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Extraction of palm tree cellulose and its functionalization via graft copolymerization

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ABSTRACT

The work in this paper was planned with the aim of extracting the cellulosic component of palm tree waste and functionalizing this cellulose through graft copolymerization with acrylic acid. The cellulose extraction included hot alkali treatment with aqueous sodium hydroxide to remove the non-cellulosic binding materials. The alkali treatment was followed by an oxidative bleaching using peracid/hydrogen peroxide mixture with the aim of removing the rest of non-cellulosic materials to improve the fiber hydrophilicity and accessibility towards further grafting reaction. Optimum conditions for cellulose extraction are boiling in 5% (W/V) NaOH in a material to liquor ratio of 1:20 for 1 h then bleaching with 60 ml/l bleaching mixture at initial pH value of 6.5 for 30 min. The pH of the bleaching medium is turned to the alkaline range 11 and bleaching continues for extra 30 min. Graft copolymerization reaction was initiated by potassium bromate/thiourea dioxide redox system. Optimum conditions for grafting are 30 mmol of potassium bromate, 30 mmol of thiourea dioxide and 150 g of acrylic acid (each per 100 g of cellulose). The polymerization reaction was carried out for 120 min at 50 °C using a material to liquor ratio of 1:20.

1. Introduction

Although bleaching of palm tree cellulose is to great extent the same as that of textiles based on cotton fiber, one has to consider two main factors in extraction and bleaching of palm tree cellulose. First, empty fruit bunch possesses ca. 17.2% lignin, 70% holocellulose, 42% alpha cellulose, 17.2% NaOH-soluble materials, 2.8 hot water-soluble materials and 0.7% ash content [1]. This is different from cotton, which acquires only 5% impurities, and the rest is α-cellulose. Second, empty fruit bunch is to some extent more sensitive to alkaline and oxidative treatments when compared to cotton fiber. In general, lignocellulosic fibers like flax, jute, bagasse, woody fibers contain various non-cellulosic materials like waxes, lignin, fats, pectins and naturally occurring colorants; etc. Removing of these impurities, efficiently through the successive preparatory steps scouring and bleaching treatments is a must to guarantee successful further processing [2–9]. Recently, there is much emphasis on the concept of energy conservation and accordingly, researchers made many different approaches to reduce the energy consumption during the successive processes involved in cellulose fibers pretreatments [10–12]. One important approach is activation of bleaching agents with different chemicals to increase its efficiency and oxidation potential [13–22]. In recent years, much research has been devoted for production of the industrial raw materials from the agricultural and industrial processing wastes in order to secure cheaper costs [23–33]. The agricultural residues such as rice straw, sugar cane bagasse, cotton stalks, corn stalks, jute waste fibers, palm tree wastes and flax shaves are available as a vast reservoir of potentially available raw material. These residues can be subjected to pulping by the alkali boiling and the obtained cellulosic pulps are further functionalized and utilized as useful industrial products.

One of the most famous approaches to synthesize new materials is the graft copolymerization technique, where synthetic polymers have definite desired performance properties are grafted onto natural polymers, which may have lack in these properties, but have another desired properties. This graft copolymerization gather the desired properties of both polymers resulting in formation of new material with improved functional properties [34]. The most common way to prepare these graft copolymers is the redox initiation method [35–45], grafting assisted with microwave irradiation [46,47], γ-ray irradiation-initiated grafting [48–50], electron beam-initiated grafting [51–54] and many other different grafting techniques [55,56].

During this work extensive experimental work was planned to find the most suitable conditions to scour and bleach empty fruit bunch as part of palm tree wastes, taking into account the quality of bleached empty fruit bunch from the molecular weight point

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of view, the cost and the environmental impact of the bleaching process. The first part of the experimental activities in this work include the utilization of peracetic acid as bleaching system to clean up empty fruit bunch and make it accessible for further chemical modification. This part of the work involves firstly studying the factors affecting the bleaching process e.g. cooxidant concentration, duration, pH and bleaching medium temperature. Second monitoring the decomposition rate of the oxidant (peracetic acid and hydrogen peroxide), and this is achieved by estimating the decomposed percent of the oxidant throughout the reaction period. Third evaluation of the treated samples via determining the whiteness index, percent weight loss, carboxyl content and carbonyl content. The second part of the experimental activities includes functionalization of the bleached empty fruit bunch cellulose via graft copolymerization with acrylic acid to increase its carboxyl content. This requires studying the factors affecting the graft copolymerization reaction, like effect of initiator components concentrations potassium bromate and thiourea dioxide, acrylic acid concentration, material to liquor ratio and polymerization temperature. Finally the so prepared poly(acrylic acid)/cellulose graft copolymer is evaluated via following up the percent total conversion and calculating the graft yield.

