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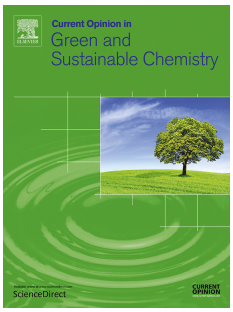

Green solvents for the dissolution and processing of biopolymers

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Green solvents for the dissolution and processing of biopolymers

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Abstract: Dissolution and processing of biopolymers perhaps is one of the oldest chemical processes in the world and there are several breakthrough inventions took place in this area. However with the advent of technological interventions, number of improvements in the processing technologies of the biopolymers has been made in order to address the efficiency and techno-economics of the developed processes. Application of alternate solvent systems is one of the strategies being popularly used in many such cases. The search of alternative solvent systems to solubilise and process biopolymers is always challenging from sustainability point of view. Biopolymers are conventionally solubilise in aqueous systems and processed employing multi step tedious protocols. Ionic liquids (ILs), deep eutectic solvents (DESs) and bio-derived solvents are emerging as alternative solvents for biomass pre-treatment and extraction of natural polymers from the resources. Application of bio-derived as well as green solvents in various industrial processes can be envisaged in near future and hence studies on such solvents for their potential towards industrial applications should be performed. Considering these points, the present review article compiles various recent literatures and reports pertaining to the sustainable processing of natural polymers using green solvents for practical applications.

Key words: Biopolymer, ionic liquid, deep eutectic solvents, bio-based solvents, dissolution, processing

1. Introduction

The judicial choice of suitable solvents and design of green processes are essential for the benefits of environment and future generation. In this direction the use of green and sustainable solvents derived from renewable resources will be 'future solvents' in the processing industries. New solvent systems also termed as 'neoteric solvents' are now widely

recognised as green solvent system for processing of biomass and preparation of new functional materials there from [1-3]. Although the biopolymers are conventionally dissolved in aqueous systems and processed using multiple chemicals but there are opportunities of using green solvent systems for their dissolution and processing. Among the green solvent systems, ionic liquids (ILs) and deep eutectic solvents (DESs) are emerging as alternative solvent systems to process and dissolve several biopolymers due to several unique characteristics of the solvent systems such as low vapour pressure, recyclability, thermal stability etc., are the few among them. In this review article dissolution and processing of few biopolymers (Figure 1) in ILs and DESs will be discussed.

As shown in Figure 1 and Table 1, most of the biopolymers covered in this article are nature derived polysaccharides made up of carbohydrate based monosaccharide units bound to each other by glycosidic linkages [4,5]. They are the oldest plant based natural polymers on the earth and are widely distributed in nature and have been regarded as structural materials and suppliers of water and energy for animals and plants (both terrestrial and sea) e.g., agarose, carrageenan, cellulose, chitin, gum polysaccharides and DNA.

Several such biopolymers have recently received much attention for their use as structural materials for sustainable development because of their eco-friendly properties such as biodegradability, biocompatibility, non-toxicity etc., and availability in large amount at a low cost [6-8].

