Novel method for extraction of cellulose from agricultural and industrial wastes

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ABSTRACT
Agricultural and industrial wastes are generated in huge quantities in Iraq and other countries. Generally they are not reused or recycled. The aim of this study was to extract cellulose from different agricultural and industrial waste sources as (rice husk, waste office paper and sugar cane) via fast and simple technique. Cellulose amounting (17.4%, 20%, and 18.2%) were extracted from these sources respectively. It can be concluded that the eco-friendly procedure employed in this study for extracting different cellulose sources is very efficient for obtaining good yield of cellulose. The powder X-ray diffraction and FT-IR were used to characterize the extracted cellulose. In terms of crystallinity and structure behaviours, a comparison with standard cellulose was made and the results showed that the extracted material was cellulose.

INTRODUCTION
The depletion of fossil fuel resources and the resulting adverse effects on the global environment and climate are of major academic, economic and political concern worldwide. One alternative is to develop a series of novel chemical processes based on renewable feedstock, typically biomass and biomass-derived chemicals\(^1\). Biomass generally refers to organic materials such as wood, grass, algae, agricultural crops and their residues and wastes, including some animal waste\(^2\). Any materials rich in cellulose, hemicelluloses, and lignin are commonly referred to as lignocellulosic biomass\(^3\). For example, wood, grass, paper, and agricultural residues like corn stover and sugarcane bagasse are typical sources of lignocellulosic biomass. Nowadays the environmental benefits of biomass/agricultural wastes associated with the producing of solid, liquid and gaseous fuels which is attracting wide attention. Various forms of agricultural wastes energy are consumed all over the world. Such waste provides a clean, renewable material source that could dramatically improve the environment, economy and energy security\(^4\).

Rice husk (RH) is one of the main agricultural products in the world. Burning of RH at ambient atmosphere leaves a residue, called rice husk ash\(^5\). RHA is a great environment threat causing damage to land and surrounding area where it is dumped. Therefore, commercial use of RH and its ash is the alternative solution to disposal problem.

Sugarcane bagasse has also attracted increasing attention due to higher biomass yields\(^6\). Sugarcane bagasse, a byproduct of the sugar production industry, consists of cellulose 43.6%, hemicelluloses 33.8%, lignin 18.1%, ash 2.3% and wax 0.8% on a dry weight basis\(^7\). It is an abundant source of lignocelluloses that
can be hydrolyzed to yield fermentable sugars for the production of value added bio-products such as lactic acid, thus increasing the economy of the process. Other applications of sugarcane bagasse are they are sources of animal feed, energy, pulp, paper and boards[8].

Waste paper is an attractive cellulosic resource for sustainable production of transportation fuels and chemicals because it is an abundant and problematic waste that can be obtained at a low or perhaps negative cost. Waste paper contains 40-55% cellulose, 25-40% hemicellulose and 18-30% lignin[9].

In Iraq (one of the developing countries), the use of agricultural waste is a new science and has high interest. The agricultural wastes can be used in the production of chemicals and liquid fuels[10]. These wastes having high volatile matter content, may find their possible utilization. As compared to biofuel, agricultural wastes also contain high oxygen and easy release of volatile matter in a combustor[11]. All these characteristics of agricultural wastes have been found to have a large influence on the burn out time of blends of agricultural wastes. The agricultural wastes produced in a particular period of the year pose potential pollution problems. Therefore, an efficient utilization of such agricultural wastes is of great importance not only for minimizing the environmental impact, but also for obtaining a higher profit[12].

The present study aimed to extract cellulose from different wastes (rice husk, waste office paper and sugarcane) via fast and simple technique. The extracted cellulose, as polycarbohydrate, as well its hydrolytic product glucose can be used in various academic and industrial applications.

**MATERIALS AND METHOD**

**The chemicals and the raw materials**

The chemicals used in this study were sodium hydroxide (Systerm, 99%), nitric acid (Scharlau, 65%), Cellulose (Riedle-De Haen 99%), Sulphuric acid (Poch, 95%). The RH was collected from a rice mill in Samawah, Iraq. All other chemicals used were AR grade or of high purity and were used directly without further purification.

