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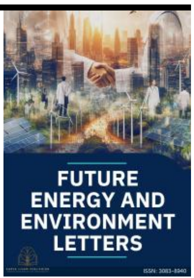

Utilising Cellulose Acetate Derived from Cotton Waste for Efficient Oil Removal in Water

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ABSTRACT

One of the most popular textile materials is cotton, and cotton waste makes up about 24% of all textile waste. For a thriving recycled cotton sector, recycled cotton has a high potential and suitable beginning material. The recycling of cotton waste offers a sustainable solution for its conversion into functional materials. Cellulose, a major constituent of cotton wools, was extracted and subsequently acetylated to produce cellulose acetate, which served as an oil adsorbent. This study aimed to extract cellulose from cotton waste and functionalise it through an acetylation process, resulting in cellulose acetate for oil adsorption applications. The methodology involved bleaching used cotton with hydrogen peroxide, followed by hydrolysis with sulphuric acid to obtain cellulose. Acetylation was then performed using acetic acid to synthesize cellulose acetate. The resulting products were characterized using infrared spectroscopy to confirm functional groups, thermal analysis to determine thermal stability, and powder X-Ray diffraction to observe crystallinity. The cellulose acetate exhibited a broader range of decomposition temperature compared to the unfunctionalized cellulose. The effectiveness of cellulose acetate as an oil adsorbent was evaluated by testing its ability to remove engine oil from water. A noticeable increase in the mass of cellulose acetate before and after the oil adsorption process underscored its efficacy in removing oil from water surfaces. In conclusion, the synthesis of cellulose acetate from cotton waste proved to be a cost-effective and recyclable alternative for oil removal from water surfaces, presenting a viable solution for addressing environmental pollution concerns.

1. Introduction

The resulting episodes of offshore oil spills, organic chemical spills, and direct discharge of industrial oil-containing effluent are increasing in frequency and causing irreparable harm to the ecosystem [1]. Cellulose-based substances can be employed as adsorbents, flocculants, and oil/water separation membranes for the treatment of water; and one of the best ways to deal with oil contamination is physical adsorption [2,3]. Consequently, it is essential to create materials with a high capacity for adsorption, low cost, and high recyclability [4]. Around 90 million tons of textile

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waste are produced worldwide each year, of which 30 million tons have been released into the environment [5]. Less than 1% of all textiles are recycled back into clothes, 25% of textile waste is reused or recycled, and 75% of textile trash is disposed of in landfills globally [6].

Cotton is a staple fibre that envelops the seeds of cotton plants like a shell. Cotton is the most important natural fibre in the textile industry, making up roughly half of all natural fibres and one of the most popular textile materials. Cotton waste also makes up around 24% of all textile waste. For a thriving recycled cotton sector, recycled cotton is a suitable and promising beginning material [7-9].

Acetylation of the plant substance cellulose results in the synthetic molecule known as cellulose acetate which is one of the most important polymers generated from plants - found in inedible plants [10]. In industry, cellulose acetate can be made into textile fibers such as acetate rayon, acetate, or triacetate. The compound also can be melted or softened by heat, or they can be dissolved in specific solvents, allowing them to be spun into fibers, molded into solid things, or cast as films [11]. In soil and ocean, cellulose acetate is extremely biodegradable. Although cellulose acetate is regarded as an environmentally beneficial substance, its chemical alteration affects (bio)degradability in natural settings.

Oil booms, skimmers, sorbents, burning in-situ, dispersants, and bioremediation are some of the numerous techniques used to remove oil from water [12,13]. One of the most economical and efficient ways to clean up an oil spill is to use absorbent material. Approximately 6% of the world's total production of solid waste created waste material is currently produced in China, which produces 26.0 million tons of textile waste, followed by the US (15.1 million tons) and the UK (1.7 million tons) [7]. When compared to modified cellulose, cellulose's adsorption capability is lower. Acetic acid modification of cellulose acetate results in a greater adsorption capacity than cellulose alone. The largest pore size, superior hydrophobicity, and wettability of cellulose acetate enable it to absorb oils and organics in water due to its increased absorbency.