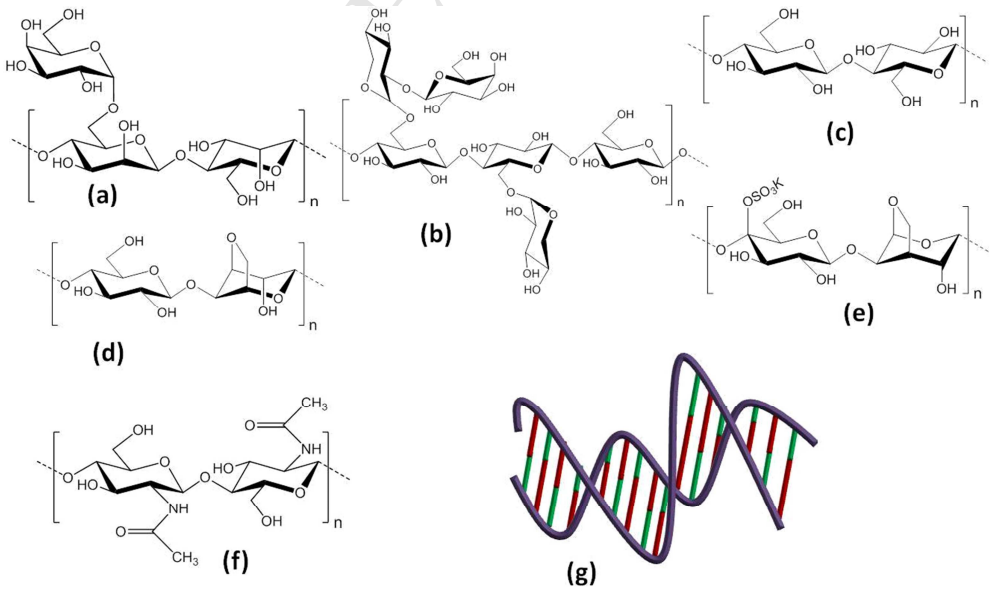

Figure 1: Repeating units of (a) guar gum, (b) tamarind gum, (c) cellulose, (d) agarose, (e) κ-carrageenan (f) chitin and (g) double helical structure of DNA

Table 1: Origin of few biopolymers and their structural information

Entry	Name	Origin/Source	Structure constituents
1	Agar/ Agarose	Cell wall of red seaweeds	Linear chain of (1,3)-linked β-D-galactopyranose and (1,4)-linked α-3,6-anhydro-L-galactopyranose
2	Carrageenan	Cell wall of red seaweeds	Linear chain of (1,3)-linked α-D-galactopyranose and (1,4)-linked β-(3,6-anhydro)-D-galactopyranose
3	Guar gum	Endosperm of seed kernel of guar plant (*Cyamopsis tetragonoloba*)	Composed of (1,4)-linked β-D-mannopyranose main chain with branched α-D-galactopyranose unit at the C-6 position
4	Tamarind gum	White kernel powder of the seeds of tamarind plant (*Tamarindus indica Linn*)	Composed of (1,4)-linked β-D-glucan with branched (1,4)-linked α-D-xylopyranose and (1,6)-linked [β-D-galactopyranosyl-(1,2)-α-D-xylopyranosyl] (glucose, xylose and galactose = 2.8: 2.25: 1.0)
5	Cellulose	Cell wall of all minor and major plants and always found associated with hemicellulose and lignin	Linear chain of β-(1,4)-linked D-glucose
6	Chitin	Cell wall of fungi and exoskeleton of annelids, molluscs, squid, and arthropods	Linear chain of N-acetyl-D-glucosamine and D-glucosamine units linked by a β-(1–4) glycosidic bond
7	DNA	Located in the cell nucleus and mitochondria of living organisms	Composed of three macromolecular constituents such as nucleobase, nucleosaccharides (Deoxyribose) and phosphate group

2. Dissolution and processing of biopolymers using green solvents

2.1. Processing of biopolymers using ionic liquids

Nature can grow a wide diversity of biomass resources that are composed of many ingredients primarily biopolymers. Biomass is processed using many conventional methods to produce biopolymers and other ingredients. Those conventional methods have several limitations in terms of difficulties in dissolution of biomass, solvent handling, solvent toxicity, high volatility of common organic solvents that produce large amount of volatile organic compounds (VOC), high temperature requirement and solvent recovery. Because of

these limitations, conventional methods are not suitable for green processing of biomass for sustainable future. Accordingly, when we consider sustainable development of green processes, it is mandatory to develop green solvent systems that have high biomass dissolving ability, high boiling point, low volatility and more energy efficiency. All these requirements match well with new solvent system named ILs. ILs are now received interest of researchers for the processing of biomass to produce high quality biopolymers, commodity chemicals and biofuels [9,10]. It is now potentially utilized for the processing of biomass such as wood, wheat straw, shrimp shell etc. [11,12] to isolate the biopolymers and it can be further utilized as solvent media for the dissolution of biopolymers and preparation of advanced functional materials [13].

