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Investigation of the Physiochemical Structure and UV Absorption Properties of Cottonseed Hull and Kernel

Rechana Remadevi[1] & Stuart Gordon[2]

[1] School of Engineering, Deakin University, Geelong, Australia

[2] CSIRO Agriculture and Food, Waurn Ponds, Victoria, Australia

Correspondence: Rechana Remadevi, School of engineering, Deakin University, Geelong, Australia.

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Abstract

This work has investigated the morphology, chemical structure and UV absorption properties of cottonseed hull and kernel, as part of an assessment of these materials for use as potential UV absorbing and/or medical compounds. The morphological analysis of the samples revealed that cottonseed kernel has a porous and homogenous morphology. By comparing the FTIR of cottonseed hull and kernel, it was found that the kernel sample has more polyphenol groups. Moreover, an examination of the UV absorption spectra showed the kernel tissue had stronger absorption spectra in both the UVA (320-400nm) and UVB (290-320nm) regions than material from the hull. Thus, the present study demonstrated that the cottonseed kernel could be a promising source of natural UV absorber.

Keywords: cottonseed kernel, porous morphology, natural UV absorber, polyphenols, UVA and UVB absorption

1. Introduction

Prolonged exposure to ultraviolet radiation is hazardous and can cause skin cancer. With the use of sunscreen products, it is possible to protect the skin from harmful ultraviolet radiation (Lowe, 2006). Based on the physical and chemical sunscreen components, there are two categories of sunscreen products available in the market: physical sunscreens and chemical sunscreens. In the majority of the physical sunscreens, the active ingredients are mainly zinc oxide (ZnO) and titanium dioxide (TiO_2). The major drawbacks with the physical sunscreens are related to the dryness caused to the skin and the breathing difficulty for the skin cells (Lewicka et al., 2011). The manufacturing of the ZnO and TiO_2 nanoparticles for cosmetic production also involves toxicity concerns. The dust produced with the nanoparticle production of these metal oxides can cause lung problems, i.e., the concentration of the nanoparticle in the lung alveola can be increased and can be absorbed in the bloodstream (Schneider & Lim, 2019). In the case of the chemical sunscreens, the main ingredients are synthetic chemicals. Prolonged use of chemical sunscreen can cause side effects on the skin (Butt & Christensen, 2000). Thus, the development of organic ingredients able to protect skin from UV radiation has therefore attracted significant interest.

Ensuring dermatological safety and at the same time meeting demands of an organic ultraviolet absorbing attribute has created a huge interest in the natural UV absorbing compounds. The lighter molecular weight polyphenols from cottonseed meal are of particular interest. These are ubiquitous plant secondary metabolites, and as extracted compounds have properties with numerous implications and the potential for exploitation in various domains of public and commercial interests. Many studies have shown the beneficial effects of plant polyphenols in skin photo-protection, including direct reduction of photo-carcinogenesis in laboratory animals as a result of polyphenolic compounds (Afaq & K Katiyar, 2011; Saric & Sivamani, 2016). Driven by the medicinal applications of polyphenolic compounds, research on the extraction of polyphenolic compounds from natural materials is one of the growing areas within medical research. Polyphenolic extraction from grape seeds, green tea and tamarindus indica seed coat were extensively studied (Cao, Sethumadhavan, & Bland, 2018; Kallithraka, Garcia-Viguera, Bridle, & Bakker, 1995; Pan, Niu, & Liu, 2003).

Cotton (*Gossypium hirsutum* L.) is an important crop that yields the natural fibre used by the textile industry. Cotton production generates two major marketable products; lint (fibre) and seed (oil and meal). The protein rich cotton seed residue produced after cotton oil extraction is called cottonseed meal. Cottonseed meal has around

45-55% of crude proteins with a considerable quantity of amino acids (Kumar et al., 2022). The meal after oil extraction is mainly used as animal feed. However, the gossypol content of the cottonseed meal is a major concern when it's used as an animal feed.

Cottonseed is an abundant source of polyphenol and is a potent natural biomolecule that can be utilised in pharmaceutical, cosmetic, and other industries. Gossypol is one of the major polyphenolic compounds contained in the cottonseed and there are studies reported on the antioxidant, antifertility, antiviral, antiparasitic- protozoan and antimicrobial activities of the gossypol (X. Wang, Howell, Chen, Yin, & Jiang, 2009). The utilisation of the cottonseed meal as a component in food depends on the percentage of the gossypol content. The Food and Drug Administration (FDA) accepted quantity of the cottonseed meal with gossypol content is less than 0.8%. Hence, most of the work in the cottonseed meal is focused on the reduction of gossypol content in the cottonseed meal (Ma et al., 2018). The traditional cottonseeds are glanded cottonseeds. This glanded cottonseed has a higher content of gossypol content (3.75g/kg) (He, Nam, Zhang, & Olanya, 2022). The yellow pigmented gossypol has a 518. 55 Dalton molecular weight and is soluble in the water-hexane mixture, acetone, chloroform, ether, and butanone (Gadelha, Fonseca, Oloris, Melo, & Soto-Blanco, 2014). There is a range of potentially higher-value compounds that could be exploited from the seed meal, which contains cellulose, proteins, lignin and other smaller phenolic compounds.

