEL or CS) and two component (CEL+CS) with varying amounts of each component were successfully prepared using procedure described in the experimental section. Thin films of CEL, CS or [CEL+ CS] with different concentrations having different thicknesses were then casted onto Mylar films. Upon cooling down to room temperature, the films underwent gelation (henceforth referred to as **Gel Films**).

In addition to the polysaccharides, the Gel Films also contained $[\text{BMIm}^+\text{C}^-]$. The IL was removed from the films by soaking them in water at room temperature for 3 days to yield “[BMIm^+Cl^-]-free” films (henceforth referred to as **Wet Films**). Finally, **Dried Films** were obtained when the Wet Films are allowed to dry. Care was taken to dry the Wet Films slowly (at least one week) at room temperature in a chamber with humidity controlled at 60% to avoid any cracking during the drying period.

Images of some of samples taken during various stages of preparation are also presented in the Scheme 1. Specifically, images of films of one-component (CEL or CS) and two component [CEL+CS] casted right after the polysaccharides were dissolved in $[\text{BMIm}^+\text{Cl}^-]$,

i.e., Gel Film are shown in top right corner of the Scheme. After soaking in water for 3 days, $[\text{BMIm}^+\text{Cl}^-]$ was removed from the gel film to yield corresponding Wet Films. Finally, Dried Films were obtained when the wet film was allowed to dry at room temperature.

XRD, FT-IR and NIR were used to follow and confirm the dissolution process and to characterize the films. Specifically, dissolution of CEL and CS in $[\text{BMIm}^+\text{Cl}^-]$ was confirmed by XRD technique. Shown in Figure 1 are XRD spectra of microcrystalline CEL, the CEL one-component Gel Film, the corresponding Dried Film as well as that of $[\text{BMIm}^+\text{Cl}^-]$ for reference. As illustrated, microcrystalline CEL exhibits diffraction peaks at $2\theta = 14.7^\circ$ and 16.3° , 22.5° and 34.6° for (101), (002) and (040) plane, respectively. These bands disappeared completely when the powder polysaccharide was dissolved in $[\text{BMIm}^+\text{Cl}^-]$. The disappearance of these bands together with the similarity between the spectrum of liquid $[\text{BMIm}^+\text{Cl}^-]$ and that of the Gel Film clearly indicate that $[\text{BMIm}^+\text{Cl}^-]$ disrupted inter- and intra-hydrogen bonds in the polysaccharide, and completely dissolves it. Similar results were also found for CS, that is $[\text{BMIm}^+\text{Cl}^-]$ also completely dissolved this polysaccharide.

Recently, there have been some reports on toxicity of ILs. However, the IL used in this work, $[\text{BMIm}^+\text{Cl}^-]$, is relatively nontoxic compared to other ILs (its EC-50 value is 897.47 (29)). Nevertheless, it is desirable to completely remove the IL from regenerated polysaccharide films to insure the films are biocompatible. Since $[\text{BMIm}^+\text{Cl}^-]$ is totally miscible with water (the logP, its octanol-water partition coefficient, is -2.4 (30)), it can be removed from Gel Films by washing the film with water. Washed water will be repeatedly replaced with fresh water until it is confirmed that there is no ILs in the washed water (by monitoring UV absorption of ILs at 214 and 293nm). FT-IR and NIR techniques were used to: (1) confirm that $[\text{BMIm}^+\text{Cl}^-]$ is completely removed from composite films when the films are washed with water; and (2) determine chemical composition of composite materials. Shown in Figure 2A is spectrum of $[\text{BMIm}^+\text{Cl}^-]$. As illustrated, overtone and combination bands of aliphatic C-H groups of the $[\text{BMIm}^+\text{Cl}^-]$ can be clearly observed at 1388nm and 1720 nm (31). These bands are specific for $[\text{BMIm}^+\text{Cl}^-]$ and can be used as indicators to determine the presence of the IL. Also shown in Figure 2A are NIR spectra of Gel Films of one-component CEL and CS samples as well as $[\text{CEL}+\text{CS}]$ two-component sample. Spectra of these Gel Films are very similar to that of $[\text{BMIm}^+\text{Cl}^-]$ because the ionic liquid was the main component of these films. After washing with water to remove the IL, and drying, **Dried Films** of one-component CEL and CS samples were found to exhibit NIR spectra drastically different from those of their Gel Films shown in Fig 2A (together with the spectrum of $[\text{BMIm}^+\text{Cl}^-]$ for reference). As shown in Fig 2B, NIR spectra of the **Dried Films** exhibit none of the indicator bands specific for $[\text{BMIm}^+\text{Cl}^-]$. Thus, it is clear that washing with water effectively and completely removed the IL from the films.

