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Cottonseed as a valuable source of oil and protein

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Abstract

Cottonseed a chief byproduct of cotton plant is a sustainable source of protein and oil. Globally ~10 million metric of plant protein is produced from cottonseed, which can fulfil the annual protein requirement of > half a billion people worldwide. Top five cotton producing countries are reported to be India, China, United States, Brazil and Pakistan. Cottonseed oil is largely cultivated worldwide and gained good reputation in global edible oil market due to its distinctive fatty acid profile including 18-24% of monosaturated, 26-35% of saturated and 42-52% of unsaturated fatty acid. Cottonseed protein is major plant-based protein with balanced amino acid composition and functional properties; however, the presence of toxic compound gossypol makes it unsuitable for direct human consumption. Cottonseed may be utilized in food industry as cooling oil and cattle feed as it has surpassed all nutritional quality standards mentioned by Food Safety and Standards Regulations, 2011 except lysine content, it also reported to have various application such as in cosmetics, and as biofuel.

1. Introduction

Cotton crop is a major source of natural plant fiber for textile industry cultivated globally in more than 80 countries and considered as important source of oilseed with approx. 25 million tons of production worldwide (Khan et al., 2022). Production of cottonseed oil rank 3rd in volume compared to corn and soybean oil with annual production approximately 4,50,000 tons (1 billion pounds) (Kumar et al., 2022a). Cottonseed is reported to have valuable coproducts such as 7% of linters, 22% of hulls, 50% of cottonseed meal and 16% of oil (Kumar et al., 2022a; Tan et al., 2022). Approximately 20% of cottonseed is utilized as cattle feed, 5% is processed by solvent extraction, 75% is processed using screw-pressing technique and the remaining is called cottonseed meal which contains approximately 45 – 55% of crude protein with balanced profile of amino acid (Cheng et al., 2020; Tan et al., 2022). According to Food and Drug Administration, cotton seed protein is considered to be safe for human consumption if it consists of 0.045% free gossypol or < 0.8% of bound gossypol (Kumar et al., 2021; Kumar et al., 2022a). Cottonseed can be of two types depending on amount of gossypol present i.e., glanded cottonseed which contain high amount of toxic compound gossypol (3.75 g/kg) and glandless cottonseed which contain trace amount of gossypol (0.06 g/kg) which is safe for human consumption (Delgado et al., 2019; He et al., 2022). According to Food Safety and Standards Regulations 2011, cottonseed can be utilized as an ingredient by food industry in preparation of various food items (Satankar et al., 2021; Kumar et al., 2022b). Cottonseed protein isolate is reported to have various properties such as surface hydrophobicity, high emulsifying abilities, water/oil absorption capacity and fluorescence intensity which shows its potential applicability in food industry (Ma et al., 2018; Kumar et al., 2022b). In this review, we have discussed the properties of cotton seed as promising source of protein and oil.

2. Cottonseed as a source of oil

Cottonseed serves as a dietary source of protein, oil, and minerals for human health and livestock feed. Cotton seed oil is mainly extracted from the kernel present inside the seed (Bellaloui et al., 2021). According to a study, cotton is largely cultivated for its fiber and for use as animal feed. It is also categorized as a polyunsaturated oil, having 70% unsaturated fatty acids. It has 20–25% palmitic acid, 2% stearic acid, 18–30% oleic acid, and 40–55% linoleic acid. Cottonseed oil is mostly used in food-related applications, including as a salad oil, for frying, to make margarine, and to make shortenings for cakes and biscuits (Fan and Eskin, 2015). While another study found that, Cottonseed oil has a P/S ratio of 2, is high in omega-6 fatty acids, free of linolenic acid, and moderately high in saturated fatty acids. Cottonseed oil contains fatty acids in the range of 21.4% to 26.4% (List, 2016). Moreover, Palmitic acid, oleic acid, and linoleic acid make up the three major fatty acids in this oil and have typical percentages of 22, 20, and 54, respectively. In cottonseed oil, PLL (27.5%), LLL (19%), POL (14%), and OLL (12.5%) are the four main triacylglycerols (Table 1). Malvalic and sterculic acids, often known as cyclopropenoid fatty acids, are two special kinds of fatty acids found only in cottonseed oil. Cottonseed oil is unique because it contains gossypol, a harmful polyphenolic compound. The most prevalent sterol in cottonseed oil is β-sitosterol. Tocopherols are abundant in cottonseed oil. About 1000 ppm of tocopherols are present in crude cottonseed oil, of which 41% and 58%, respectively, are β- and γ-tocopherols respectively (Ghazani and Marangoni, 2016). Furthermore, the fatty acid composition of cottonseed oil includes tiny levels of 2.33% stearic acid, 1% myristic acid, 0.6% palmitoleic acid along with 52.89% linoleic acid, 25.39% palmitic acid, and 16.35% oleic acids (Yang et al., 2019). Additionally, Cottonseed oil contains fatty acids it contains 70% unsaturated fatty acids including 18% oleic, 52% linoleic, and 26% primarily palmitic and stearic (Sundar et al., 2019). Cottonseed oil typically contains 65-70% unsaturated fatty acids, including 18-24% monounsaturated, 42-52% polyunsaturated, and 26-35% saturated fatty acids, with a polyunsaturated to saturated fatty acid ratio of 2:1 (Shahrajabian et al., 2020). In a different study, Unsaturated fatty acids (UFA) make up 72.45% of cotton seed oil's fatty acid composition, while saturated fatty acids (SFA) make up 24.96% of it. (Gutiérrez et al., 2020).

Table 1. Oil composition of cottonseed.