Cao et al have reported that the polyphenols from cottonseed might help in reducing human cancer cell growth (Cao et al., 2018). Furthermore, it's well known that polyphenolic system has a higher UV absorption (i.e., through effective pi-conjugation, orbital (de)localisation and mesomeric (+M) effects of the hydroxyl moieties play a major role in the ultraviolet absorption) (Gierschner, Duroux, & Trouillas, 2012). Gossypol is one of the major polyphenolic compounds contained in the cottonseed, it has carbonyl and phenolic hydroxyl groups as well as its bulky binaphthalene structure (X. Wang et al., 2009).

There have been no reports on the UV absorption of seed material. Hence, the main objective of this study was to explore the UV-absorbing ability of cotton seed kernel and hull. In this work, the hull and kernel were separated from the cottonseed and examined for its physical and chemical properties. The separated hull and kernel samples were powdered with a pulveriser. The powdered kernel and hull samples were characterised by examining the morphology under electron microscopy, by particle size analysis, chemical structure by FTIR and by the UV absorption characterisation using the UV-Vis-NIR spectrophotometer.

2. Materials and Methods

2.1 Materials

The cottonseed sample assessed in this work came from commercially grown Australian Upland cotton (*Gossypium hirsutum L.* variety Sicot 73) grown in southern NSW during the 2018/19 growing season. The cottonseed sample was obtained just after ginning, which occurred three months after harvest. The cottonseed has been kept in the gin yard as per industry standard in a plastic wrapped module (at <12% moisture). Between sampling at the gin and this study, the cottonseed was stored in dark, dry conditions.

2.2 Methods

2.2.1 Sample Preparation

Cottonseeds were immersed in water for three hours and were then carefully dehulled manually to obtain the whole kernel and hull fractions. The separated hull and kernel were de-linted (removed the fibres from the surface) and dried in a conventional oven at 50 degrees for five hours to remove the water content from the seeds. Then the seeds were powdered using a rotary cutter mill (Pulverisette 19, Fritsch GmbH, Germany).

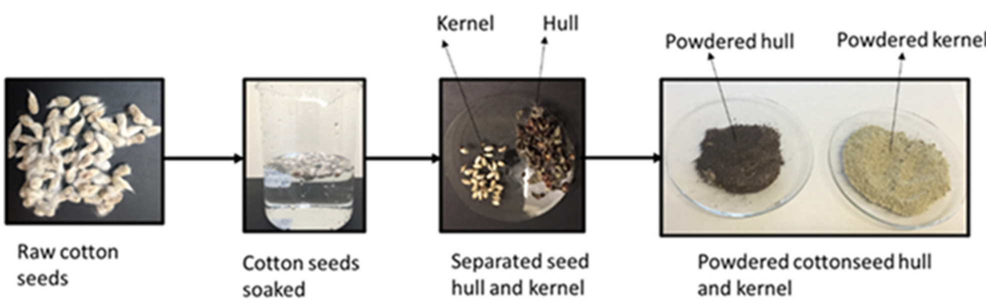

Figure 1. Sample preparation

2.3 Characterisation

2.3.1 Analysis of Morphology

The morphology of the hull and kernel samples was analysed using a scanning electron microscope (SEM). The samples were gold sputter-coated (Leica EM ACE600) followed by imaging under a Zeiss Supra 55vp scanning electron microscope at 3 kV accelerating voltage. Several fields were examined to ensure representative images were recorded.

2.3.2 Particle Size Measurement

The particle size of the milled hull and kernel samples were measured using the dry unit of the Mastersizer 3000 with an air pressure of 0.5 bar. This method was validated, by titrating air dispersion pressure against change in measured size distribution. The volume-based particle size distributions were recorded. The values presented are the average of at least three determinations.

2.3.3 Analysis of the Chemical Structure

The Fourier-transform infrared (FTIR) spectra analysis of all the powdered samples was completed under the Attenuated Total Reflectance (ATR) mode using the Vertex 70 (Bruker, Germany) spectrometer with a scan resolution of 4 cm-1 and 32 scans per sample between 400 cm^{-1} and 4000 cm^{-1}. Data were collected after baseline correction by OPUS 5.5 software.