In 1934, Graenacher *et. al.*, established the dissolution of biopolymer for the first time in ILs and reported the dissolution of cellulose in a mixture of 1-ethylpyridinium chloride and nitrogen containing base [14]. After few decades, in 2002, Swatloski and co-workers also reported the dissolution of 25 *wt*% cellulose in an IL comprising 1-butyl-3-methylimidazolium chloride (BmimCl) [15]. Thus ILs can directly dissolve the cellulose biomass without any pre-treatment and further purified cellulose can be regenerated by addition of water or other precipitating solvents such as ethanol and acetone without severe degradation of the cellulose. Cellulose dissolution in ILs was also investigated by other researchers [16]. Tsioptsias *et al.*, have tested 1-allyl-3-methylimidazolium chloride (AmimCl) for the dissolution of cellulose and make a microporous and mesoporous low density aerogel materials that can be used as decompression of the supercritical CO_2 [17].

Chitin is the second most abundant biopolymer after cellulose. It can also be processed using ILs based green solvents system for the development of chitin based advanced functional materials for sustainable development. Conventionally chitin is processed using solvent systems such as halogenated solvents (trichloroacetic acid and dichloroacetic acid), formic acid-halogenated solvent mixture, and *N*,*N*-dimethylacetamide-LiCl mixture [18]. These solvent systems have some drawbacks such as corrosion generation, difficulties during the dissolution and recovery of biopolymers, degrade the chemical structure of biopolymer etc.. Thus, it is required to develop environmentally benign solvent system to overcome the drawbacks of conventional solvent systems. In this line of research, Xie and co-workers reported the dissolution of chitin in an IL comprising BmimCl at 110 °C first time in 2006 [13]. After that, chitin was dissolved in several ILs such as 1-butyl-3-methylimidazolium acetate (BmimA), 1-allyl-3-methylimidazolium bromide (AmimBr) and 1-Ethyl-3-methylimidazolium acetate (EmimA) in higher concentration [19-21]. Prasad *et al.*,

(2009) also reported the dissolution and preparation of weak gel of chitin in AmimBr [22]. These reports proposed the dissolution of neat chitin but the crustacean shell can be directly dissolved in IL and pure chitin powder can be extracted. Qin *et al.*, reported the direct dissolution of sea shell in EmimA and extraction of pure chitin [12].

Due to the better dissolution or processing capabilities of ILs, other biopolymers such as guar gum, tamarind gum, agarose, carrageenan, DNA and proteins can also be dissolved and processed in ILs. Among the plant derived gums, guar gum was dissolved in BmimCl and soft functional ion gel having self-healing and solvent responsive healing was prepared [23,24]. The seaweed polysaccharide, carrageenans (κ,ι and λ) was reported to be soluble in BmimCl and composite gel with cellulose having very high shear strain was produced [25]. Delicate bio molecules such as DNA are reported to be soluble in ionic liquids in very high concentration and very long stability upon room temperature storage [26-28].

2.2. Processing of biopolymers using deep eutectic solvents (DESs)

DESs are another new class of solvents obtained by mixing two immiscible components one of which act as hydrogen bond acceptor (normally quaternary ammonium salts) and other is hydrogen bond donor (normally acids, alcohols, amines etc.) in suitable molar ratios followed by heating. DESs are found to be less thermo chemically stable and more volatile than ILs, but easier to prepare since this needs only mixing of at least two compounds and gentle heating where as preparation of ILs required a synthesis step and hence the DESs can be prepared in a much cost effective way. Processing of biomass and dissolution of biopolymers such as cellulose, chitin, gum and marine polysaccharides is much of interest using DESs. In this field of research, DESs was reported to solubilise polysaccharides such as chitin up to 9% w/v [29]. Further DESs were successfully utilized in pre-treatment process of biomass. Kumar *et al.* (2015) described the delignification process of pine wood, wheat straw and rice straw using DES to produce high quality cellulose pulp directly from biomass [30]. Following the same approach, choline chloride derived DESs were also reported to solubilise xylans [31]. Delicate bio molecules such as DNA solubility with structural stability in DES is investigated by Mondal et al., (2013) and they have also investigated the suitability of the solvent for functionalization of DNA [32,33].