It is noteworthy to add that the IL used was recovered by distilling the washed aqueous solution (the IL remained because it is not volatile). The recovered $[\text{BMIm}^+\text{Cl}^-]$ was dried under vacuum at 70°C overnight before reuse. If needed, recovered $[\text{BMIm}^+\text{Cl}^-]$ was decolorized by heating with activated charcoal at 100°C for ca 24hrs. *As such, the synthetic method is not only green but recyclable because all chemicals used are fully recycled.*

Properties, activities and responses of a sample are known to be dependent on its concentration (or rather on its active ingredient). It is, therefore, important to verify that in [CEL+CS] composite materials, each component is homogeneously distributed throughout the material in order to obtain desired and reproducible properties/activities/responses. Since electrical properties of CEL and CS are known to be somewhat different, homogeneity of composite materials containing two or more of these compounds can be determined by scanning electron microscope (SEM) because this technique is known to be dependent on electrical properties of a sample.

Analysis of the film materials by SEM reveals some interesting features about the texture and morphology of the materials. As expected, one-component CEL and CS (Figure 3A and B, respectively) are homogeneous. Chemically, the only difference between CS and CEL is the few -NH_2 groups in the former (see Scheme 1). However, their structures, as recorded by the SEM, are substantially different. Specifically, while CS seems to exhibit smooth structure, CEL seems to arrange itself into fibrous structure. Interestingly, a 10:3 CEL:CS composite material (Fig 3C) is not only homogeneous but it is more similar to structure of CS than that of CEL, namely, it has a rather smooth structure without any fibrous forms.

Chemically, the regeneration of both CEL and CS was confirmed by FT-IR spectroscopy. As illustrated in figure 4, the FT-IR spectrum of microcrystalline CEL (Figure 4C) exhibits three pronounced bands at around 3400cm^{-1} , $2850 - 2900\text{cm}^{-1}$ and $890 - 1150\text{cm}^{-1}$. These bands can be tentatively assigned to stretching vibrations of O-H, C-H and -O- group, respectively (32 – 34). The fact that the **Dried Film** also exhibits these three bands and is very similar to that of the microcrystalline CEL clearly indicates that CEL was completely regenerated by this synthetic method. Similarly, the FT-IR spectrum of a CS **Dried Film** (Figure 4D) is similar to the FT-IR spectrum of the CS powder from which it was made. These spectra display characteristic CS bands around 3400cm^{-1} (O-H stretching vibrations), $3250 - 3350\text{cm}^{-1}$ (symmetric and asymmetric N-H stretching), $2850 - 2900\text{cm}^{-1}$ (C-H stretching), 1657cm^{-1} (C=O, amide I), 1595cm^{-1} (N-H deformation), 1380cm^{-1} (CH_3 symmetrical deformation), 1319cm^{-1} (C-N stretching, amide III) and $890 - 1150\text{cm}^{-1}$ (ether bonding) (32 – 34). These results indicate that both CEL and CS were successfully regenerated by the synthetic method developed here without any chemical transformation.

Results from NIR measurements further confirm regeneration of polysaccharide composite materials. Shown in Figure 4A are NIR spectra of microcrystalline CEL and regenerated CEL **Dried Film** (4A) and CS powder together with regenerated CS **Dried Film** (4B). As illustrated in 4A, both CEL microcrystalline and regenerated CEL film exhibit bands around 1492nm, 1938nm and around 2104nm. These can be attributed to the overtone and combination transition of the -OH groups. Since CS also possesses the same O-H groups in addition to -NH_2 group, NIR spectra of CS powder and film (4B) also have additional bands at around 1548nm and 2028nm which expectedly can be attributed to the -NH modes (34, 35). The similarity between the NIR spectra of starting polysaccharides and regenerated polysaccharide further confirms that CEL and CS were successfully regenerated by this preparation method.

As described above, mechanical strength of wet CS is so poor that practically it cannot be used by itself for applications based on its unique properties. Measurements were made to determine tensile strength of pure CS film and (CS+CEL) composite films with different CEL concentrations in order to determine if by adding CEL into CS, [CEL+CS] composite material would have adequate mechanical strength for practical applications. Results obtained, shown in Fig 5, clearly indicate that adding CEL into CS substantially increase its tensile strength. For example, up to 5× increase in tensile strength can be achieved by adding 80% of CEL into CS, and that the tensile strength of the composite material can be adjusted by adding judicious amount of CEL. More importantly, the tensile strengths of [CS+CEL] composite materials are comparable with those of existing CS materials including those prepared by either grafting or copolymerization with other chemicals (36 – 41). Thus it is evidently clear that the [CEL+CS] composite materials have overcome the major hurdle currently imposed on utilizations of the materials, namely they have superior mechanical strength and still are able to retain their biocompatible and unique properties.