2.3.4 UV Absorption Analysis

A UV-Vis-NIR spectrophotometer (Cary 5000 Scan, Varian Inc., Palo Alto, CA, USA) was used to test the UV absorption of the powdered cottonseed hull and kernel samples with a scan rate of 600 nm/min. The wavelength of the light beam ranged from 200 nm to 800 nm. The spectrophotometer consists of a 110 mm diameter integrating sphere, featuring an inbuilt high-performance photomultiplier. Each powder sample was placed in a powder cell specifically designed for the instrument. Initially, a baseline was recorded using a polytetrafluoroethylene (PTFE) reference cell covering the reflectance port. The sample is then mounted over the port and the reflection of the sample surface is collected by the sphere. The reflectance is therefore measured relative to the PTFE disk. The diffuse reflectance measurements were converted into absorption (arbitrary units) using the Kubelka–Munk function see Eq (1):

$$(f\,(R) = (1 - R)^2/2R) \tag{1}$$

3. Results and Discussion

The morphology of the cottonseed hull and kernel were examined under the scanning electron microscope. From the electron micrographs, it was found that there were fine fibres on the outer layer of the hull. The hull outer layer looks more irregular and heterogeneous (Figure 2a and Figure 2b). However, the inner side has a smoother surface than the outer side and there were no fibres (Figure 2c and Figure2d).