Structure of few ILs and DESs used for the dissolution of biopolymers are depicted in Figure 2.

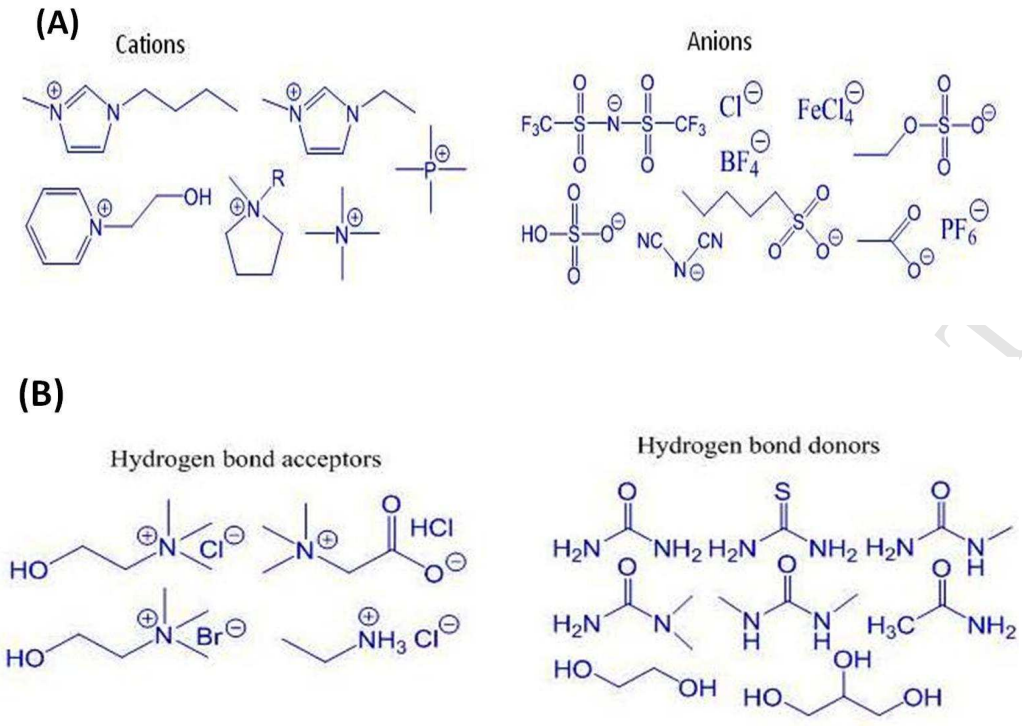

Figure 2 : Structure of few ionic liquids (A) and deep eutectic solvents (B) used to dissolve and process biopolymers.

2.3. Processing of biopolymers using biomass derived solvents

Biomass derived solvents are demonstrated as solvent systems for the processing and pre-treatment of biomass. Dumesic and co-workers have reported the biomass derived solvents namely gamma valerolactone (GVL) for the processing of biomass for the first time in 2014 [34]. They have tested GVL/water solution (80:20 *v/v*) for processing of biomass such as corn stover, hardwood and softwood and producing carbohydrate sugars derivatives. According to literature, the conventional process for the production of carbohydrate sugars from biomass is very difficult due to the slight degradation of sugars, conversion of these sugars into their corresponding furan compounds, corrosiveness and high-priced cost limits its application in this direction [35, 36]. Thus, biomass derived solvents are alternative green solvent for the sustainable processing of biomass for the production sugars derivatives in a cost effective way. In the new processing strategy, after the treatment of the biomass, the carbohydrates sugars are produced without any degradation. The researchers have further tested the processing of biomass in GVL/water solution followed by diluted acid treatment to break down the cellulose and hemicellulose into their constituent sugars without any degradation [37]. Further, they were able to isolate lignin from biomass (corn stover) via biomass fractionation using GVL [38]. Apart from these reports, Shuai and co-workers

(2016) have also reported the GVL as a solvent for the mild pre-treatment of lignocellulosic biomass. They have isolated glucan and xylan from biomass and further pre-treated biomass was converted to sugars (glucose and xylose) [39]. The results of above discussed research suggested that the overall process could be cost competitive for isolation of biomass derived constituents.