Source	Compound Identified	Yield/ Concentration	Reference
Cottonseed oil	Unsaturated fatty acids	70%	Fan and Eskin, 2015
	Palmitic acid	20–25%,	
	Stearic acid	2–7%,	
	Oleic acid	18–30%	

Source	Compound Identified	Yield/ Concentration	Reference
	Linoleic acid	40–55%	
Cottonseed oil	Fatty acids	21.4-26.4%	List, 2016
Cottonseed oil	Palmitic acid	22%	Ghazani and Marangoni, 2016
	Oleic acid	20%	
	Linoleic acid	54%	
	PLL	27.5%	
	LLL	19%	
	POL	14%	
	OLL	12.5%	
Cottonseed oil	Linoleic acid	52.89%	Yang et al., 2019
	Palmitic acid	25.39%	
	Oleic acids	16.35%	
	Stearic acid	2.33%	
	Myristic acid	1%	
	Palmitoleic acid	0.6%	
Cottonseed oil	Unsaturated fatty acids	70%	Sundar et al., 2019
	Oleic acid	18%	
	Linoleic acid	52%	
	Palmitic and Stearic acid	26%	
Cottonseed oil	Unsaturated fatty acids	65-70%	Shahrajabian et al., 2020
	Oleic acid	18-24%	
	Linoleic acid	42-52%	
	Palmitic and Stearic acid	26-35%	
Cottonseed oil	Unsaturated fatty acids	72.45%	Gutierrez et al., 2020
	Saturated fatty acids	24.96%	

3. Cottonseed as a source of protein

Worldwide, plants contribute about 70% of consumable protein (Alford et al., 1996; Bansode et al., 2022). Cottonseed protein has a lot of potential because it is more affordable and accessible than animal protein, and it can be easily introduced into the diet as a high-quality protein that will encourage growth (Kumar et al., 2021). Currently, more than two thirds of the world's population lack access to nutritious food, and protein malnutrition is the second biggest health issue after poor food availability (Tontisirin et al., 2002). Every day, 80,000 infants are born who will not live to be five years old due to malnutrition and starvation (Uchendu and Atinmo, 2011). In order to overcome this starvation and malnutrition, different protein sources must be made available. Given that cotton is grown in numerous developing nations, it can definitely contribute significantly to addressing these demands (Kumar et al., 2021). According to a report, from 2014-17 approximately 8.3 and 9.4 million metric tons of protein was available. Hence, seeds of cotton (*Gossypium hirsutum* L.) contain high-quality proteins (Balandrán-Quintana et al., 2019). For example, globulins (salt soluble) account for about 60-70% of seed proteins, regarded as the major dominant storage proteins in cottonseed, whereas gliadins (alkali soluble) and albumins (water soluble) are present in lower concentrations (Bellaloui et al., 2015). The major amino acid present in cottonseed is arginine (15-34% of total protein), followed by cysteine and methionine found in less amount (1-2%) (He et al., 2015) (Table 2). Cottonseed proteins have a high content of ionizable amino acids (aspartic and glutamic acids, histidine and lysine). These proteins are soluble at basic pH and are readily denatured by thermal treatment above 80°C. The increase in temperature triggers the Maillard reactions, involving interaction between gossypol and lysine (Buffo and Han, 2005). Cottonseed by-product, i.e., cottonseed meal remained after oil extraction is one of the commercial cottonseed protein sources. It contains about 33-41% protein and also harmful terpenoid which is cardio- and hepatotoxic for human and animal (Balandrán-Quintana et al., 2019). Various studies have been used to identify the advantages/disadvantages of adding cottonseed to the diet that how food preparation impact the nutritive value of cottonseed flour. Early researchers confirmed that cottonseed protein meal and flour were effective growth-promoting substances (Niu et al., 2021). Animals fed 9 and 18% calories from protein containing either 0, 50 or 100% cottonseed protein showed a calcium increase when casein was the sole protein source and a decrease when cottonseed was the only protein source (Alford et al., 1996). Glanded cottonseed fed to monogastric animals had been shown to reduce the oxygen-carrying capacity of the blood and result in shortness of breath and edema of the lungs (Cheeke, 2022). Gossypol is abinaphthyl, dialdehyde, polyhydroxyl pigment, which is highly reactive and deleterious to humans. In a study, an investigation was conducted to develop free-gossypol cottonseed (Sihag et al., 2021). Sunilkumar et al. (2006) used tissue-specific RNA interference technology to disrupt the production of gossypol to develop transgenic seeds with 99% reduction of gossypol content. However, transgenic seeds are found to be non-toxic, used as feed ingredient for shrimps (Richardson et al., 2016). Furthermore, Ma et al. (2018) produced cottonseed protein isolates (free gossypol content, 0.012%) utilizing various solvent extraction methods (hot, cold, and supercritical). Cold solvent extraction and supercritical fluid extraction produced isolates with good functional qualities (high emulsifying capabilities, high water/oil adsorption, and surface hydrophobicity), allowing them to be used as food additives. Proteins extracted from gossypol-free cottonseed meal could be employed as food additives in general. However, more research is required to reduce the toxicity of cottonseeds (Balandrán-Quintana et al., 2019). It was determined that cottonseed flour has protein efficiency ratio (PER) equivalent to that of casein. Fractionation of cellular proteins during isolate preparation produces favorable and unfavorable effects. The storage protein isolates are low in lysine and sulfur amino acids concentration and low protein quality. While on the other hand, non-storage protein isolated are high in protein quality (PER>2.5) and IAA. Edible cottonseed protein products, approved by the US FDA, have a maximum of 0.045% free‘gossypol (Gilani and Lee, 2003). Zhang et al. (2009) prepared protein isolates from defatted cottonseed meal via alkaline protein solubilization, followed by isoelectric precipitation. Optimized extraction conditions involving pH, temperature, stirring, solvent: defatted meal ratio results in 40-70% protein isolation (Zhang et al., 2009; He et al., 2013). In another study, an edible cottonseed protein concentrate (72.2%) was prepared using a two-solvent extraction method utilizing acetone in aqueous and anhydrous form (Gerasimidis et al., 2007). The gossypol reduction was about 65%, results in the formation of concentrate with higher oil and water absorption capacity than wheat flours and good foaming property. Cottonseed proteins are also used to synthesize protein-based films which can be utilized as edible items but not as packaging materials. The use of cottonseed protein has several advantages in the food processing arena (Buffo and Han, 2005). Cottonseed has more than four times the protein than whole wheat protein, has a low spoilage rate, and is economical. Furthermore, cottonseed's bland flavor does not mask other foods, and its chemical composition and light color are characteristics which are conducive to use in the formulation of foods with enhanced nutritive value (Buffo amd Han, 2005; Kumar et al., 2021).

Table 2. Amino acid concentration in cottonseed.

