Synthesis of Recyclable Magnetic Cellulose Nanofibers from Ionic Liquids for Practical Applications in Separation Science

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Abstract: The present study focused on coupling cellulose nanofibers (alternative materials for plastics and metals) with a magnetic ionic liquid (synthesized by a microwave-assisted method) through mixing to yield magnetic cellulose nanofibers (MCNFs) that can be recycled by attracting them to a magnet. Accordingly, two types of ionic liquids were synthesized: (a) 1-butyl-3-methylimidazolium tetrachloroferrate(III) ([bmim]FeCl4) and (b) 1-glycidyl-3-methylimidazolium tetrachloroferrate ([glmi]FeCl4), which were characterized by the fast atom bombardment mass spectrometry (FAB−MS) technique. Impregnation of the cellulose nanofibers with the ([bmim]FeCl4) ionic liquid caused the latter to be physically adsorbed onto the nanofibers to produce {MCNF@[bmim]FeCl4}, whereas the corresponding ([glmi]FeCl4) ionic liquid was chemically bonded to the cellulose nanofibers to yield magnetic {MCNF@[glmi]FeCl4} nanofibers. Under the experimental conditions used, the corresponding magnetic moments were 0.222 A m^2 kg^-1 for {MCNF@[bmim]FeCl4} and 0.095 A m^2 kg^-1 for {MCNF@[glmi]FeCl4}.

Key words: cellulose nanofiber, ionic liquid, magnetization, recycling

1 Introduction
Ancient Egyptians used the stem of the papyrus plant to make paper, which was later adopted by the Greeks and subsequently used extensively during the rule of the Roman Empire.1 The first papermaking process was documented in China during the Eastern Han period (25–220 BC).2 However, recent years have witnessed the development of digital technology to store text. Accordingly, paper documents are seldom used, as they are being replaced by digital data and tablets. Consequently, the demand for paper is expected to decline, thus reducing the demand for wood. Accordingly, new fields of wood utilization are being explored. For example, biomass energy and bioplastics are being investigated to develop potential applications that might result in new industries that use wood rather than oil and coal. In this way, the use of plants can benefit from this carbon neutral source and concomitantly reduce CO2 emissions, a current greenhouse gas of much controversy.

On the other hand, cellulose nanofibers (CNFs) are new materials that have attracted considerable attention because of their advantageous characteristics. Just over a decade ago, Abe et al. discovered a method to produce 15 nm wide CNFs from wood. CNF is a general term used to describe materials made from cellulose, a principal component of plants; fibers with diameters ranging from only a few to hundreds of nanometers and lengths of 5 μm or more can be produced. CNFs in the cell walls of wood are embedded in matrix substances such as lignin and hemicellulose; thus, cellulose can be isolated as nanofibers by removing the matrix substances after a very simple mechanical treatment. These CNF materials are approximately five times stronger than iron and one-fifth of the weight of iron. Furthermore, they exhibit a linear thermal expansion coefficient equivalent to that of quartz glass with low environmental impact and ecotoxicity.
In addition to fundamental research, various industries that deal with automobile parts, home appliances, personal computer housings, plastic molded containers, tires, rubber rolls, packings, belts, cosmetics, food additives, painting, and diapers, among others, are currently using CNFs as a practical, alternative material to steel and glass\(^6-9\). As such, CNFs are attractive and useful materials in sustainable societal efforts and are thus drawing much attention as alternative materials to replace steel and conventional plastics.

Currently, some companies have begun the production (and sales) of CNFs using equipment capable of producing several hundred tons or more of the fibers\(^1\). A search using the keywords cellulose nanofiber in Science Finder revealed that only 91 papers were reported in 2010, while 589 articles were published nearly a decade later (2018), and the number is still increasing. Thus, dramatic developments are expected in the future, both industrially and academically. However, the recycling of these new attractive materials has received scant attention. For instance, chlorofluorocarbons, which are ideal refrigerants that were thought to be stable and safe, ultimately found their way into the atmosphere in large quantities that are now being recognized as significant contributors to the formation of holes in the ozone layer\(^10\). It is imperative, therefore, that repeating the same mistakes be avoided by exploring new material designs and discovering new methods to recycle such nanofibers after usage.