3. Biopolymer based functional ion gel materials

The biopolymer based ion gels are defined as a semi-solid soft ion conducting gel materials prepared by incorporation of biopolymers in neoteric solvents and these have been found to be suitable for various applications such as stimuli-responsive materials, electrochemical devices, sensors, actuators, biomedical applications and many more (Figure 3).

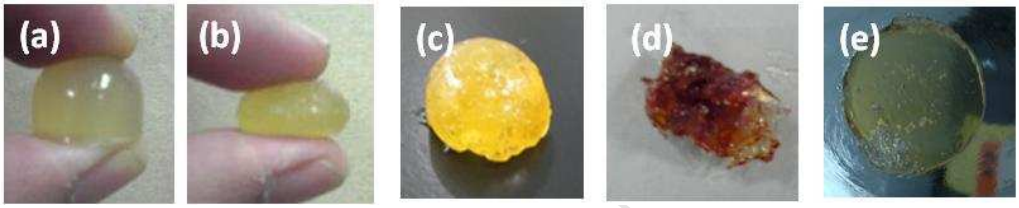

Figure 3: Few representative biopolymer based ion gels (a) κ-carrageenan [25] (b) Cellulose [40] (c) Guar gum [41] (d) Chitin [22] (e) Tamarind [42]

After the discovery of dissolution of cellulose in ILs [15], the solvent has been widely used for the preparation of ion gels and the ion gel can simply be prepared by dissolution of biopolymers in ILs via heating-cooling process (Figure 4). The biopolymers such as cellulose, chitin, guar gum, agarose and carrageenan have been used to prepare ion gels in neoteric solvents. These novel gel systems are soft, viscoelastic and flexible that can be used for various applications mainly preparation of stimuli-responsive advanced functional materials or transformed to value-added sustainable materials. Few important biopolymer based ion gels are discussed below.

3.1. Terrestrial plant derived biopolymer based ion gels

After the discovery of cellulose dissolution using BmimCl in 2002, Kadokawa *et al.,* (2008) have reported the preparation of cellulose ion gel in BmimCl [40]. The cellulose ion gel was prepared by standing the cellulose solution in BmimCl (15 *wt*%) at room temperature for few days via exclusion of excess IL from the gel matrix. Similarly, chitin was found to dissolve upto 7 *wt*% in AmimBr and weak gel of the same could be prepared [22]. Among the plant based gums, gelation of guar gum (GG) (15% *w/w*) by heating-cooling process was observed in BmimCl [41]. The gel can be converted to electric conducting thin films and the gel also

showed self and solvent responsive healing ability [23,24]. Further, tamarind gum was used to prepare ion gels using both synthetic ILs namely BmimCl and BmimBr as well as bio-based ILs namely choline acrylate, choline caproate and choline caprylate by heating cooling process. The gels were found to have good thermal stability and exhibited very good thixotropic nature and adherence to human finger muscles [42].