**Extraction of cellulose**

Different types of wastes (rice husk (RH), waste office paper and sugarcane) were chosen as sources of cellulose & as illustrated below.

**Extraction of cellulose from RH**

RH was used as a source of cellulose. The RH was washed twice with water and dried at room temperature for 24 h. A weight (35 g) sample of the cleaned RH was stirred with 700 mL of nitric acid (1.0 M) at room temperature for 24 h, and washed with distilled water. The wet material was subsequently dried in an oven at 100 °C for 24 h. The rice husk treated with acid was weighed then transferred into a 1.0 L plastic container. To purify the cellulose by removing silica and lignin from RH fibres, 500 mL of sodium hydroxide (1.0 M) solution was added. Then the solution was stirred for 24 h at room temperature. It was then filtered using suction filtration. The dark brown filtrate (sodium silicate solution with lignin) was kept in a covered plastic container. The solid was filtered and washed several times using distilled water. The solid was treated with an alkali solution (NaOH 6.0 M) for 6 h. The solid was then filtered to be used for cellulose extraction and the filtrate was titrated with acid at a room temperature using sulphuric acid (5.0 M) under continuous stirring until constant pH in the range of 5–6 was reached. The resulting suspension material was then separated by vacuumed filtration and washed roughly with distilled water. This method gave 6.0 g of cellulose (17.14%) from RH. Scheme 1 summarizes the methodology of the extraction of cellulose from RH.

**Extraction of cellulose from waste paper**

Waste paper was used as the raw material for extraction cellulose by a simple and economic method. Waste paper was collected from waste boxes of the offices in AL-Muthana University. Waste paper (5.0 g) was cut into small pieces, and mixed with sodium hydroxide solution (7.5%) in a plastic container equipped with stirrer. The mixture was stirred for 6 h then filtered. The filtrate was titrated against sulphuric acid (5.0 M) solution until the pH reached 5.0. After separating the mixture, the solid was washed with distilled water and dried at room temperature. Scheme 2 shows the methodology of cellulose extraction from waste paper. This method gave about 1.0 g (20.0%) of cellulose.

**Extraction of cellulose from sugarcane**

Sugarcane bagasse is the second most commonly
used nonwood plant material for paper production in many parts of the world\textsuperscript{13}. The annual production of sugarcane throughout the world exceeds 54 million tons on dry basis\textsuperscript{14}. Sugarcane was collected from the farm of sugarcane factory in Maysaan governorate, Iraq. Extraction of cellulose was carried out according to the method\textsuperscript{15}. Sugarcane was cut into small pieces, and dried for 1 week at room temperature. After drying the sugarcane was grinded to powder. A weight of 22.0 g was washed with distilled water and left in 600 ml of water for 24 h and then filtered and dried at room temperature for another 24 h. Sodium hydroxide solution (0.25 M) was added in a plastic container equipped with stirrer. The mixture was stirred for 18 h and then filtered. The filtrate was naturalized with nitric acid (20.0 %). After that the mixture was filtered and washed with distilled water until the filtrate did not turn to pink when phenonaphthalene and drop of NaOH were added to it. Scheme 3 shows the methodology of cellulose extraction from sugarcane. The solid was dried at 105\textdegree C for 3h. This method gave 4.0 g (18.2 %) of cellulose.
RESULTS AND DISCUSSION

Cellulose was extracted from waste RH, waste office paper and sugarcane using new simple method (Scheme 1, 2, and 3). Due to the structural complexity of the polycarbohydrates pre-treatment is required to disrupt the structure of lignocelluloses materials. The alkali treatment of RH and waste paper make cellulose soluble due to the formation of sodium salt[16,17] and separated it from other constituents. While the acid neutralization regenerates the insoluble cellulose with modified structure process of pure cellulose. The extracted cellulose was characterized using FT-IR and XRD pattern, which were compared either with the standard cellulose, or with the literature