Waste cotton is an abundant and low-cost resource. Its conversion to cellulose acetate for use in oil removal applications optimizes the use of already-existing materials and supports a circular economy. Although cellulose acetate has been extensively researched and shown to be useful in a number of environmental applications, the majority of current research focusses on how it is made from primary cellulose sources. Limited research has explored the use of post-consumer waste materials, such as used cotton, for producing cellulose acetate, despite the potential to address two pressing issues: textile waste management and the need for cost-effective adsorbents for oil spill remediation. By assessing the viability of turning used cotton into cellulose acetate and assessing its efficacy as an oil adsorbent, this study fills this gap and promotes waste valorization and environmental sustainability. Thus, the objective of this research is to prepare cellulose acetate by extracting cellulose from cotton waste for oil removal study. The synthesized cellulose acetate was characterized using infrared spectroscopy, thermogravimetric analysis (TGA), and X-ray diffraction (XRD) to determine its functional groups, thermal stability, and crystallinity, respectively. The sorption capacity and reusability of the cellulose acetate were then evaluated for oil removal study.

2. Methodology

2.1 Material and Chemical

This experiment used 30% hydrogen peroxide, 30% sulphuric acid, acetic acid, sodium hydroxide, hydrochloric acid, deionized water, and distilled water. Two types of cotton were utilized: one was brand-new and acquired from a nearby store, and the other was worn cotton (or waste cotton) from everyday use.

2.2 Bleaching and Hydrolysis of Cotton

The bleaching and hydrolysis of cottons methods were adapted from Rashid *et al*., [14] following the procedure as described [14]. The cottons were bleached with 150 mL of 30% hydrogen peroxide at room temperature for 1 hour. The bleached pulp was washed repeatedly using distilled water. After being vacuum-dried at room temperature, 3 g of bleached pulp was added to a beaker containing 120 mL of distilled water. The mixture was then stirred magnetically for 20 minutes at 250 rpm.

2.3 Hydrolysis of Cotton

Cottons were hydrolyzed using sulphuric acid at 30% v/v concentrations. The experiment was carried out in a 500 mL Erlenmeyer flask with 1 g of bleached cotton and 300 ml of sulfuric acid. For 90 minutes, the mixture was continuously stirred at 250 rpm. To stop the hydrolysis process, cold distilled water was added to the mixture. The resulting residues were dried at 50°C for 24 hours after being repeatedly cleansed with distilled water to achieve neutral pH (pH 6-7).

2.4 Acetylation of Cotton-Derived Cellulose

2 g of cellulose was added to a flask containing 70 mL of distilled water to start the acetylation process, and the mixture was then stirred to create slurry (pH 8). The mixture was combined with 4.8 mL of acetic acid and stirred continuously for one hour at 40°C. HCl was added to stops the process after 30 minutes. The acetylated cellulose was continuously rinsed in distilled water until the pH balances out, and was then dried at 50°C. The general illustration for hydrolysis and acetylation is shown in Figure 1.

2.5 Characterization of Extracted Cellulose and Cellulose Acetate

Characterization using Fourier transform infrared spectrophotometer was recorded at wavenumber of 4000 - 650 cm^{-1} to examine the functional group. Thermogravimetric analysis (TGA) was used to determine the weight loss of the product and their thermal stability. The temperature range was 30°C to 600°C, and the heating rate is 10°C/min. X-ray diffraction (XRD) patterns were used to identify the crystal structure and phase compositions of products. X-ray diffraction (XRD) spectra were recorded using the X-ray source Cu Kα. The intensity was determined in a 2θ angular range between 10° and 80°.

2.6 Saturated Adsorption Capacity

The oil adsorption experiment was conducted at room temperature. An important indicator for adsorbent materials is their saturation adsorption capacity (*Qm*). After weighing the mass of cellulose acetate (initial mass - *Mi*), the sample is immersed in 1 mL of engine oil. The sample was removed with tweezers after five minutes, and the area was then thoroughly cleaned with a non-woven fabric. The final mass of the cellulose acetate (*Mf*) was recorded.