Ionic liquids (ILs) are novel and attractive solvents in various chemical fields (organic synthesis, electrochemistry, liquid phase extraction, catalysis, and polymerization) and are typically composed of bulky asymmetrical organic cations, such as imidazolium, and inorganic anions, such as tetrafluoroborate and tetrachloroferrate. Their unique properties (e.g., thermal stability, vapor pressure, miscibility with water and organic solvents, and tunable viscosity) together with their safe use and ability to extract various organic compounds and metal ions largely depend on their structures\(^11\). Recent progress in functional ILs has been reviewed by Ohno et al.\(^12\) to highlight their unique morphology. This review discussed their applications (i) as solvents for dissolving materials hardly soluble in ordinary solvents (from the viewpoint of energy conversion), (ii) as electrolyte solution substitutes for batteries and electrochemical devices, (iii) as solvents for biomolecules with particular dissolution of proteins, and finally, (iv) in their zwitterionic and polymerized forms. The numerous uses of ILs in separation sciences were also recently reviewed by Berthod et al.\(^13\) for their exceptional properties as non-molecular solvents possessing a negligible vapor pressure, high thermal stability, and unique solvating properties due to their polarity and ionic character of molten salts. The latter authors also touched upon other uses, including their use in nuclear waste reprocessing. Furthermore, being highly thermally stable they were introduced in polar gas chromatography capillary columns working at relatively high temperatures (passing 300\(^\circ\)C), as well as in liquid chromatography and capillary electrophoresis. Additionally, tailor-made ILs have been introduced for the mass spectrometry detection of trace anions at the few-femtogram level\(^10\). An earlier review highlighted advancements in the use of ILs in separation science, including gas chromatography, high-performance liquid chromatography, capillary electrophoresis, extraction and microextraction techniques, and mass spectrometry\(^14\).

Herein, novel materials are developed that involve CNFs from plants (alternative materials for plastics and steels) coupled to magnetic ILs to produce magnetic CNFs, which could then be recycled for applications in various fields (see Fig. 2). A general disadvantage of plant CNFs is that they tend to be insoluble in conventional solvents, although they dissolve in ILs\(^15\). Consequently, CNFs appear to have a

Fig. 1  A typical natural cellulose fiber from a plant and its constituent molecular chains. Reproduced from Han\(^5\) through a creative commons license 4.0; https://creativecommons.org/licenses/by-nc/4.0/
pronounced affinity for ILs. Thus, the first challenge of the present study was to prepare magnetic ILs via a microwave-assisted synthesis, subsequent to which the second objective was their use in preparing magnetic cellulose/IL (MCNF-IL) nanofibers. The latter could prove useful in separation science as they can be recycled by the use of magnets, thereby increasing their usefulness as alternative materials.

2 Experimental Section
2.1 Chemical reagents
1-Methylimidazole |CH$_3$C$_3$H$_3$N$_2$; purity >98%|, 1-chlorobutane |C$_4$H$_9$Cl; purity >98%|, iron (III) chloride hexahydrate |FeCl$_3$·6H$_2$O; purity >99%| and 1-chloro-2,3-epoxypropane |C$_3$H$_5$ClO; purity >99%| were supplied by the Fujifilm Wako Pure Chemical Co. The TEMPO (oxygen type; 2,2,6,6-tetramethylpiperidine-1-oxyl) substrate was provided by Nippon Paper Industries Co., Ltd. and used for the synthesis of CNFs.

2.2 Synthesis of the [bmim]FeCl$_4$ionic liquid
The IL 1-butyl-3-methyl-imidazolium tetrachloroferrate (III), [bmim]FeCl$_4$, was first reported by Hayashi et al. The IL involved microwave irradiation, as reported in an earlier study that dealt with the synthesis of the tetafluoroborate system [bmim]BF$_4$. The preparation of [bmim]FeCl$_4$ involved the addition of distilled and purified 1-methylimidazole (8.21 g, 0.10 mol), 1-chlorobutane (20.82 g, 0.13 mol) and iron (III) chloride hexahydrate (16.22 g, 0.10 mol) to a high-pressure Pyrex glass reactor, followed by microwave heating in the absence of any solvent (Reaction 1). The microwave equipment consisted of an Anton Paar Monowave 300 apparatus equipped with a high-pressure Pyrex glass reactor (100 mL).

$$\text{N} + \text{N} + \text{HCl} + \text{FeCl}_3 + \text{H}_2\text{O} \rightarrow \text{NiFeCl}_4 \text{H}_2\text{O}$$

Reaction 1 was performed under microwave irradiation at 140°C for 30 min using a proportional-integral-differential (PID) controller. The organic phase was repeatedly treated with diethyl ether and ethyl acetate to remove any unreacted 1-chlorobutane and 1-methylimidazole. Diethyl ether was subsequently removed in vacuo, and the residue was washed three times with small volumes of water to remove any remnant chloride ions. A later work-up of drying in vacuo at 100°C gave the desired product. Thereafter, the product was extracted with diethyl ether and a small amount of ion-exchanged water. After a drying period the dark brown [bmim]FeCl$_4$ was obtained in approximately 53% yield. Bringing a neodymium magnet (magnetic flux density = 10 T) close to the solution before the
drying process confirmed that the black fluid was attracted to the magnet (Fig. 3).