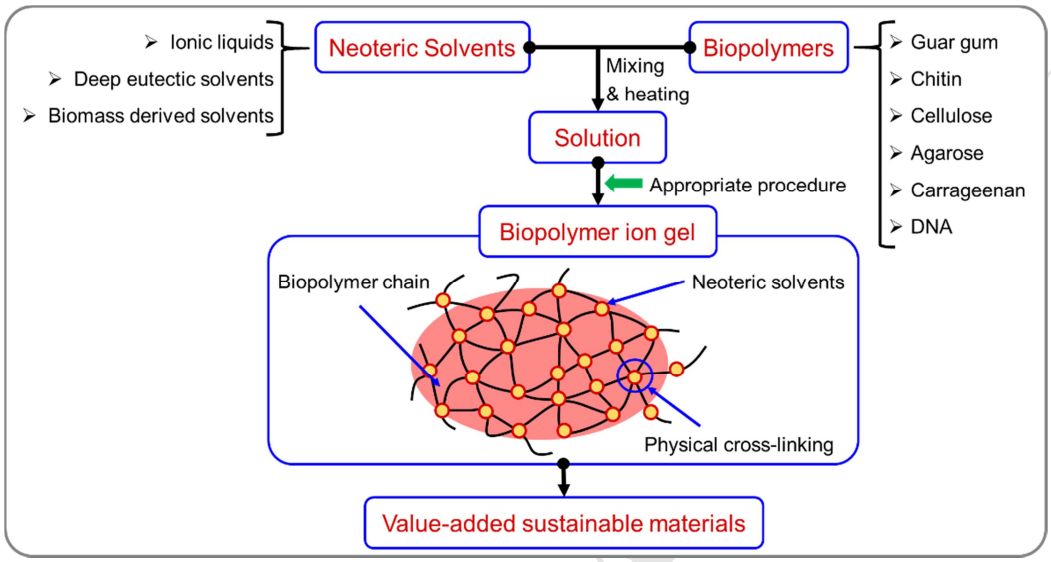

Figure 4: Schematic representation for the production of biopolymer ion gels with neoteric solvents.

3.2. Sea plant derived biopolymer based ion gels

Prasad *et al.*, (2009), have reported the carrageenan-ILs based functional materials using different type of carrageenans such as κ-, λ-, and ι- and IL such as BmimCl [25]. The ion gel of carrageenan was prepared by first dissolving the biopolymers in respective IL via heating at 100 °C followed by cooling to room temperature to obtain the ion gel materials. Similarly for ion gel preparation, agarose was dissolved in certain imidazolium and cholinium based ILs via heating-cooling process. Singh *et al.*, (2010), have identified the imidazolium and pyridinium based ILs for dissolution, regeneration and ion gel formation of agarose [43]. Further Trivedi *et al.*, (2012), also reported the formation of agarose ion gels using several imidazolium and pyridinium based protic and mixed protic-aprotic ILs [44]. The ion gels thus prepared can be used as smart polymeric conducting materials and self-healing gel materials. It can also be used in several electrochemical devices such as soft organic diodes, batteries, fuel cells, photovoltaic devices [21,45].

3.3. Hybrid ion gel systems

Further the ion gels system was also established through the preparation of binary hybrid ion gels using two or more different biopolymers in ILs. The cellulose and chitin based binary hybrid ion gel was prepared using two imidazolium based ILs such as BmimCl and AmimBr

[21]. In a typical process, the solution of chitin (~5 *wt*%) in AmimBr and cellulose (~10 *wt*%) in BmimCl was prepared individually and both the solution was mixed in the desired ratio at high temperature to obtained hybrid ion gel materials. The cellulose-chitin hybrid ion gel was used as an electrolyte in the electric double layer capacitor [21].

4. Future prospects

As discussed above, green solvents such as certain ionic liquids and their structural analogues known as deep eutectic solvents were found to be suitable for the processing of various biopolymers and functional material preparation but still attempts to be made to make the developed processes cost effective and industry friendly. Further, although the green solvents are claimed to be recycled and reused but the purity of the recycled solvents and their efficiency especially for the ones obtained after bio-mass treatment is an important issue, which must be addressed seriously. So far, most of the green solvent mediated processes for biopolymer generation is limited to the laboratory experiments and not reached to the industries. The industrial non compatibility is primarily due to the high cost and inefficient recycling and waste disposal issue related to the solvents and hence research must be focused in developing cost effective biodegradable and biocompatible green solvents for practical applications. In order to address this issues, more research works should be done in the application of deep eutectic solvents rather than ionic liquids since the former can be prepared in relatively greener way in comparison to the later and hence cost effective. Further, there are several polysaccharides still left for which suitable processing technologies are not available. Processing of some unexploited polysaccharides including seaweed based ones such as ulvans and fucoidans should be targeted in new functional green solvents. There is a need for the development of commercially viable extraction processes based on ionic liquids for the seaweed polysaccharides having commercial importance. Further much research efforts are required to establish the suitability of bio derived solvents for the processing of biomass in a cost effective manner.