Table 1 (as in Section 3.2) shows the initial and final masses (*Mi* and *Mf*, respectively) of cellulose acetate during this study. Then, *Qm* was obtained using the following equation:

$$Q_m = \frac{M_f - M_i}{M_i} \tag{1}$$

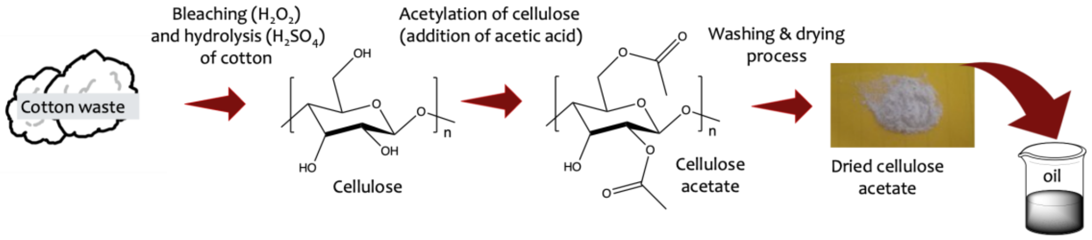

Fig. 1. Illustration of general procedures in this study

3. Results

3.1 Characterization of Extracted Cellulose and Cellulose Acetate

Figure 2 shows the IR spectra, TGA curves and X-ray diffraction spectra of cellulose and cellulose acetate. The extracted cellulose from cotton waste and cellulose acetate had vibrational frequencies for OH (~3335 cm^{-1}), and CO (~ 1640 cm^{-1}) (see Figure 2(a)). Wavenumber 3336.36 cm^{-1} absorption band attributed to OH vibrations. A strong connection between water and cellulose is indicated by an absorption band about 1640.85 cm^{-1}. A wider OH vibration absorption band and a downward wavenumber shift were observed after the acetylation procedure (3335.11 cm^{-1}) [15].

The thermal degradation of cellulose and cellulose acetate from new and old cotton was investigated using TGA. The TGA curve in Figure 2(b) depicts the sample's weight decrease – in which exhibited the typical profile expected for cellulosic materials [16,17]. While cellulose (extracted from used cottons) and cellulose (from new cottons) showed two-step decomposition, both cellulose acetate samples prepared from the waste and new cottons demonstrated three-step decomposition as reported previously [18]. In the temperature range of 30 - 95°C, cellulose (extracted from used cottons) and cellulose (extracted from new cottons) showed initial weight losses of 5.03 and 2.45%, respectively, which were linked to moisture removal followed by breakdown at 115 and 100°C. At 600°C, TGA of cellulose (extracted from used cottons) and cellulose (extracted from new cottons) revealed weight losses of 75.48 and 73.50%, respectively. This result suggested that cellulose contains certain non-volatile components.

At range of 30 - 102°C, the TGA of both cellulose acetates from cellulose (extracted from used cottons) and cellulose (extracted from new cottons) revealed weight losses of 12.01 and 8.08%, respectively. The primary cause of the weight losses in the first phase is the evaporation of water that is physically bonded inside the cellulose framework. Compared to cellulose, its porous structure caused significant weight losses. Weight loss of 36.14 and 32.36% at 378 and 227°C represent how the major chains of cellulose acetate deteriorate when heated, and weight loss of 32.84 and 32.89% at 600°C maybe caused by ash formation. From this analysis, the prepared cellulose acetate demonstrated higher thermal stability up to 600°C compared to the cellulose sample. Higher degrees of acetylation tend to increase stability [19].

Peaks at 2θ = 14.91 and 22.69° were observed in the X-ray diffraction spectra (see Figure 2(c)), as was previously reported [20]. The sharp peaks represented high crystallinity of the cellulose acetate powder. The observation of the same XRD patterns (with identical peak positions and sharpness) for both new and recycled cottons suggests that recycling did not significantly alter the crystalline structure of the cellulose acetate derived from the cottons. This implies that recycled cotton retains similar structural integrity and crystallinity to new cotton, making it a viable source for cellulose acetate production.

