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Synthesis and characterization of carboxymethyl cellulose from office waste paper: A greener approach towards waste management

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ABSTRACT

In the present study, functionalization of mixed office waste (MOW) paper has been carried out to synthesize carboxymethyl cellulose, a most widely used product for various applications. MOW was pulped and deinked prior to carboxymethylation. The deinked pulp yield was 80.62 ± 2.0% with 72.30 ± 1.50% deinkability factor. The deinked pulp was converted to CMC by alkalization followed by etherification using NaOH and $ClCH_2COONa$ respectively, in an alcoholic medium. Maximum degree of substitution (DS) (1.07) of prepared CMC was achieved at 50 °C with 0.094 M and 0.108 M concentrations of NaOH and $ClCH_2COONa$ respectively for 3 h reaction time. The rheological characteristics of 1–3% aqueous solution of optimized CMC product showed the non-Newtonian pseudoplastic behavior. Fourier transform infra red (FTIR), nuclear magnetic resonance (NMR) and scanning electron microscope (SEM) study were used to characterize the CMC product.

1. Introduction

The conversion of waste materials into useful products would alleviate a variety of socioeconomic problems such as providing a greener approach to manufacturing. Recycling of waste has huge environmental and economical benefits as recycling of one ton of waste paper saves 17 trees and 7000 gallons of water (ITC, 2014). Across the world, lots of waste is raised on a daily base and yet the economic systems of these states continue to dwindle unabated. These wastes could be recycled into the products of societal and economic interests. Paper is a significant component of our daily life and likewise one of the most prominent cellulosic biomass wastes produced in an ample amount in several subjects (Gulsoy et al., 2013). The number of times paper can be reprocessed by paper industry is limited due to the shortening of the fiber length and the resulting reduction in tensile strength. Thus, the loss of paper making properties causes it to occupy 30–40% of landfill sites in developed countries (Adhikari et al., 2008). In accession to this, the cellulosic rich fibers, left over from the process of papermaking, are discharged with the wastewater in amounts of several thousand tons a year (Nikolov et al., 2000). Feeble mechanical strength of waste paper has some drawbacks to use in the paper industry alone. However, derivatives of waste paper can find applications in other industrial areas. Thus, chemical adjustment of its cellulosic fibers in the yield of different cellulose derivatives is an additional possible way for its employment and management (Ünlü, 2013).

Cellulose is the most abundant polymer on earth, which fixes it also the most common organic compound. Fair yield of cellulose via photosynthesis is estimated around 830 million metric tons per annum. As 40% of dry-weight of crops is composed of cellulose and its annual output is approximately 200 million tons (Ünlü, 2013). Plants contain approximately 33% cellulose whereas wood contains around 50% and cotton contains 90%. Cellulose is a linear and fairly rigid homopolymer consisting of D-anhydroglucopyranose units (AGU). These units are linked together by β-(1–4) glycosidic bonds formed between C-1 and C-4 of adjacent glucose moieties (Klemm et al., 2001). Most of the cellulose is extensively used as a raw material by the paper industry for the production of paper and cardboard products (Bachheti et al., 2010; Dutt et al., 2011) and a small fraction is used in the production of commodity materials and value added carboxymethyl cellulose and methyl cellulose, etc. Moreover, it can be chemically altered to pay value added cellulose derivatives such as carboxymethyl cellulose, methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, cyanoethyl cellulose, and so forth (Varsney and Naithani, 2011). Among all these modified cellulosic products, CMC is manufactured in significant amounts due to its wide commercial applications with

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regard to volume demand. It accepts a broad circle of applications within different industries including food ingredients, pharmaceuticals, cosmetics, paper products, adhesives, lithography, ceramics, detergents, and materials (Saputra et al., 2014). Such diverse applications along with its low pricing make CMC as one of the major market shareholder within all the cellulose ether product categories.

Now a day's cotton and wood pulp are basic raw material for producing modified cellulose products. Competitive demand of these crude materials for many other industries will not be affordable in future for the formation of modified cellulose products. Thus, there is an urgent demand for low cost, non-competitive and sustainable raw materials for the production of modified cellulose products. Recently some new and underutilized raw materials like bamboo shaving (Chen and Lou, 2014), water hyacinth (Saputra et al., 2014), cotton linters (Khullar et al., 2005; Xiquan et al., 1990), textile waste (Bidgoli et al., 2014), recycled news paper (Ünlü, 2013), unused paper (Mahkami and Talaeipour, 2011), paper sludge (He et al., 2009) and broad bean hull (Al-Subhi, 2014), were also explored for the CMC synthesis, but none of them been commercialized so far. The central aim of the present work is to utilize the abundantly available, underutilized waste paper cellulosic rich biomass as an alternative feedstock rather than expensive cotton linters and wood pulp for CMC production, which now, are discouraged due to strict environment conservative regulations. Waste paper cellulose is highly amorphous in nature, hence unlike commercially available cellulose, it is more accessible to chemical change (Adhikari et al., 2008). Further, the mixed office waste paper has high cellulose, low lignin and less ink contents in comparison to waste newsprint or other types of paper waste, hence a high degree of functionalization can be attained.