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References

1. R. A. Sheldon, *Green Chemistry*, **2014**, *16*, 950−963. •
2. F. M. Kerton, Alternatives Solvents for Green Chemistry (Ed: J. H. Clark & G. A. Kraus). *RSC Green Chemistry Book Series*, **2009**, ISBN: 978-0-85404-163-3.

3. R. D. Rogers and K. R. Seddon, Ionic Liquids: Industrial Applications for Green Chemistry. *ACS Symposium Series*, **2002**, *818*, ISBN: 978-0-84123-789-6.
4. A.C.J. Voragen, C. Rolin, B. U. Marr, I. Challen, A. Riad, R. Lebbar, S.H. Knutsen. Ullmann's Encyclopaedia of Industrial Chemistry. 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 29, **2012**, pp,417-472.
5. J. M. Berg, J. L. Tymoczko and L. Stryer, *Biochemistry* (5th Edition). W.H. Freeman Press, New York, **2002**, ISBN: 10: 0-7167-3051-0.
6. J. Clark and D. Macquarrie, Handbook of Green Chemistry & Technology, Wiley-Blackwell Publishing, USA, **2002**, ISBN: 978-0-632-05715-3.
7. G. S. Dhillon, S. Kaur, M. Verma and S. K. Brar, Biopolymer based nanomaterials: Potential applications in Bioremediation of Contaminated waste water and Soils. In: Analysis and Risk of Nanomaterials in Environmental and Food Science (Ed: Farré, M. and Barceló, D.), Wilson & Wilson, Elsevier, UK, **2012**, *Vol. 59*, 91–130.
8. D. N. Iqbal and E. A. Hussain, *International Journal of Pharma and Bio Sciences*, **2013**, *4*, 423–435.
9. D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chemistry*, **2013**, *15*, 584–595.
10. S. S. Y. Tan and D. R. MacFarlane, *Ionic Liquids in Biomass Processing*, In: *Ionic Liquids* (Ed.: B. Kirchner), Springer-Verlag Berlin Heidelberg, **2010**, 311–339. •
11. D. A. Fort, R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna and R. D. Rogers, *Green Chemistry*, **2007**, *9*, 63–69.
12. Y. Qin, X. M. Lu, N. Sun and R. D. Rogers, *Green Chemistry*, **2010**, *12*, 968–971.
13. H. Xie, S. Zhang and S. Li, *Green Chemistry*, **2006**, *8*, 630–633
14. C. Graenacher, *Cellulose solution*. U.S. Patent No.: 1943176, **1934**.
15. R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *The Journal of American Chemical Society*, **2002**, *124*, 4974–4975. •
16. J. Kadokawa, M. Murakami, A.Takegawa, Y. Kaneko. *Carbohydrate Polymers*, **2009**,75,180-183
17. C. Tsioptsias, A. Stefopoulos, I. Kokkinomalis, L. Papadopoulou, C. Panayiotou. *Green Chemistry*. **2008**,10,965-971
18. M.Terbojevich, C. Carraro, A. Cosani, E. Marsano. *Carbohydrate Research* 1988, 180,73–86
19. S. S. Silva, A. R. C. Duarte, A. P. Carvalho, J. F. Mano and R. L. Reis, *Acta Biomateriallia*, **2011**, *7*, 1166–1172.
20. Y. Wu, T. Sasaki, S. Irie and K. Sakurai, *Polymer*, **2008**, *49*, 2321–2327.