The IL [(bmim)FeCl₄] was characterized by mass spectrometry using a JEOL JMS-700 FAB-MS. The mass spectral analysis of the synthetic sample showed peaks at m/z = 139.2 (positive mode) and 197.8 (negative mode), confirming that the product was indeed [(bmim)FeCl₄]. Unfortunately, the structural determination of the magnetic [(bmim)FeCl₄]IL by NMR proved unsuccessful.

2.3 Synthesis of the [(glmi)FeCl₄]ionic liquid

The one-pot and solvent-free synthesis of this IL was similar to that for [(bmim)FeCl₄]. Accordingly, 1-methylimidazole (8.21 g, 0.10 mol), chloromethylxirane (12.03 g, 0.13 mol), and iron (III) chloride hexahydrate (16.22 g, 0.10 mol) were added to the high-pressure Pyrex glass reactor (10 mL) followed by microwave irradiation from the Anton Paar Monowave 300 apparatus. After completion of the reaction, the product was washed with diethyl ether, acetonitrile, and ion-exchanged water. Subsequent removal of the solvents and drying gave the final IL [(glmi)FeCl₄] (Reaction 2).

\[
\begin{align*}
\text{NH}_3 + \text{CH}_2 = \text{CHCl} + \text{FeCl}_3 + 6\text{H}_2\text{O} & \xrightarrow{\text{MW}} \text{FeCl}_4^{-} \text{glmi} \text{NH}_{3} + \\
\text{(glmi)FeCl}_4^{-} + \text{NO solvent} & \xrightarrow{\text{MW}} \text{(glmi)FeCl}_4^{-}.
\end{align*}
\]

A FAB-MS mass spectral analysis revealed peaks at m/z = 139.1 (positive mode) and 197.8 (negative mode); an additional peak at m/z = 282 (positive mode) was observed in addition to the peak of the target substance. This is thought to include a dimerized byproduct that may have resulted from the ring opening of the ethylene oxide groups. The characteristic magnetic properties of [(glmi)FeCl₄] were confirmed with a neodymium magnet (magnetic flux density = 10 T) before solvent removal, as shown in Fig. 4. Since this phenomenon was not observed for [(glmi)Cl], we infer that the Cl⁻ ion was ion-exchanged with FeCl₃ 6H₂O to produce the [FeCl₄]²⁻ ion.

3 Results and Discussion

3.1 MCNFs obtained by mixing the magnetic ionic liquid [(bmim)FeCl₄] and CNF

The dark brown and highly viscous [(bmim)FeCl₄]liquid was mixed with TEMPO-oxidized CNFs, and the mixture was allowed to stand at room temperature (~25°C) for 1 d, ultimately yielding gel-like CNFs as displayed on the tip of a needle (see Fig. 5a). Figure 5b shows the magnetic cellulose nanofibrous gel [(MCNF@[(bmim)FeCl₄]) approaching the neodymium magnet (magnetic flux density = 10 T) and ultimately adhering to it (Fig. 5c). Clearly, the mass of the [(MCNF@[(bmim)FeCl₄])gel is attracted to the neodymium magnet as it moves through the air to be deposited on the magnet. In contrast, the [(bmim)Cl]IL synthesized in a manner similar to [(bmim)FeCl₄], but in the absence of the iron (III) chloride hexahydrate, was not attracted to the neodymium magnet when brought close to it. Similarly, a 1.0 mL ethanolic mixture of iron (III) chloride hexahydrate powder (0.1 g) and TEMPO-oxidized CNFs failed to be attracted to the neodymium magnet. Consequently, mixing the magnetic IL with CNFs produced magnetized CNFs because of the affinity between the IL and the CNFs at the molecular level.