2. Experimental

2.1. Materials and chemicals

Empty fruit bunch was collected from palm tree farm. Hydrogen peroxide, sodium hydroxide, glacial acetic acid, sodium carbonate, sulfuric acid, potassium permanganate, potassium bromide, potassium iodide, potassium bromate, thiourea dioxie, acrylic acid and sodium thiosulfate were all laboratory grade chemicals. The non-ionic wetting agent Texazym T was kindly supplied by Inotex Company.

2.2. Methods

2.2.1. Alkaline treatment of empty fruit bunch wastes

Sodium hydroxide solution was used to extract noncellulosic binding materials from empty fruit bunch composition. For this purpose, empty fruit bunch wastes were well air dried in sunny area. Then the empty fruit bunch wastes are finely grinded in an ordinary mill (Fig. 1).

After grinding, the empty fruit bunch wastes were treated, separately with sodium hydroxide solutions having concentrations ranging from 0.5% to 10% (W/V) and 2 g/l non-ionic wetting agent. The system was boiled under reflux for 60 min using the material to liquor ratio 1:20. At this end, the treated samples were removed from the alkaline solution by filtration, washed several times with hot distilled water, rinsed several times in cold distilled water until the rinsing water becomes neutral and finally dried in open air.

2.2.2. Preparation of the bleaching agent

Peracetic acid was prepared according to a reported method [57], that glacial acetic acid (0.5 mol) was mixed with concentrated sulfuric acid (0.375 mol) and the resulting mixture was allowed to cool to reach 0 °C. This cold acids mixture was then added, dropwise to hydrogen peroxide solution, so that the final reaction volume does not exceed 100 ml and at the end of addition, the system temperature was raised to 25 °C and maintained at this temperature for 90 min. The progress in the reaction of peracid formation was monitored by withdrawing samples from the reaction medium at different time intervals and estimating the amounts of consumed hydrogen peroxide and formed peracid throughout the reaction duration.

2.2.3. Bleaching

Alkali treated empty fruit bunch was treated with a bleaching liquor containing varying concentrations from the freshly prepared peracid mixture (20–120 ml/l) together with 2 g/l nonionic wetting agent. The bleaching reaction was allowed to proceed for different durations (15–240 min) and the bleaching runs were carried out at different pH values, which were initially adjusted by addition of sodium carbonate. Other bleaching trials were carried out at different reaction temperatures ranging from 30 °C to 70 °C, by use of material to liquor ratio 1:30.

The percent decomposed peracetic acid and hydrogen peroxide was followed up by estimating the residual peracid and hydrogen peroxide concentration throughout the reaction duration [58]. At the end of the bleaching reaction, the bleached samples were removed from the bleaching liquor by filteration and washed several times with hot water then rinsed thoroughly with cold water and finally dried in open air.

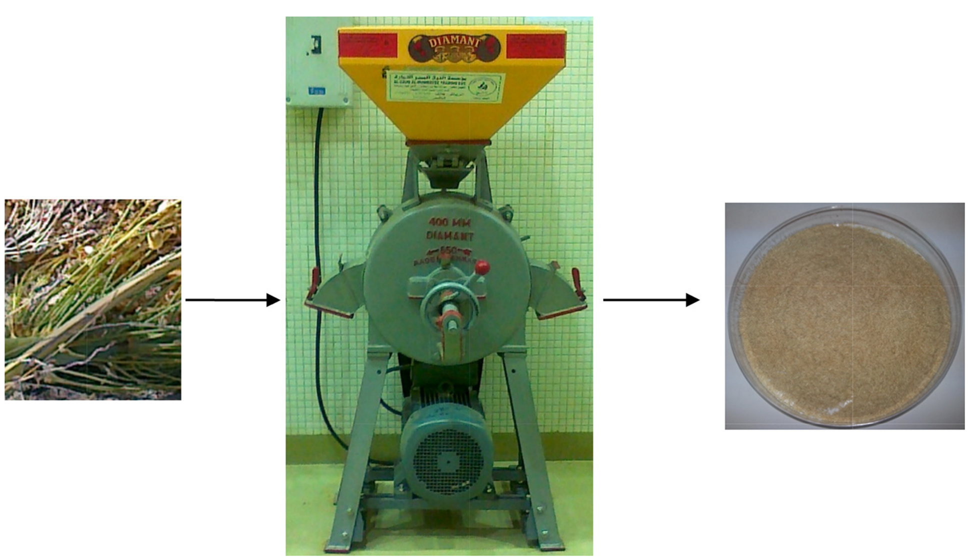

Fig. 1. Grinding of empty fruit bunch.