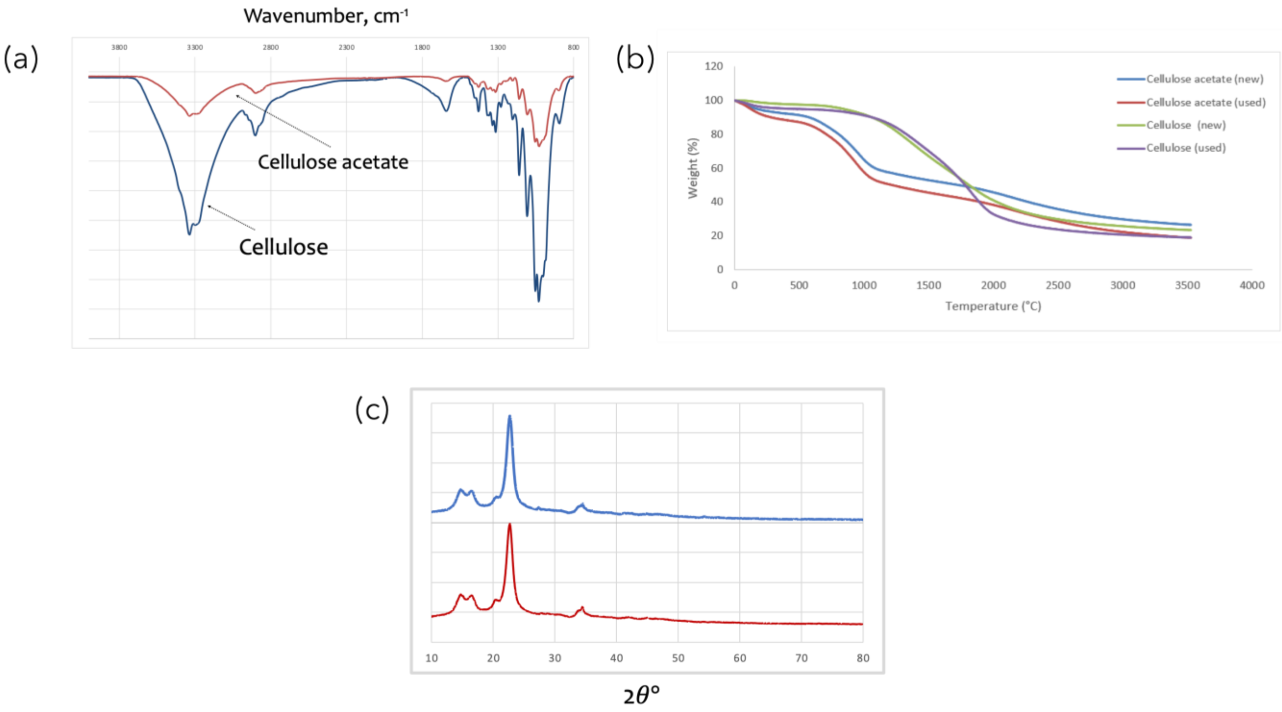

Fig. 2. (a) IR spectra of cellulose (extracted from cotton waste) and cellulose acetate showing vibrational frequencies for OH (~3335 cm^{-1}), and CO (~ 1640 cm^{-1}); (b) TGA curves of cellulose and cellulose acetate prepared used and new cottons; and (c) X-ray diffraction spectra of cellulose acetate prepared from cotton waste (blue) and from clean new cotton (red)

3.2 Oil Adsorption Study

The evaluation of adsorbent materials' effectiveness relies significantly on their saturation adsorption capacity. Table 1 summarizes the adsorption capacity of cellulose acetate derived from both new and used cotton. The saturation adsorption capacity (calculated based on Eq. 1) of cellulose acetate from used cotton was measured at 0.1233 ± 0.0108 g/g, whereas that from new cotton was 0.2379 ± 0.0061 g/g (see Figure 3). The lower saturation adsorption capacity observed in cellulose acetate derived from used cotton, despite having similar crystallinity, probably attributed to the residual substances present on the used cotton fibers. These substances, such as oils, dirt, or detergents absorbed during prior use, can interfere with the adsorption process by partially blocking the pore structure or active sites of the cellulose acetate. Furthermore, these residuals could alter the surface energy or chemical properties of the polymer, reducing its ability to interact effectively with oils and organics.