3.2 MCNFs obtained by mixing the magnetic ionic liquid [(glmi)FeCl₄] and CNF

In the present study, magnetic CNFs were synthesized by chemically bonding a magnetic IL with an epoxy ring to the OH group of the CNFs, yielding magnetic 1-glycidyl-3-methylimidazolium tetrachloroferrate/CNFs [(MCNF@[(glmi)FeCl₄])]. The process involved mixing the [(glmi)FeCl₄]IL and the CNFs in an aqueous alkaline (NaOH) solution at room temperature followed by stirring for 24 h at 60°C. The resulting solid material was treated with acetone (1.0 L) while stirring for 10 h, followed by washing several times to remove [(glmi)FeCl₄] and any other impurities that were physically adsorbed onto the cellulose fibers. Characterization of the purified product revealed that some of the [(glmi)FeCl₄] was chemically bonded to the cellulose through the ~OH group of the CNFs via opening of the ethylene oxide moiety to yield [(MCNF@[(glmi)FeCl₄])] (Reaction 3). Figure 6 shows a photograph of the magnetized...
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Fig. 5 Magnetic response of cellulose nanofibers soaked in [bmim]FeCl₄ that yielded [MCNF@[bmim]FeCl₄]; (a) Photograph of magnetized cellulose nanofibers [MCNF@[bmim]FeCl₄] attached to the tip of a needle, (b) [MCNF@[bmim]FeCl₄] drawn toward the Neodymium magnet, (c) magnetized [MCNF@[bmim]FeCl₄] adhering to the Neodymium magnet.

Fig. 6 Magnetic response of cellulose nanofibers soaked in [glmi]FeCl₄ yielding a magnetized [MCNF@[glmi]FeCl₄] powder being attracted to the Neodymium magnet.

3.3 Evaluation of the physical properties of the magnetic materials

The magnetic properties of the two types of MCNFs were measured using a vibration sample magnetometer BHV-50 (Riken Denshi Co. Ltd.). Results from the magnetometer are presented in Table 1. Evidently, [MCNF@[bmim]FeCl₄] showed a greater magnetic moment than that of [MCNF@[glmi]FeCl₄], which is likely due to the significant retention of [glmi]FeCl₄ on the CNFs through chemical bonds. No doubt, further research into the synthesis could produce a significantly greater quantity of pure [MCNF@[glmi]FeCl₄]; thus, it may be possible to achieve greater magnetic susceptibilities for the latter MCNFs.

Interestingly, Galland et al.¹⁹ reported the use of CNFs as a dispersant agent for magnetic nanoparticles. Compared with those from that report, the magnetic susceptibilities of the MCNFs in this study tend to be lower; however, no direct comparison with this earlier work is possible because the usage of CNFs in each study is entirely different. Nonetheless, it may be possible to modify the MCNFs in the future to augment their magnetic properties.

4 Concluding Remarks

We have shown that using an IL with high affinity for CNFs leads to the formation of MCNFs coupled to ILs, which are potential materials for use in separation science and for the disposal/removal of pollutants and/or toxic substances in various liquid ecosystems. Future research is expected to produce MCNFs with greater magnetic susceptibilities by discovering and optimizing the syntheses of new ILs that can bind more strongly to CNFs.

However, the future of this material is not limited to recycling applications. For instance, Zhou et al.²⁰ reported that the preparation of magnetic CNFs could expand their functions to include novel magnetic hydrogel beads formed from carboxylated cellulose nanofibrils, amine-functionalized magnetite nanoparticles, and poly(vinyl alcohol) blended chitosan fabricated by an instantaneous gelation method. The beads were subsequently employed as adsor-
bents for the disposition/removal of Pb(II) ions from aqueous media\textsuperscript{20}. The adsorption capacity of the beads for Pb(II) was 171.0 mg g\textsuperscript{-1}, with the carboxylate groups on the carboxylated cellulose nanofibril surface playing an important role. Moreover, the Pb(II)-loaded hydrogels could easily be regenerated in weakly acidic solutions while maintaining an adsorption effectiveness of 90\% for up to four cycles. Accordingly, various, other applications of magnetic CNFs are probable.

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Conflicts of Interest
The authors declare no conflict of interest. This study received no other financial support that could have adversely affected its outcome.

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\begin{table}[h]
\centering
\caption{Magnetic properties of two kinds of magnetic cellulose nanofibers MCNFs: [MCNF@bmim]FeCl\textsubscript{4} and [MCNF@glmi]FeCl\textsubscript{4}.}
\begin{tabular}{l c c}
\hline
 & [MCNF@bmim]FeCl\textsubscript{4} & [MCNF@glmi]FeCl\textsubscript{4} \\
\hline
Sample area / mm\textsuperscript{2} & 28.27 & 28.27 \\
Sample thickness / mm & 2.50 & 2.50 \\
Sample weight / kg & 6.63 \times 10\textsuperscript{-5} & 3.34 \times 10\textsuperscript{-5} \\
Magnetic field strength / A m\textsuperscript{-1} & 3.98 \times 10\textsuperscript{6} & 3.98 \times 10\textsuperscript{6} \\
Coercivity / A m\textsuperscript{-1} & 3.83 \times 10\textsuperscript{1} & 1.36 \times 10\textsuperscript{4} \\
Magnetic moment vs. weight / A m\textsuperscript{2} kg\textsuperscript{-1} & 0.222 & 0.095 \\
\hline
\end{tabular}
\end{table}
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