Source	Amino acid	Concentration/Yield	Reference
Cottonseed protein isolates*	Isoleucine	121-146	Gilani and Lee, 2003
	Leucine	95-120	
	Lysine	55-109	
	Methionine + Cystine	76-145	
	Phenylalanine + Tyrosine	140-152	
	Threonine	85-114	
	Tryptophan	109-134	
	Valine	143-149	
Glandless cottonseed flour (mg/gm protein)	Lysine	48	Alford et al., 1996
	Histidine	31	
	Arginine	130	
	Aspartic acid	110	
	Threonine	34	
	Serine	39	
	Glutamic acid	208	

Source	Amino acid	Concentration/Yield	Reference
	Proline	46.3	
	Half-cystine	28	
	Glycine	47	
	Alanine	45	
	Valine	46	
	Methionine	16	
	Isoleucine	35	
	Leucine	68	
	Tyrosine	31	
	Phenylalanine	64	
	Available lysine	45	
	Tryptophan	-	
Glandless cottonseed kernels (mg/gm protein)	Lysine	45	Alford et al., 1996
	Histidine	27	
	Arginine	121	
	Aspartic acid	91	
	Threonine	30	
	Serine	42	
	Glutamic acid	216	
	Proline	34	
	Half-cystine	12	
	Glycine	41	
	Alanine	39	
	Valine	44	
	Methionine	14	
	Isoleucine	30	
	Leucine	54	
	Tyrosine	29	

Source	Amino acid	Concentration/Yield	Reference
	Phenylalanine	54	
	Available lysine	41	
	Tryptophan	12	
Cottonseed meal protein isolate (%)	Arginine	8.6-13.2	Li et al., 2010; Tan et al., 2022
	Histidine	2.5-3.5	
	Isoleucine	3.6-4.1	
	Leucine	6.8	
	Lysine	3.5-3.7	
	Methionine	1.2-1.3	
	Phenylalanine	5.1-7.4	
	Threonine	3.2-3.7	
	Tryptophan	1.1	
	Valine	5.1-6.2	
	Alanine	4.1-6.1	
	Aspartic acid + Asparagine	9.7-9.8	
	Cysteine	0.4-2.0	
	Glutamic acid + Glutamine	19.6-22.1	
	Glycine	4.3-7.8	
	Proline	3.6-4.7	
	Serine	5.3-5.4	
	Tyrosine	1.7-3.0	
Cottonseed meal (%)	Alanine	3.8	Li et al., 2010
	Arginine	12.1	
	Asparagine	4.2	
	Aspartic acid	5.2	
	Cystine	1.9	
	Glutamine	10.2	

Source	Amino acid	Concentration/Yield	Reference
	Glutamic acid	11.7	
	Glycine	5.7	
	Histidine	2.9	
	Hydroxyproline	0.1	
	Isoleucine	3.2	
	Leucine	6.0	
	Lysine	4.4	
	Methionine	1.8	
	Phenylalanine	5.4	
	Proline	5.0	
	Serine	4.6	
	Tryptophan	1.2	
	Threonine	3.3	
	Tyrosine	2.9	
	Valine	4.5	
Cotton seed flour (%)	Alanine	4.1	Li et al., 2010; Cheng et al., 2020
	Arginine	13.6	
	Aspartic acid	9.9	
	Glutamic acid	22.3	
	Glycine	4.5	
	Histidine	3.2	
	Isoleucine	3.7	
	Leucine	6.3	
	Lysine	4.8	
	Methionine	1.4	
	Phenylalanine	6.0	
	Proline	3.9	
	Serine	4.5	

Source	Amino acid	Concentration/Yield	Reference
	Threonine	3.4	
	Tyrosine	3.4	
	Valine	5.1	
Cotton seed (*G. arboreum*: FDK-124, LD-1019, LD-949, LD-327) (g/100g)	Albumins	27.3	Singh and Kaur, 2019
	Globulins	49.6	
	Glutelins	16.3	
	Prolamins	6.6	

*=expressed as a percentage of the respective IAA in the FAO/WHO (1991) scoring pattern)

4. Conclusion and future perspectives

The utilization of raw byproducts generated by agro-industrial waste have attracted the attention of food industries towards production of bio-friendly, nutritious, and sustainable products which can be directly utilized in human diets. Cottonseed is reported to be abundant in basic amino acids associated with several bioactivities such as angiotensin-converting enzyme inhibitory activity, antioxidant, immune-modulatory and antimicrobial activity. Although cottonseed is sustainable source of edible oil and plant protein the presence of toxic compound gossypol makes it unsafe for consumption, which can be overcome by degossypolyzation of cottonseed to permissible limits (450 ppm) as per guidelines of World Health Organization and U.S. Food and Drug Administration.

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Cotton and Other Natural Fibre based Sustainable products for Futuristic Applications

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1. Introduction

Textile materials like jute, cotton, wood, papers, etc., all are highly flammable due to their cellulosic backbone. Various synthetic chemicals based on phosphorous and nitrogen are available on the market for the manufacture of flame retardant textiles. In most cases, a large quantity of chemicals has been used, in addition to formaldehyde gases are released during processing and also from the finished fabric [1,2]. Consequently, the sustainability of the process is one of the main problems in the production of flame-retardant textiles, so that they do not burn easily when used. Over the past few years, researchers have adopted various ways to manufacture durable and sustainable flame-retardant textiles. As part of our research, we explored for the first time the use of the plant biomolecule in the manufacture of fire-resistant natural fibre textiles. Three widely available plant-based bio-macromolecules that invariably go into waste are: banana (musa) pseudostem sap (BPS), coconut (cocos nucifera) shell extract (CSE) and pomegranate (punica granatum) rind extract (PRE) [3-5]. In our research covering a period of about 10 years, we chose them, systematically applied separately on cotton, jute, wool fabrics and critically studied for their flame-retardant properties. Encouraged by the initial success, research groups of India have improved our research to better understand the underlying principle and refined the application to maximize fire-retardant textile production.

Scientific research has revealed that pleasant smell has enormous effect on creating good moods and positive mental function [6]. Pleasant fragrance smell has positive effect on pain, concentration, memory, mood, romance, anxiety, sleep disorder etc., some of the pleasant fragrance used to make the human beings feel better and relaxed the stress level of brain and rejuvenate the body action [7]. Some of them are efficient to ease the migraine and headaches and assist to sleep. Overall pleasant smell has certain well-being effect on the human beings and it is very much essential in many useful places of our day to day life. Pleasant fragrance has essential importance in living room, car, office, bed room, washroom etc., In the market, different synthetic essential oil based (lavender, jasmine etc.,) fragrance pockets are available for the pleasant action [8]. a new natural fibre based fragrance pack has been prepared. Handmade paper based sheath material, cotton based non-woven core material and citronella essential oil have been explored for engineering of the fragrance pack. Mosquito repellency and the fragrance release behavior of the pack have been measured qualitatively and quantitatively by using various technical instruments and in depth scientific discussions are documented in the present context.