To understand this oil adsorption mechanism, it is crucial to understand the structural alteration that occur when cellulose is acetylated. Cellulose acetate has a partially hydrophobic nature due to its acetyl groups, making it oleophilic (oil-attracting or hydrophobic). This characteristic makes it easier for oil molecules to adsorb by promoting interaction with non-polar oil chains and repelling the more polar water. Its oil adsorption capabilities are significantly improved by this hydrophobic alteration [21]. In addition, the adsorption process also involves weak van der Waals forces, hydrogen bonding (from residual hydroxyl groups), and other molecular interactions between cellulose acetate and oil molecules.

Table 1
The evaluation of cellulose acetate derived from used cotton and new cotton materials

	Initial mass, M_i (g)	**Final mass, M_f (g)**	**Mass difference (g)**
Cellulose acetate (from used cotton) (n = 3)	0.1983	0.2243	0.0260
	0.1995	0.225	0.0255
	0.1965	0.2183	0.0218
	Average		0.0244 ± 0.0023
Cellulose acetate (from new cotton) (n = 3)	0.1636	0.2015	0.0379
	0.1649	0.2051	0.0402
	0.1603	0.1985	0.0382
	Average		0.0388 ± 0.0013

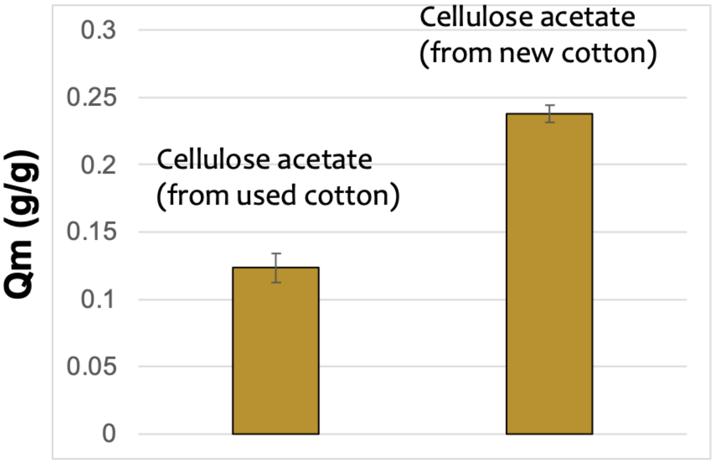

Fig. 3. The saturation adsorption of cellulose acetate on oil removal in water

4. Conclusions

The preparation and characterization of cellulose acetate from new cottons and cotton waste were successfully achieved. The synthesized compounds were characterized using infrared (IR) spectroscopy, X-ray diffraction (XRD), and thermogravimetric analysis (TGA). IR analysis confirmed the acetylation of cellulose, with characteristic functional groups indicating successful synthesis from both new and used cottons. XRD analysis revealed no significant differences in crystallinity between cellulose and cellulose acetate, nor between cellulose acetate derived from new and used cotton, indicating structural integrity was maintained across sources. However, the evaluation of adsorption effectiveness highlighted that cellulose acetate from used cotton exhibited a lower saturation adsorption capacity (0.1233 ± 0.0108 g/g) compared to that derived from new cotton (0.2379 ± 0.0061 g/g). The statistically significant difference between the two adsorbents, likely related to the source used to prepare them. Overall, the findings demonstrate that cellulose acetate from cotton waste retains comparable structural properties and offers potential for environmentally sustainable applications, particularly in pollution reduction, though pre-treatment to remove residual contaminants may enhance its adsorption performance.

Future research on hydrophobic cellulose acetate needs to focus on carrying out a comprehensive assessment of the environmental impacts associated with the production, consumption, and disposal of waste-derived cellulose acetate. This is essential to comprehend the broader implications of this strategy and ensuring that its application is aligned with sustainable and environmentally responsible practices. Future research comparing cellulose acetate to other adsorbents, such as polypropylene, activated carbon, and natural fibres (such rice husks), can yield important information. Although activated carbon is effective, its cost and capacity for regeneration are constrained. The potential benefits of cellulose acetate are highlighted by the fact that polypropylene is not biodegradable and that natural fibres frequently need to be chemically modified. To broaden its range of applications, cellulose acetate can also be combined with other functional changes. To create materials with both hydrophobic qualities and photocatalytic activity, for instance, inorganic particles possessing photocatalytic qualities might be chosen as modification additives.

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