21. S. Yamazaki, A. Takegawa, Y. Kaneko, J.-I. Kadokawa, M. Yamagata and M. Ishikawa, *Electrochemical Communications*, **2009**, *11*, 68–70.
22. K. Prasad, M. Murakami, Y. Kaneko, A. Takada, Y. Nakamura and J.-I. Kadokawa, *International Journal of Biological Macromolecules*, **2009**, *45*, 221–225.
23. M. Sharma, D. Mondal, C. Mukesh, K.Prasad. *Carbohydrate Polymers.* **2013**, 98, 1025-1030. •
24. M. Sharma, D. Mondal, C. Mukesh, K.Prasad**.** *RSC Advances.*, **2013**, *3*, 16509 – 16515
25. K. Prasad, Y.Kaneko, J. Kadokawa. *Macromolecular Bioscience* **2009**, *9*, 376-382
26. C. Mukesh, D.Mondal, M. Sharma, K. Prasad. *Chemical Communications*, **2013**, *49*, 6849 – 6851.
27. M. Sharma, D. Mondal, N. Singh, J. Bhatt and K. Prasad. *RSC Advances*, **2015**, 5**,** 40546 - 40551.
28. N. Singh, M.Sharma, D. Mondal, M. M. Pereira, K. Prasad**.** *ACS Sustainable Chem. Eng*. **2017**, 5, 1998−2005 •
29. M. Sharma, C. Mukesh, D. Mondal, K. Prasad**.** *RSC Advances.*, **2013**, *3*, 18149 – 18155
30. A. K. Kumar, B. S. Parikh and M. Pravakar, *Environmental Science and Pollution Research International*, 2015, 23, 9265–9275

31. E. S. Morais, P. V. Mendonça, J.F. J. Coelho, M. G. Freire, C. S.R. Freire, J. A. P. Coutinho, A. J. D. Silvestre. *ChemSusChem.* 2018, 11,753-762.

32. D. Mondal, M. Sharma, C. Mukesh, V. Gupta, K. Prasad. *Chemical Communications* **2013**, 49, 9606-9608. •

33. D. Mondal, J. Bhatt, M. Sharma, S. Chatterjee, K. Prasad**.** *Chemical Communications*, **2014**, 50, 3989-3992

34. J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger and J. A. Dumesic, *Science*, **2014**, *343*, 277–280. •

35. N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple and M. Ladisch, *Bioresource Technology*, **2005**, *96*, 673–686.

36. Y. Sun and J. Cheng, *Bioresource Technology*, **2002**, *83*, 1–11.

37. M. A. Mellmer, D. M. Alonso, J. S. Luterbacher, J. M. R. Gallo and J. A. Dumesic, *Green Chemistry*, **2014**, *16*, 4659–4662

38. J. S. Luterbacher, A. Azarpira, A. H. Motagamwala, F. Lu, J. Ralphbc and J. A. Dumesic, *Energy & Environmental Science*, **2015**, *8*, 2657–2663

39. L. Shuai, Y. M. Questell-Santiago and J. S. Luterbacher, *Green Chemistry*, **2016**, *18*, 937–943

40. J.-I. Kadokawa, M.-A. Murakami and Y. Kaneko, Carbohydrate Research, 2008, 343, 769–771.

41. K. Prasad, H. Izawa, Y. Kaneko and J.-I. Kadokawa, *Journal of Material Chemistry*, **2009**, *19*, 4088–4090. •

42. M. Sharma, D. Mondal, C. Mukesh and K.Prasad. *Carbohydrate Polymers* **2014**, *102*, 467-471.

43.T. Singh, T. J. Trivedi and A. Kumar, *Green Chemistry*, **2010**, *12*, 1029–1035

44.T. J. Trivedi, D. N. Srivastava, R. D. Rogers and A. Kumar, *Green Chemistry*, **2012**, *14*, 2831–2839.

45. M. Taghavikish, S. Subianto, Y. Gu, X. Sun X. S. Zhao and N. Roy Choudhury. *Scientific Reports*. **2018**,8,10918