Generally natural leather is a collagen based animal hide, has been obtained after various chemical based processing of the skins of cattle, pig, goat, dog, horse, aviator etc. It is composed of keratin, other amino acids like alanine, glycine, arginine, proline etc., and these amino acids are joined by peptide linkages among themselves [9]. Natural leather has variety of end usage as it is well commercialize in the market for manufacturing of jacket, wallet, belt, seat cover, footwear parts, watch strap etc. Main advantages of using the natural leather are its breathable, partly water proof, crease free, resistance to fire, resistance to dry abrasion nature. However, in recent days, exploration of natural leather is gradually going down because of the involvement of unethical issue of animal killing. Besides, conventional leather processing require larger quantity of toxic chemicals like salt, quick lime, sodium sulphide (for liming process, removing hair from raw hide and skin), strong acids (for pickling), chrome metal salt (for tanning), etc. These chemicals are harmful as they increase the chemical oxygen demand (COD), biological oxygen demand (BOD) and total dissolved solid (TDS) level of water [10-12]. Moreover, high cost, some few fixed colours in the finished products, bad odour, not easy to cut or sew, batch to batch quality variation etc., are adding newer challenges in the field of leather technology. Therefore, development of artificial leather is getting attention for the industries and researchers. Different researches are going on for the improvement of the quality of artificial leather so that it can meet all the standards of natural leather based compound. Most of the artificial leathers composed of one natural or synthetic fibre based base fabric, are not sustainable. Therefore, for minimizing hazardous effluent problem of leather industries, minimizing animal killing issues and for lowering the usage of non-sustainable synthetic leathers made from polyurethane, polyvinyl chloride, sysnthetic rubber etc., a leather like flexible composite has been developed by using natural fibre and natural rubber (plant product) based formulations. Very few research works are reported on the exploration of natural ligno-cellulosic fibres (paper, pineapple fibre, hemp fibre etc) for making flexible composite material and no systematic scientific data has been reported in this regard [13,14] . To the best of our knowledge, till date, no research has been reported on the manufacturing of flexible composite from ligno-cellulosic ramie fibre and natural rubber based formulation. Developed product is almost resemblance of natural leather. Ramie fibre has high strength and fineness and may be suitable for making leather like flexural composite. Current context delivers a detail process of developing flexural composite and the physical, chemical and other useful properties of the developed product has also been registered systematically and compared scientifically with natural leather.

2. Flame retardancy of cotton textile by plant bio-molecule

Our research has revealed that the pomegranate rind extract (PRE) has the highest effect towards imparting flame retardancy to a cotton fabric, as compared to the other two extracts (namely, BPS and CSE) [15]. While the control cotton fabric showed a limiting oxygen index (LOI) value of 18, pomegranate rind extract (PRE) treated cotton fabric showed an LOI value of 32, in comparison to 27 and 30 for banana pseudostem sap (BPS) and coconut shell extract (CSE) treated fabrics, respectively with 25% loading on the fabric surface [16,17]. The physical significance of LOI is that it quantifies the minimum amount of oxygen required just to initiate burning of a cotton fabric and consequently, a higher LOI value indicates a higher non-flammability, i.e., simply put, improved fire resistance of a fabric. The thermal stability of the treated fabrics was assessed through a forced combustion test. Both the control and the treated cotton fabrics were subjected to combustion in a specially fabricated cone calorimeter machine with a heat flux of 35 kW/m^2, keeping in mind the susceptible minimum burning limit of the upholstery, curtain and other like home-furnishing textiles [18,19]. We were astonished at the outcome of the study. It was found that the average peak heat release rate of the 400g/L PRE treated fabric is half (45kW/m^2) compared to the peak heat release rate of the control cotton fabric (80kW/m^2) with no after-flame and afterglow. This implies that in case of an accidental fire, if we use the person's dress materials prepared by PRE application or make a tent with such fabric, the person can endure the miss- happening to a longer duration because of lower heat, and no after flame and afterglow, compared to the dress or tent made with the untreated pristine fabric. Similar observations can be made with CSE and BPS, showing their potential for self-extinguishing effect, when applied with 2-3% Sodium Tri Polyphosphate [20-22].

From the mass spectroscopy analysis, our research has also confirmed that the resulting fire retardancy of the bio-macromolecule treated cellulosic fabric can be attributed to the combined reaction effect of the phenolic source (polyphenolic tannin, gallic acid, ellagic acid, betacyanin, coumarin, etc.), carbon source (carbonic dihydrazide, nona hexacontanoic acid, 1 hydroxy 2 pentanone, sugar based material), blowing agent, nitrogen containing bases like guanidine, asparagine (amino acid of protein) etc., found in extracts from PRE. To confirm the formation of flammable gases, volatile gases released during the combustion of the treated fabrics were also analyzed by GC-MS [7-10]. It has been observed that the peaks (mass/charge) assigned to the levoglucosan andits derivatives (77, 65, 91, 162) are very less intensive in the smoke of the treated fabric, whereas smoke of the control cotton fabric shows flammable levoglucosan based components and tar like products, terpenoids, etc. It has been noticed that tannin based active ingredients of plant extracts blocks the primary –OH groups of cellulose and helps in aromatization of the cellulosic cotton fabric in increasing the carbon content in charmass, and restricts the flammable gas formation at higher temperature [11,12]. The mechanism reveals that mainly tannin based large molecular weight phenolic groups present in the bio-macromolecules, assist in the char formation and also restrict depolymerization of cellulose and the flammable gas formation, thus followed a condensed phase mechanism of flame retardancy.