Taken together, results presented clearly indicate that we have successfully developed a novel, green and recyclable method to dissolve CEL and CS and to synthesize novel, biocompatible all polysaccharide composite materials containing CEL and CS. As anticipated, adding CEL to CS material increases mechanical strength of the CS-based composite material. It is expected that the [CEL+CS] composite materials will have properties of CEL and CS, namely, superior mechanical properties (from CEL) and bactericide and fungicide, drug delivery as well as good adsorbent for pollutants and toxins (from CS). Initial evaluation of their ability to adsorb organic pollutants is described in following section.

Adsorption of endocrine disruptors including polychlorophenols and bisphenol A

The pseudo first order and pseudo second order kinetic models were used to obtain the rate constants and equilibrium adsorption capacity of different composite materials for different chlorophenol analytes and bisphenol A. The pseudo first order kinetic model parameters were calculated from the plots of $\ln (q_e - q_t)$ versus t while those of the pseudo second order kinetic model were obtained from the plots of t/q_t versus t (Figure 6). The results are shown in Table 1 for a 100% CS film and Table 2 for a 100% CEL film. It is evident from the tables that in all cases, the correlation coefficients (R^2) and the Model Selection Criteria, (MSC), are higher for the pseudo second order kinetic model than those corresponding for the pseudo first order kinetic model. In addition, the theoretical and experimental equilibrium adsorption capacities, q_e , obtained for the pseudo first order kinetic model varied widely for the different analytes. The results seem to suggest that the adsorption of various Chlorophenols and BPA onto CS and CEL composite materials is best described by the pseudo second order kinetic model. This good correlation of the system provided by the pseudo second order kinetic model suggest that chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and analyte might be significant (42).

The pseudo second order kinetic parameters were used to compare the sorption performance of different composite materials. Table 3 shows a comparison of the kinetic parameters of a

100% CEL film and a 100% CS film. Clearer observation can be seen in Figure 7 which plots variation of the equilibrium sorption capacity q_e , of the various analytes for these two film materials. As illustrated, for all analytes, equilibrium adsorption capacities for 100% CS material are much higher than those corresponding for 100% CEL material. This is as expected, because CS is known to be an effective adsorbent for various pollutants. Of particular interest is the fact that both the 100% CEL and 100% CS films have relatively much higher adsorption capacity for 2,4,5 tri Cl-Ph than all the other analytes that were studied. These results clearly indicate that novel composite materials with high chemical and mechanical stability and good adsorption capacity can be synthesized by judiciously adjusting the ratio of CS and CEL in the composite material.

Conclusions

In summary, we have successfully developed a novel, simple and recyclable method to synthesize novel, high performance, biocompatible and biodegradable composite materials from CEL and CS. In this method, $[BMIm^+Cl^-]$, an ionic liquid (IL), was used as a solvent to dissolve and synthesize the [CEL+CS] composite materials. Since the IL can be removed from the materials by washing them with water, and recovered by distilling the washed solution, the method is totally recyclable. XRD, FT-IR, NIR and SEM were used to monitor the dissolution process, to characterize the composite material and to confirm that CEL and CS were successfully regenerated by the method without any chemical transformation. While not presented here, we have successfully demonstrated that [CEL+CS] composite material can serve as an effective adsorbent for removal various endocrine disruptors including polychlorophenols and bisphenol A. This is because the [CEL+CS] composite material have combined advantages of their components, namely superior chemical stability and mechanical stability (from CEL) and excellent adsorption capability for pollutants (from CS). Specifically, results of tensile strength measurements clearly indicate that adding CEL into CS substantially increase its tensile strength. Up to 5× increase in tensile strength can be achieved by adding 80% of CEL into CS, and that the tensile strength of the composite material can be adjusted by adding judicious amount of CEL. More importantly, the tensile strengths of [CS+CEL] composite materials are comparable with those of existing chitosan based materials including those prepared by either grafting or covalently attaching CS to man-made polymers. Results of kinetics of adsorption of polochlorophenols and BPA by the composite material clearly confirm that unique properties of CS remain intact in the material, namely, the composite material is very good adsorbent for these polutants, e.g., up to 1.95 mM of 2,4,5-trichlorophenol can be readily adsorbed per gram of the material. Preliminary results presented in this study are very encouraging and clearly indicate that higher adsorption efficiency can be obtained by judiciously modifying experimental conditions (e.g., replacing films of composite material with microparticles to increase surface area, and pH of solution). These possibilities are subject of our current intense study.