FT-IR analysis of extracted cellulose

FT-IR is useful for several types of analysis such as identify unknown samples through absorption of functional groups, to confirm the acidic nature of samples, determine the quality or consistency of a sample and determine the amount of components in a mixture[18]. FT-IR of the extracted cellulose from waste RH, waste office paper and sugarcane compared with that of standard cellulose as shown in Figure 1. The FT-IR spectra of extracted cellulose from waste RH, waste office paper and sugarcane showed strong absorption at 3450-3425 cm⁻¹ which is attributed to O-H stretching vibration. This absorption band is composed of two vibrations located at 3285 cm⁻¹ (attributed to intermolecular hydrogen bonds) and 3335 cm⁻¹ (attributed to intramolecular hydrogen bonds). The peak absorbance band at 2918 and 2850 cm⁻¹ is attributed to –C–H symmetric and asymmetric vibrations. The O–H vibration of the pure cellulose shows absorption band located at 3353 cm⁻¹. The vibration band at 1649 cm⁻¹ in all samples is due to the O–H of water. The presence of this band indicates that the remaining water molecules were strongly bonded to cellulose macromolecules via hydrogen bonding. The vibration at 1429 cm⁻¹ in the pure cellulose is due to the –CH₂– group. This absorption band shifted to 1446 in both spectra of waste paper and sugarcane, while the waste RH showed different bands at 1512, 1461, 1425 cm⁻¹ which are attributed to the methylene groups. The vibration at 1163 cm⁻¹ is assigned for C–O–C stretching which appears almost simultaneously with the vibration located at 983 cm⁻¹ (attributed to β-linkage that present in the structure of cellulose). The vibration located at 1161 cm⁻¹ on the standard cellulose spectrum is assigned to the

Figure 1 : The FT-IR measurements for pure cellulose, extracted RH cellulose, waste paper cellulose and sugarcane cellulose
anti-symmetric bridge C–O–C stretching vibration[9]. The vibration band shifted to 1112 cm\(^{-1}\) in RH spectrum, 1116 and 1124 cm\(^{-1}\) in both waste paper and sugarcane respectively. From the FT-IR, most of the bands of the extracted cellulose are match well with that of the standard cellulose. This indicate that the cellulose was successfully extracted from the waste RH, waste paper and sugarcane and that sufficient removal of lignin and hemicelluloses was done from the used raw biomass

**Powder x-ray diffraction (XRD) of extracted cellulose**

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material (e.g. minerals, inorganic compounds) and can provide information on unit cell dimensions[20]. The X-ray diffractograms of the extracted cellulose in the present study is shown in Figure 3.2. Different peaks are observed in all samples at 2 Theta 16, 22.6, 27, 34.7 and 39. These are characteristic of the crystal polymorphs of cellulose. The peak at 2 Theta 16 corresponds to the (110), crystallographic peaks at 2 Theta 22.6 and 34.7 correspond to the (002) and (102) planes, respectively. The peak at 2 Theta 39 corresponds to the (004) planes. The crystallinity index obtained from X-ray diffractograms for the extracted cellulose was found to be 42.3 and 47.7 respectively. All these data are in agreement well with the literatures[21,22]. During the aggregation forming the microfibrils, realignment of monocrystals may occur, leading to the further increase of crystallinity of microfibrils obtained in this work.

**CONCLUSION**

Utilization of waste biomass as renewable resource for energy and chemicals has the potential to contribute to a cleaner environment. It can reduce the need for fossil fuels and chemical products, while reducing the environmental pressures associated with the disposal of waste materials. Agricultural wastes and biosolids contain large quantities of lignocellulosic constituents could be converted to value-added products. Throughout the current study cellulose which has many industrial and medical applications, was extracted efficiently from three types of waste (Rice husk, sugarcane and waste office paper). Rice husk, sugarcane and waste office paper as a source for cellulose was used in an attempt to utilize this unwanted wastes products from the rice milling and industry. The FT-IR and XRD clearly show that the method which followed in this work to extracted cellulose could give a cellulose with properties in agreement well with the pure cellulose.

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