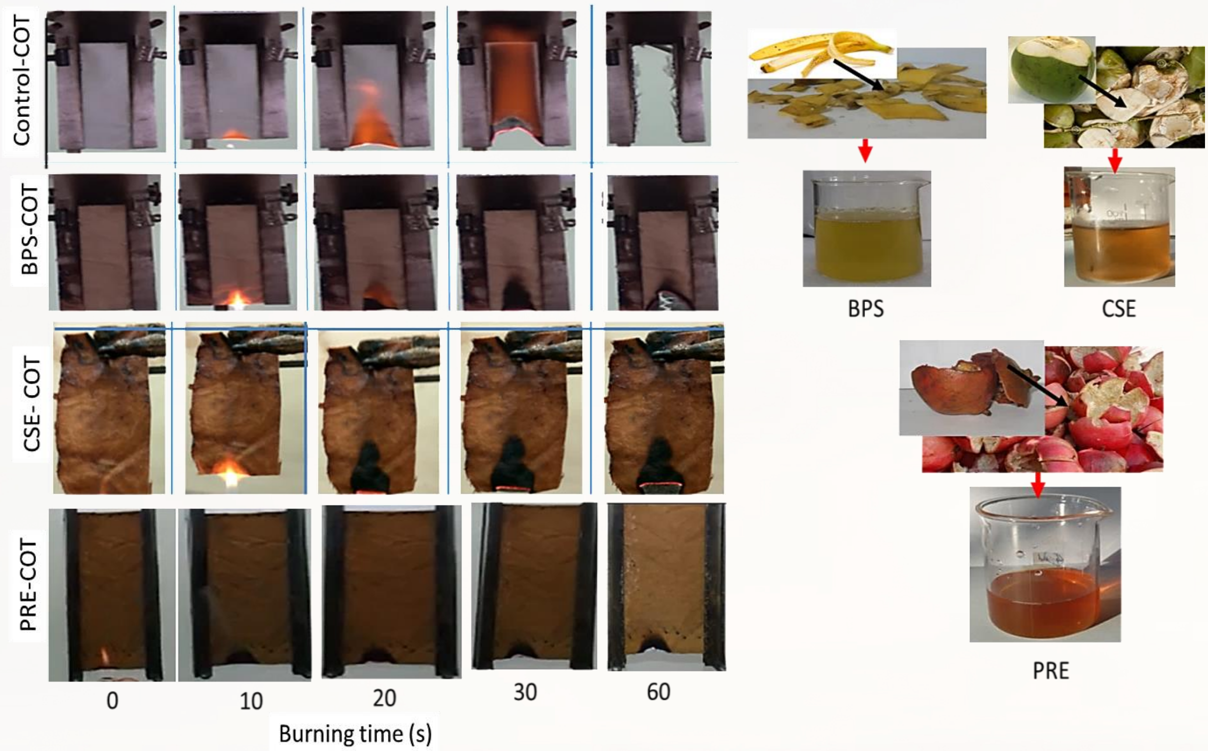

Fig 1. Flame retardant cotton fabric prepared from wastage plant extracts of banana peel, coconut shell and pomegranate rind [1-5].

2.1 Implementation of products or services using natural fibres

Fabrics made from natural fibres, like cotton and jute are used in hospitals and homes, as bed sheets and covers, table cloth, curtains, for packaging and in making non-permanent structures like pandals. Every year, a lot of fire related accidents happen, causing destruction of property and life throughout the world due to fire, as well as the toxic smoke and high temperature originating from the highly combustible cellulosic textiles. Bio-based flame retardant fabric of natural fibres can be used as home textiles, such as table cloth, sofa cover, curtains, mops, packages etc. For example, a bio-based flame retardant cotton fabric made curtain shows 70% higher LOI, no after flame and afterglow and thus, get self-extinguished within 2 min. In addition to it, toxic smoke composed of carbon monoxide, levoglucosan etc., and temperature generated during the combustion of the textile is also 60% lower as compared to the untreated normal fabric. The bio-based flame retardant treated fabric shows the success result with an add-on of 20-25% on the fabric surface at neutral pH. A small scale trial of 10 meter cotton fabric was also carried out on the winch machine in the laboratory of ICAR-CIRCOT. The treated fabric was found with good fire resistant property in terms of oxygen index (LOI: 29) and the secondary burning stopping within 1min. Our developed treatment was found effective not only on the cotton based textiles but also in jute, sisal, wool fibre made fabrics [23]

3. Natural Fibre based fragrance products

Three layers of non-woven have been used as core material or as essential oil holding material in the core. Citronella based natural essential oil has been incorporated uniformly in the middle non-woven layer of the cotton by using micro pippet. Thereafter, oil infused non-woven fabric has been guarded with other non-woven layers (same specification) in up and down side. Henceforth, the total sponge like non-woven arrangement has been packed inside the natural fibre made handmade paper as shown in Fig 1. In the total arrangement, cotton non-woven has been acted as core material and the handmade paper of different porosity has been acted as sheath material. Thereafter, packet has been packed in alluminium foil and labelled with proper technical parameters of the pack.The technical steps involved in well-being pack preparation, has been represented in Fig 2.

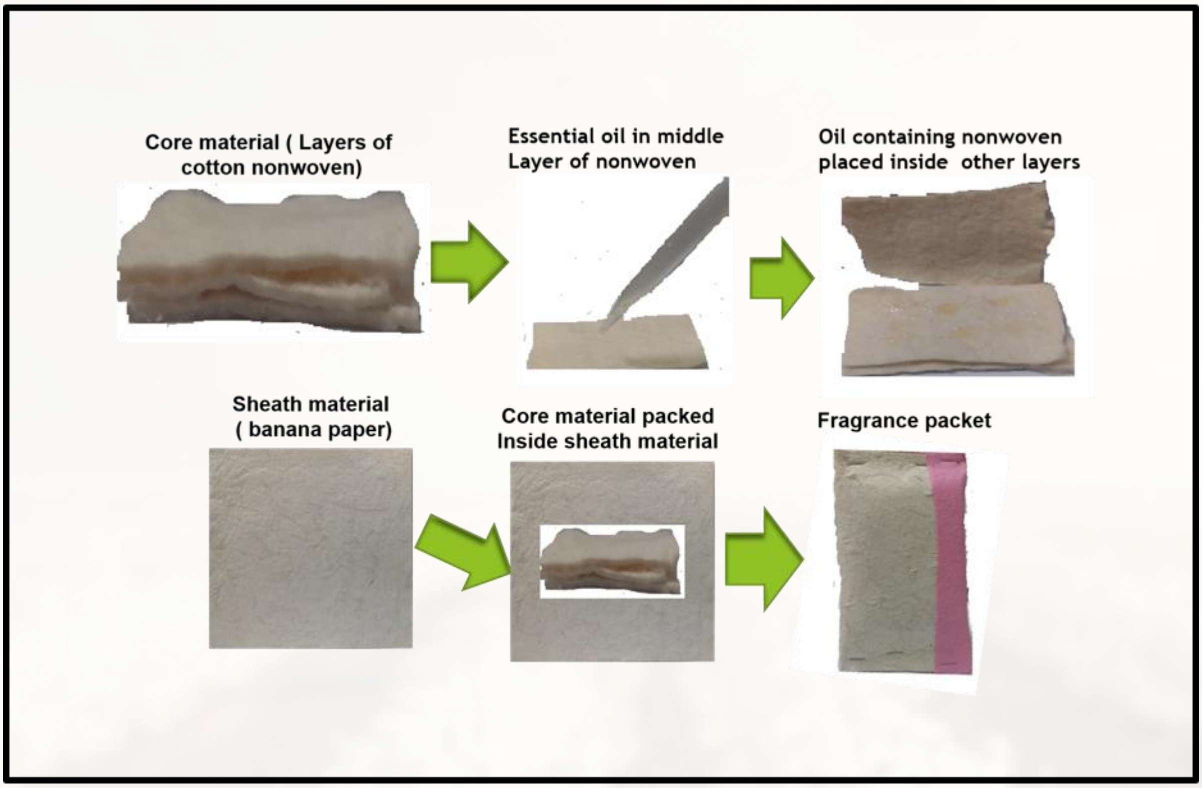

Fig 2. Technical steps for the preparation of cellulosic fibre based well-being material [23].