Previously attempts have also been made for the synthesis of CMC from waste paper (Mahkami and Talaeipour, 2011; Ünlü, 2013). However, to date, to the best of our knowledge, no research has described the pre-steps of processing like deinking and pulping etc. truly required for a CMC of higher grade from real waste paper in true sense. Moreover, the reuse of waste paper essentially depends on the process of pulping followed by deinking. Deinking is a sophisticated and essential process for reuse of waste paper. The complete process of deinking has not been performed in these studies while in some other attempts (Mahkami and Talaeipour, 2011) authors has undertaken fresh unprinted paper which does not contain ink or other impurities and thus cannot be classified under "waste". Prompted by the aforesaid facts, the possibility of using mixed office waste paper as a feedstock for production of CMC was examined and findings are reported herein.

2. Experimental

2.1. Materials

Mixed office waste (MOW) paper was used as a raw material. The samples were collected from the different Research Divisions of Forest Research Institute, Dehradun, Uttarakhand (India). MOW mainly consisted of photocopier and computer printout papers. The wastepaper was manually sorted to remove non-paper objects such as stickers, staples, rubber bands, and others. The sorted waste paper stock was stored in polyethylene bags at room temperature until needed. All the chemicals used were of analytical grade.

2.2. Methods

2.2.1. Characterization of MOW

Proximate chemical composition of the MOW was studied as per the Technical Association of the Pulp and Paper Industry (TAPPI) standard methods. TAPPI method Nos. T 421 om-02; T 09 m-54; T 19 m-50; T 203 cm-99; T 222 om-02; T 211 om-02 and T 207 cm-99 were used for the determination of moisture content, holocellulose, pentosans, alpha-cellulose, lignin, ash, hot water solubles respectively. The MOW was processed using valley beater (Valley Iron Work Co., Appleton, WI, USA) at room temperature for defiberization and production of pulp for 20 min. Pulp was air dried and powdered in a Willey mill (A. Gallenkamp Co., Ltd., London) to 60 mesh size. The powdered material was used for proximate analysis.

2.2.2. Pulping and deinking

The reuse of waste paper essentially depends on the process of pulping followed by deinking. Deinking is a sophisticated process for reuse of waste paper. In the present study MOW paper was pulped and deinked in the hydrapulper followed by the flotation cell. The process of deinking involves removal of ink particles from the fiber surface and the separation of the dispersed ink particles from fiber suspensions by washing or flotation (Bajpai and Bajpai, 1998; Prasad et al., 1993). The ink particles are physically bonded to the fibers because of high heat, making it difficult to remove from the cellulosic fiber. In the flotation deinking, air bubbles rise through the agitated liquid in the tank containing suspended waste paper pulp and contaminant particles. The rising bubbles collect hydrophobic contaminants and ink agglomerates. The attached particles are then transported to a froth layer, from where they are easily removed. The MOW was manually torn into a size of approximately 1-in. squares, pulped and subsequently subjected to deinking. Prior to pulping of waste paper, two hundred gram of oven dried MOW was soaked in water (500 ml) for overnight at room temperature. Wet MOW was charged in hydrapulper with NaOH (2% *w*/*w*), Na_2SiO_3 (2% *w*/*w*), H_2O_2 (1% *w*/*w*) at a 12% pulp consistency for 30 min at 55 ± 2 °C. This pulp was transferred to a flotation cell with Tween-80 (0.1% *w*/*w*) at 40 ± 2 °C for 10 min flotation time. The consistency of the pulp was maintained 1% in the flotation cell by addition of water. After the completion of deinking, the pulp was recovered on muslin cloth from the drain valve of the flotation cell. The pulp was then washed at 2% consistency in a plastic container followed by filtration through a pulp screen. The washing process was repeated three times. After washing, the residual water present in the deinked pulp was drained by the laboratory hydro extractor machine. The hydro extracted deinked MOW pulp was shredded in the pulp shredder and stored in airtight plastic containers at 4 °C. The deinking efficiency of the process was evaluated by means of brightness measurements, as indicated in TAPPI method T452 om-08. The effectiveness of deinking depends on the technique used, printing conditions, quality of ink, and kind of printing substrate.

2.2.3. Sample preparation

Hydroextracted deinked MOW pulp was placed in oven at 105 ± 2 °C for overnight drying. The oven-dried samples were then passed through a laboratory mixer in order to avoid the lump forming in the pulp. Then the disconcerted deinked MOW pulp was processed for carboxymethylation.

2.2.4. Carboxymethyl cellulose synthesis

CMC was produced by etherification of the hydroxyl groups with sodium monochloroacetate (SMCA) in the presence of aqueous alkali. The carboxymethylation of MOW paper proceeds through the Williamson's ether synthesis reaction steps (Tijsen et al., 2001) with an undesired side reaction. In the main reactions the sodium hydroxide reacts first with the hydroxyl groups of the cellulose to give alkoxide. The carboxymethyl groups are then formed in a SN_2 reaction between the cellulose alkoxide and SMCA (Eq. (1)).