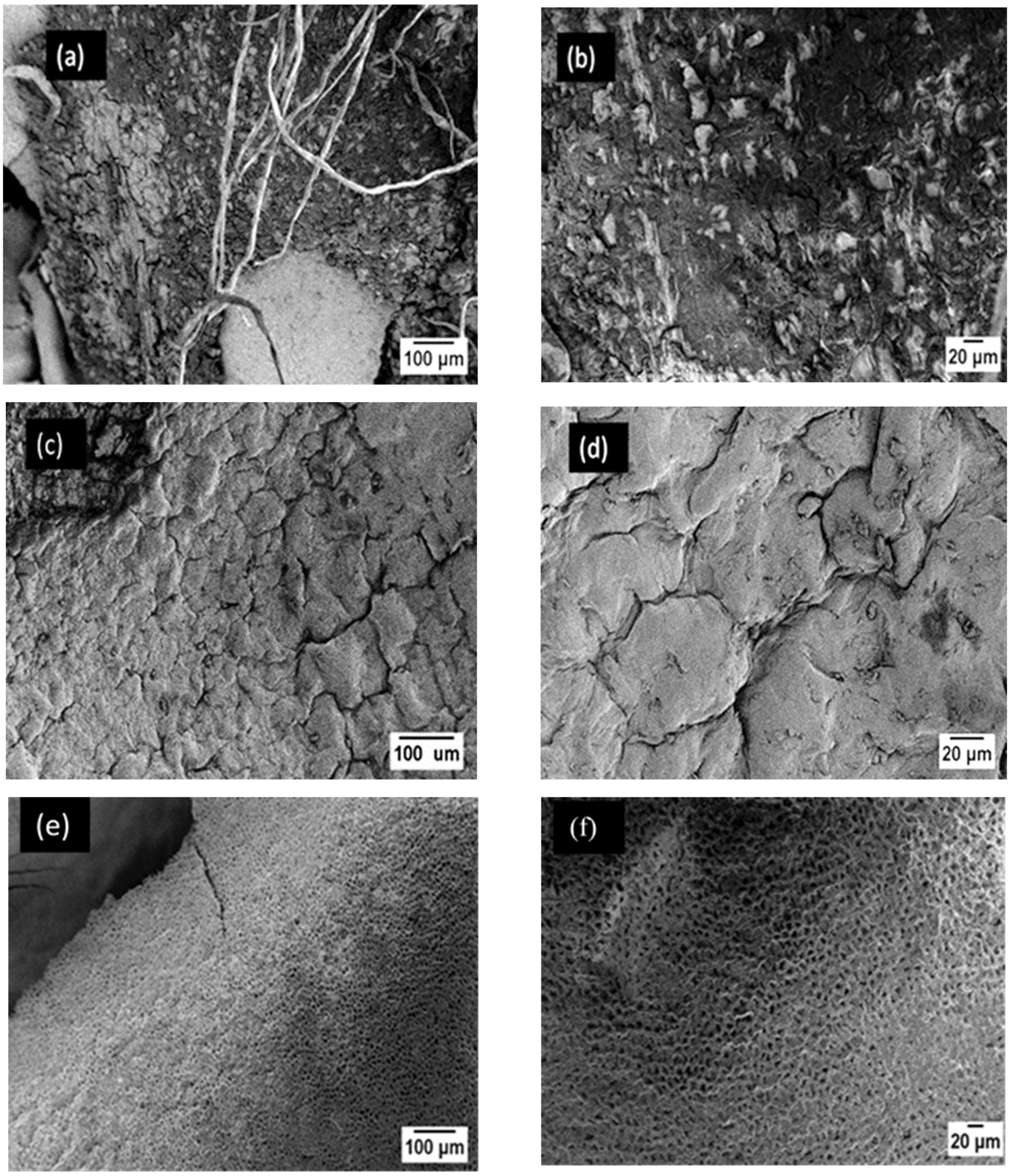

Figure 2. (a)(b) Cotton seed hull outer surface (c)(d) cotton seed hull inner surface faced to the seed kernel (e)(f) Cotton seed kernel

The morphology of the cottonseed kernel was entirely different from the hull. The kernel material was more porous, and the pores were uniformly distributed on the surface (Figure 2e and Figure 2f).

The Fourier-transform infrared spectroscopy (FTIR) was used to investigate the chemical structure of the samples (shown in Figure 3).

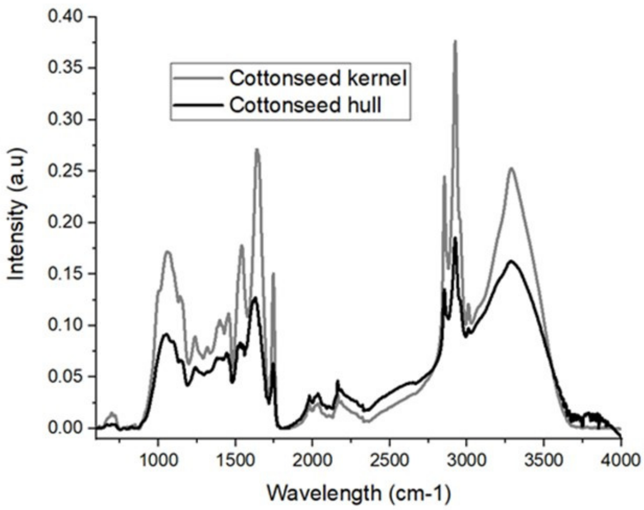

Figure 3. FTIR analysis of cotton seed kernel and seed hull

Table 1. Summarises the FTIR peaks of the samples

FTIR band (cm-1)	Assignment
3600 -3200	O-H vaibrations and N-H vibrations
2900-2850	C-H stretching vibrations
1743	C=O stretching vibrations etser group(from lipids and fatty acids of the seed)
1563	Bending vibration of N-H of amide II present in the protein part of the meal.
1456	Bending vibration of C-H from the protein
1380	In plane -C-H bending of phenyl
1107 – 1103	C-O-C pyranose ring skeltal vibration
1038	In plane -C-H bending of phenolic -O-H groups

Both samples have shown vibrational modes around 3600 -3200 cm^{-1}designated as the presence of -OH functional groups (X.-Q. Wang et al., 2017). In literature, it was reported that gossypol is giving bands at 3100-3600cm^{-1} region. The band at 3365 cm^{-1} for –OH was associated with phenol, and bands at 3130 and 3015 cm^{-1} were assigned as unsaturated and aromatic (phenyl) –CH vibrations (Mirghani & Che Man, 2003). The spectra at 2900cm^{-1} and 2850cm^{-1} were assigned mainly to C-H vibration bands from the aldehyde groups (X.-Q. Wang et al., 2017). The spectra at 2518, 1881, 1642,1551, 1492, and 1404 cm^{-1} are assigned to aromatic aldehydes, phenyl ring stretching, and –C–OH in-plane bending. The bands in the region 1750- 1650 cm^{-1} attributed C=O stretch in the carboxylic acid group. The peak near to 1160cm^{-1} related to beta-(1-4)-glycosidic bond cellulose (X.-Q. Wang et al., 2017).

The peak in the spectral region around 1107 cm^{-1} – 1103 cm^{-1} can be assigned to the C-O-C pyranose ring skeletal vibration (X.-Q. Wang et al., 2017). There were new peaks found in the cottonseed kernel's FTIR spectra. They were at 1380, 1106, 1038 and 830 cm^{-1} and which are assigned to the in plane -C-H bending of phenyl, phenolic -O-H and two adjacent phenyls. From the infrared spectroscopic analysis, it was found that the kernel sample has more phenolic rings in the structure.