3.1 Mosquito repellency of the fragrance pack

The prepared natural fibre based fragrance pack is also capable to repel mosquitoes. As per earlier mentioned procedure, natural fibre based fragrance pack has been opened and kept on and approximately 50 nos. of mosquitoes were released in the test chamber at a time. Periodically, observations were made on death/ migration of the mosquitoes to the untreated chamber. Observations are made initially, ten minutes and half an hour to see if there was any long standing effect on mosquitoes in terms of moving away/ death etc. Test has been repeated two times for constant observation. For knowing the longevity and the effectiveness of the prepared pack, the fragrance pack has been kept open for one week and the concerned test has been conducted on day 3 and day 5. Detail test report has been represented in Table 6. It has been observed that the concerned pack is 100% effective against mosquitoes up to 3 days. Then the repellency effect has been gradually decreased. As per literature, mosquitoes are searching for carbon di oxide, lactic acid scents. Actually, active ingredients present in the citronella oil (geranilol, citronellal) come out from the pack as fragrance and may mask the smell of carbon di oxide and lactic acid in the surroundings.

3.2 Mechanism of fragrance release from natural fibre pack

Grey cotton non-woven has been used as core material of the fragrance pack, for slow release of the active ingredients of essential oil. Grey cotton contains thin layer of fat, wax, pectin and protein like materials. All of the mentioned materials are lipophilic in nature and fat, waxy layer present on the cotton non-woven have capability to hold the essential oil and assist in slow releasing of the active ingredients present in it. Essential oil deposited on the surface of cotton non-woven also has been fortified by FTIR analysis, depicted in Fig 9. It has been observed from the FTIR analysis that grey cotton nonwoven showed sharp peak at 3300cm^{-1}, assigned with the –OH stretch vibration and two other important peaks ranging from 1000 to 1100cm^{-1}, could be associated with the vibration of pyran structure (-C-O-C stretch) and C-O group stretching of cellulose. Peaks observed at 1200 and 1245cm^{-1} responsible for –OH bending vibration[Dave et al 2014]. However, cotton nonwoven treated with citronella oil showed some clear distinct peaks. Sharp peak observed at 2935cm^{-1}, could be responsible for C-H methyl and methylene asymmetric stretching [24]. Grey cotton also showed one small peak at this wave-number range and it also associated with the CH_2 symmetric stretching vibration. However, as observed from the figure, after deposition of oil, intensity of the said peak has been increased. Distinct peak also has been observed at 1750 and 1705cm^{-1}, could be attributed with the aldo, keto, estero or acido (C=O) stretching vibration [24]. These groups are present in geranial and citronellal active ingredients of the citronella oil. These groups of the active ingredients could be reacting with the free fatty acids and esterifies carboxylic group of pectin (small peak at 1749cm^{-1} in grey cotton) present in the grey cotton. Clear peaks also have been observed at 1380 and 1485cm^{-1} may be assigned with the C-H symmetric vibration and methylene C-H vibration [24].

Possible reaction between essential oil and nonwoven has been represented in Fig8. From the Figure it also has been observed that after oil incorporation, diameter of the grey cotton fibre has remained unchanged. It means citronella oil only has been deposited on the surface of the cotton fibre and adhered with the waxy layer (oleophilic in nature) of the cotton. As there no swelling has been observed it can be concluded that essential oil did not penetrate inside the structure of the cotton fibre. Therefore, extent of the fragrance released per unit time from the core material has been controlled by the pores and the pore volume of the core material and also on the pores of the paper based sheath layer. It means from one side, waxy layer of cotton surface, porosity and thickness of the core material has assist for the control release of the fragrance. In addition, paper based sheath layer of standard porosity (air flow rate: 2200ml/min) provide extra protection (control release) on fragrance release properties in the surrounding zone.

3.3 Packing mechanism and cost of fragrance packet

Packing mechanism is another important part of this project as the storage durability of the natural fibre based fragrance pack is depending on it. As per logic, outer packing cover of the material should have very limited level of porosity so that no fragrance volatile can come out from the pack during the storage time. Connected with this mechanism, both side plastic coated aluminium foil (porosity: 100mL/min) has been used for packing purpose and sticker printed with all the protocols have been attached on the outer side of the aluminium foil as represented in Fig 3.

Fig3. Aluminum foil with printed user guidelines used for packaging purpose [23]

Cost of the engineered fragrance pack also has been calculated in detail with combining the cost of cotton non-woven, essential oil, paper material, printing charges (on pack and on aluminum foil), aluminum foil packing, time and labour charges. Selling price of each pack reaches approximately Rs. 25 in Indian currency. However, price of each pack may decrease if it has been prepared in larger quantities.

Fragrance pack has been prepared by using cotton nonwoven, paper and citronella oil. Natural fibre and citronella oil based fragrance pack is totally eco-friendly and easily biodegradable. The product is suitable to provide rejuvenating and refreshing fragrance up to seven to eight days (using 24h everyday) in its surrounding atmosphere, after opening the package. Moreover, the concerned fragrance pack can also repel mosquitoes up to four to five days. Grey cotton nonwoven acts as physical barrier for quickly leaching of fragrance from the pack and the fatty layer, pectin etc. present in the grey cotton assist to hold the hydrophobic essential oil and slowly released it in the surroundings. Prepared product may be effectively used in office, washroom, bed room, living room, car etc., It also may be equally useful to remove the bad smell if its placed in wardrobes, cupboards, drawers , travel bags etc.