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Figure 1.
X-ray diffraction spectra of microcrystalline CEL, CEL gel film, regenerated CEL film and [BMIm⁺Cl⁻]

Figure 2.
Near-IR of [BMIm⁺Cl⁻] and different stages of CEL and CS films.

a) SEM images of cellulose

b) SEM images of chitosan

c) SEM images of a cellulose/chitosan composite material

Figure 3.
SEM micrographs of the various films

Figure 4. NIR and FT-IR spectra of microcrystalline CEL, regenerated CEL film (A and C), CS powder and regenerated CS film (B and D).

Figure 5.
Plot of tensile strength as a function of CEL concentration in [CS+CEL] composite films.

Figure 6.
Pseudo second order linear plots for a 100%CS composite material

Scheme 1.

Procedure used to synthesize [CEL+CS] composite materials

Table 1

Kinetic parameters for adsorption of Chlorophenols and BPA onto 100% CS film

Analyte	qe, expt (M/g)	Pseudo first-order kinetic model				Pseudo second-order kinetic model			
		qe(M/g)	K ₁ (min ⁻¹)	R ²	MSC	qe(M/g)	K ₂ (M ⁻¹ min ⁻¹)	R ²	MSC
2-CIPh	1.30E-03	1.48E-03	0.089	0.9865	3.305	1.32E-03	385.9	0.9998	8.02
3-CIPh	1.62E-03	3.25E-03	0.050	0.9745	2.669	1.68E-03	133.5	0.9960	5.21
4-CIPh	1.64E-03	6.49E-04	0.051	0.9849	2.861	1.66E-03	214.6	0.9996	7.52
3,4 Di-CIPh	2.23E-03	7.23E-04	0.048	0.8769	0.761	2.27E-03	169.8	0.9999	8.72
2,4,5 Tri-CIPh	1.05E-02	9.90E-03	0.016	0.9843	3.917	1.20E-02	2.1	0.9991	6.60
BPA	1.74E-03	5.88E-04	0.040	0.8947	1.680	1.80E-03	168.3	0.9995	7.24

Table 2
Kinetic parameters for adsorption of Chlorophenols and BPA onto 100% CEL film

Analyte	Pseudo first-order kinetic model					Pseudo second-order kinetic model				
	qe, expt (M/g)	qe(M/g)	K ₁ (min ⁻¹)	R ²	MSC	qe(M/g)	K ₂ (M ⁻¹ min ⁻¹)	R ²	MSC	
2-CIPh	4.11E-04	1.45E-04	0.029	0.6469	0.041	3.93E-04	702.3	0.9871	3.95	
3-CIPh	3.19E-04	4.95E-04	0.044	0.9747	2.678	3.20E-04	293.8	0.9822	3.72	
4-CIPh	5.79E-04	1.69E-04	0.055	0.9559	1.788	5.81E-04	2054.2	0.9999	9.13	
3,4 Di-CIPh	7.98E-04	9.44E-04	0.142	0.9665	2.397	8.19E-04	315.6	0.9996	7.47	
2,4,5 Tri-CIPh	1.87E-03	1.01E-03	0.011	0.9714	3.287	1.95E-03	25.4	0.9967	5.32	
BPA	7.27E-04	4.62E-04	0.014	0.9715	3.156	8.05E-04	78.9	0.9911	4.39	

Table 3
Comparison of pseudo-second order kinetic parameters for 100% CEL and 100%CS composite material

Analyte	100%CEL				100%CS			
	qe(M/g)	K ₂ (M ⁻¹ min ⁻¹)	R ²	MSC	qe(M/g)	K ₂ (M ⁻¹ min ⁻¹)	R ²	MSC
2-CIPh	3.93E-04	702.3	0.9871	3.95	1.32E-03	385.9	0.9998	8.02
3-CIPh	3.20E-04	293.8	0.9822	3.72	1.68E-03	133.5	0.9960	5.21
4-CIPh	5.81E-04	2054.2	0.9999	9.13	1.66E-03	214.6	0.9996	7.52
3,4 Di-CIPh	8.19E-04	315.6	0.9996	7.47	2.27E-03	169.8	0.9999	8.72
2,4,5 Tri-CIPh	1.95E-03	25.4	0.9967	5.32	1.20E-02	2.1	0.9991	6.60
BPA	8.05E-04	78.9	0.9911	4.39	1.80E-03	168.3	0.9995	7.24