The particle sizes of the samples are shown in Figure 4. From the results, it can be seen that the average particle size for the hull samples was 653 um and that of the kernel sample was 623 um. The result indicates that the kernel and hull powdered prepared with the pulveriser has almost similar particle size.

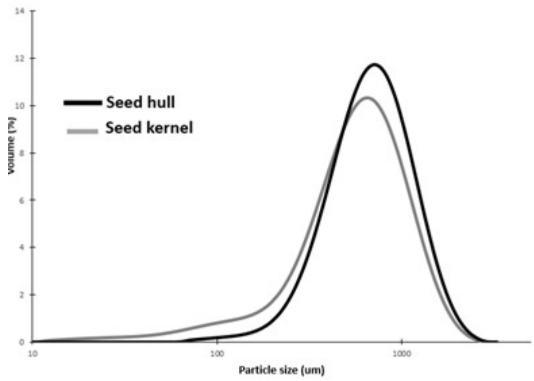

Figure 4. Volume-based particle size distribution of silk samples

These particles were used to study the UV absorption properties of the samples. Figure 5 shows the UV absorption spectra of both the cottonseed hull and kernel samples. It was found that the kernel sample exhibited absorption at 280 nm, 330 nm and 360 nm. These absorptions are due to the presence of polyphenolic compounds in the cotton kernel (Aleixandre-Tudo & Du Toit, 2018; J. Wang et al., 2016). The presence of polyphenolic compounds in the cotton kernel is evidenced in the infrared spectra of the kernel sample. Polyphenols compounds contain π conjugated systems with hydroxyl-phenolic groups.

The π type molecular orbitals electronic transitions provide the UV-visible spectrum of this group of compounds (Aleixandre-Tudo & Du Toit, 2018). From the UV absorption study, it can be seen that cottonseed kernel has given a strong UV absorption in both UVA (320-400 nm) and UVB (290nm-320nm) regions. However, the seed hull samples didn't show significant UV absorption.

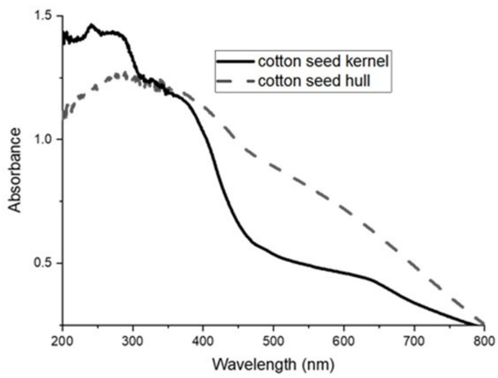

Figure 5. UV–VIS absorption spectra of cotton seed hull and kernel samples

It was reported that inorganic sunscreen blockers such as Titanium dioxide (TiO2) are more effective in UVB and Zinc oxide (ZnO) in the UVA range, so there is a combination of these two required for broader protection (Smijs & Pavel, 2011). The valence band of the TiO2 possesses several densely packed electron states, which allow many absorption possibilities, as long as the energy absorption exceeds the width of the bandgap. This is the reason TiO2 crystals absorb more in the UVB part while ZnO absorbs more UVA radiation, even though the ZnO bandgap energy exceeds that of TiO2. It was reported that the micro sized TiO2 is the most effective in UVB and micro sized ZnO in the UVA range, the combination of the two oxides only can provide the required broad band UV protection (Smijs & Pavel, 2011). The results obtained from this study showed that the cottonseed kernel microparticle has UV absorption in both UVA and UVB regions. Thus, cottonseed kernel is a prospective material to use as an organic UV absorber in the cosmetic industry.

4. Conclusion

This study demonstrates the morphology, chemical structure, and UV absorption of cotton seed material. The microstructure of the cottonseed kernel was different from the hull. The kernel material showed more porous, and the pores were uniformly distributed on the surface. The FTIR studies revealed that more phenolic groups were present in the kernel samples. The UV absorption studies of the samples showed that the kernel sample has an absorption in both UVA (320-400nm) and UVB (290-320nm) regions. The cottonseed kernel showed notable

UV absorption properties, this could be due to the higher polyphenol content. This work represents the first example of cottonseed in its separated form, which paves a new way for cosmetic applications in the field of organics UV blockers and opens potential application of cottonseed kernel as a useful natural UV shielding agent in the therapeutic industry. It is anticipated that the results from this research work will lead to the development of formulations for organic UV absorber material suitable for cosmetic applications. This is a novel introduction to the UV absorption ability of the cottonseed material which may find applications in future.

Declaration of Competing Interest

The authors declare that they have no conflicts of interest in this work.

Acknowledgements

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