4. Natural fibre based flexible composite

A natural fibre based flexural composite has been developed by using suitable chemical formulation of natural rubber, sulphur dispersion, accelerator, activator, stabilizer, filler antioxidant etc. with needle punched ramie non-woven fabric. Developed natural fibre based flexural composite products have been examined in terms of different physical properties like absorbency, wicking, swelling, shrinkage. The performance properties i.e abrasion resistance, tensile strength, tear strength, puncture resistance, permeability, porosity and dynamic loading and recovery of the developed product has also been examined and compared with the wet blue (chrome treated) leather of goat. Absorbency time and rate of vertical wicking of the wet blue leather are almost equal as compared to the developed flexural composite whereas composite product shows 20% higher permeability and less shrinkage as compared to the natural leather. Tensile strength of the developed product was 50% less whereas tear strength is almost equal as compared to the natural leather, having same weight and thickness. Surface and cross-sectional morphology of the flexural composite and natural leather has also been characterized by scanning electron microscopy analysis. The thermo-gravimetry (TG), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) analysis of developed composites have also characterized. and compare with the natural leather.

4.1 Treatment process

Ramie fibre based needle punched non-woven was treated with natural rubber based formulation as mentioned in Table 1. Thereafter, the treated material was dried or coagulated at 80-90°C for 10 min. Dried samples have been hot pressed (HP) for 30s at 40kg/cm^2 at 120°C. Henceforth, the sample has been vulcanised at 140°C, for 3-5 min and followed by washing with open water flow for 5-7 min with vigorous rubbing. Finally, the washed samples were dried and buffed with emery paper grade 1 (finer distribution) for 2-3 min. Fig 4 shows the process condition and recipe used for developing different samples.

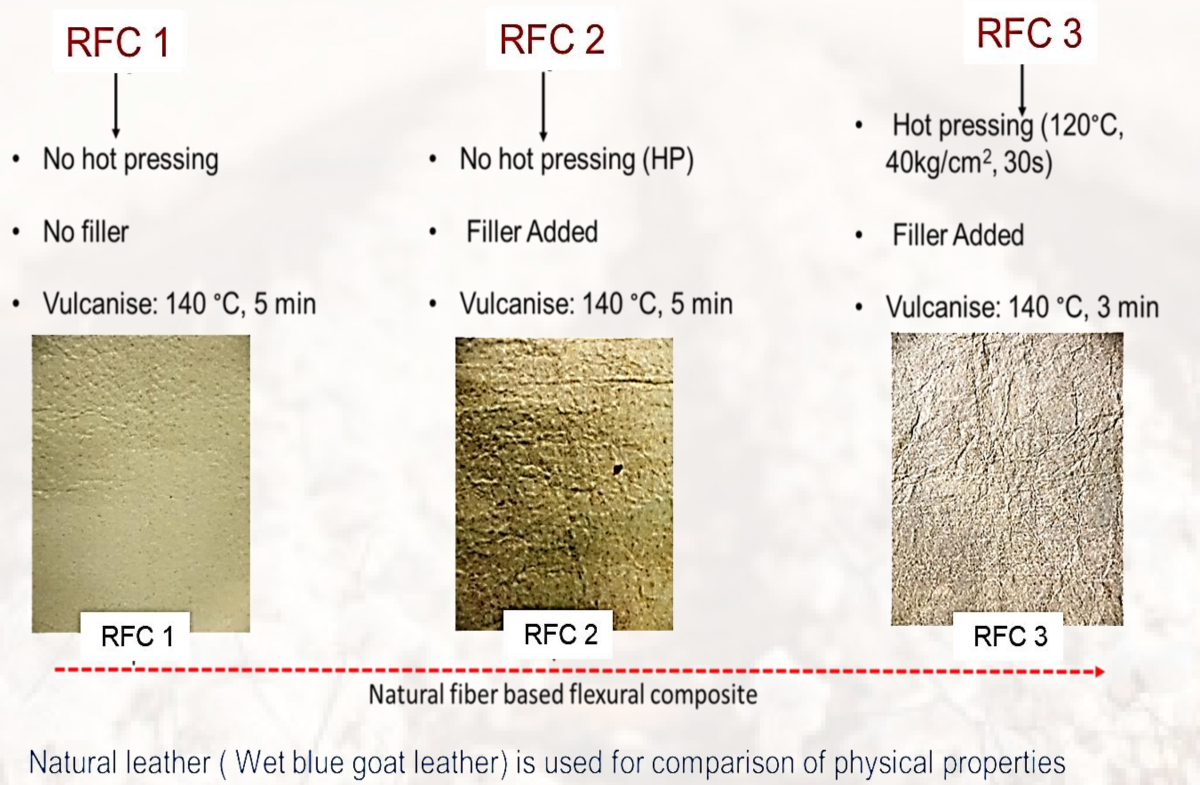

Fig4. Different formulation and process condition followed for development of the samples [25]

4.2 Chemical mechanism involved and structure property correlation

Chemical composition of the developed flexural composites and natural leather are completely different and all the physical properties of the developed products, defined earlier is directly or indirectly correlated with the chemical structure of the material. Natural rubber contains CH_2 group and its polymer has been cross-linked among them with sulphur during vulcanisation process at higher temperature. Accelerator and activator just has been controlled the vulcanisation process (reduced vulcanisation time and temperature) by free radical generation mechanism but not take part into the chemical reaction. Sodium salt of bovine was also used in the formulation for improving the nitrogen content of the material and it is observed from the elemental analysis of the developed composite. Wax contains ester group and was used for better feeling and it also assist to reduce the surface roughness, ozone crack resistance material. Vulcanised flexible composite is dimensionally stable and did not show any kind of shrinkage in vertical and horizontal direction. Primary hydroxyl (-OH) group of cellulose is very reactive in nature and it may reacts with the vulcanised rubber chain through electron transfer mechanism. Reactivity of free $-CH_2OH$ group of cellulose is comparatively lower and affects the absorbancy, wicking and swelling nature of the samples. Although wax, antioxidant present on the surface of the developed product also affected the functional properties. Structure was permanently set after vulcanisation, reflects shrinkage behaviour of the products.

On the other hand, natural leather is composed of protein-based groups, different amino acids etc. Wet blue leather involves the process of chrome treatment on the pickled leather and high valent chromium was attached with the resultant protein based structure. Long chain peptide group of natural leather is elastic in nature due to the conversion of alpha to beta form and it reflects high recovery rate in dynamic loading behaviour. On the other hand, ramie fibre has poor extension properties and vulcanised rubber attached with the cellulosic structure, partly assist the recovery behaviour. High toughness (more tensile strength, puncture resistance) of the natural leather, may be linked with high degree of polymerisation of polymer chain, elastic nature, oriented structure of collagen unit present in it.

4.3 Mechanical properties of the developed flexible composite

RNW-C and various rubber formulation treated ramie based flexible composites (RFC) have been evaluated for its tensile strength, tear strength and the puncture resistance and the reaults are represented in Table 5. It was observed from Table 5 that the tenacity of all the ramie based flexural composites is significantly higher as compared to the RNW-C. Tenacity of RFC 3 is found significantly higher (25%) as compared to the RFC 1, may be due to the higher ramie fibre content in the structure. However, tenacity of RFC 3 is about 50% lower as compared to the wet blue goat leather samples. The tear strength of all ramie based flexural composite samples was similar to the WBL. It may be due to the flexibility of the rubberised natural fibre based flexural composite samples. Puncture resistance, another important parameter for upper footwear has performed for understanding the toughness property of the ramie based flexural composites. Puncture resistance of the non-woven fabric has improved significantly (30-35%) after treatment with rubber based formulation. It is one of the clear signature of the toughness of the developed product which has been confirmed later by dynamic loading test. However, wet blue natural leather sample has shown almost four times more puncture resistance, five to six times higher puncture energy as compared to the flexural composite developed from ramie based non-woven fabric.

Swelling test of the samples has been carried out to understand the reaction of the developed composite samples with water. Control ramie sample instantly soaked with water and sink into it, however, all the rubber formulation treated samples are floated on the water surface as depicted in Fig 7. It may be due to the lower density of the rubber (0.92g/cc) as compared to the natural fibre based ramie (1.45g/cc). It also may be due to the fact that some air molecules have been entrapped inside the structure and reduce the specific weight of the sample. Hot water shrinkage of the samples are another important part related with the dimensional stability of the product developed. For measuring this property, Samples have been dipped in boiled water for 7 minutes and length of it is measured in horizontal and vertical direction. It was observed that developed composite samples showed no shrinkage in longitudinal and horizontal direction. Flex resistance of the samples also has been examined and it shows that natural leather (WBL) is stable up to 9000 cycles while RFC1 has broken after completion of 1000 cycles. It may be due to the lower toughness and extensibility of the developed product as compared to the WBL. Incorporation of filler in the rubber formulation has improved the surface texture, however, flexing property of the product has been decreased. Physical properties of the developed flexural composites have been compared with the PU based synthetic leather of same weightage and thickness. All the necessary data is represented in Table 5.

Table 5. Tensile and other physical properties of the materials [25]

Physical parameters	**RNW-C**	**RFC 1**	**RFC 2**	**RFC 3**	**WBL**	**Synthetic leather made by PU**
		No HP No filler	No HP Filler	HP Filler		
Tenacity (N/mm^2) in length direction	1.02* (5.6%)	4.10* (3.6%)	5.05* (4%)	5.51* (5%)	12-13* (3.2%)	7.67* (1.4%)
Tensile strain at break (%)	42.11* (4.2%)	28.17* (4.2%)	27.32* (3.7%)	32.08* (4.9%)	70.48*(3%)	45.34* (2%)
Tear strength	36.45* (2.5%)	274.21* (2.6%)	255.13* (2.5%)	245.2* (2%)	276* (1.4%)	225.4* (2.3%)
Puncture resistance (N)	137	210	200	220	585	425* (1.2%)
Energy for puncture (mJ)	768**	820**	830**	725**	4090**	2304*
Flex resistance (Cycles)	32	1000	500	550	9000	8500
Swelling (%)	300	27.7	47.4	60.63	32	20
Hot water shrinkage (%)	Length wise 4.5% and width wise 5.26%	No shrinkage in both direction	No shrinkage in both direction	No shrinkage in both direction	Length wise it is 3% and width wise 2%	No shrinkage in both direction

Note: *Mean value of three samples and parentheses represent CV%

Natural fibre based flexural composite sample has been developed by using natural rubber based formulation. Most of the ingredients required for mimicking the natural leather i.e for making flexural composite is nontoxic in nature and more clearly very less quantity of chemicals have been consumed for making the product as compared to the larger quantity of chemical consumption for leather processing. Developed product is almost resemblance of natural leather. Property of the developed flexural composite has been compared with the natural leather of almost similar thickness and weight. It was found from all the physical and chemical analysis that flexural composite (RFC-1) has shown almost similar behaviour in terms of capillary action, absorbency time, swelling, tear strength, shrinkage, breathability, density etc., with natural leather. Abrasion resistance, one of the important parameter for the flexural composite to be use as a footwear material has shown 9-10% more weight loss as compared to natural leather. However, tensile strength and breaking strain of the developed product are almost 50% less as compared to the natural leather. In addition of it, puncture resistance, energy also need to be improve and continuous work is going on in this direction. Besides, chemical analysis, surface topography and thermal stability behaviour of the products also have been established and compared in contrast with natural leather. Developed products really have a potential to be use as hand bag, wallet, pencil bag kind of materials.

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Cotton Crops – The importance of ultra-low volume spraying

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Since the discovery of the insecticide DDT, farmers growing cotton have sprayed their crops with insecticides to reduce damage caused by bollworms and other insect pests. This has varied between the use of aircraft applying in some cases a mixture of DDT, with methyl parathion and toxaphene This mixture was used in the USA to combat boll weevil as much as bollworms. Subsequently following publication of Rachel Carson's book "Silent Spring", the use of DDT was withdrawn. The introduction of crop monitoring and selecting an insecticide most suited to the predominant pest did in some countries lead to more specific recommendations. However, in Africa, where cotton is mostly grown on small farms, only a small proportion of farmers were able to obtain sufficient water to apply insecticides using knapsack sprayers. This was followed by research to determine if sprays could be applied with a much smaller volume of spray applied per hectare.

Initially the use of the Micron ULVA or Turbair X sprayer, designed by Bals (1974) to use a rotary atomiser were tried in several countries to apply less than 5 litres of spray per hectare, i.e ultra-low volume spraying, a technique introduced initially to control swarms of locusts over vast areas. Trials in Malawi confirmed that ULV sprays on cotton were as effective as treatments using knapsack sprayers (Matthews, 1973). By positioning the nozzle downwind of the operator's body, there was less risk of the operator being sprayed. The formulation of insecticides for ULV spraying was provided from Holland by Philips-Duphar, where Maas, (1971) had examined various solvents that varied in their dissolving power, volatility, viscosity and phytotoxicity. Among the vegetable oils, cotton seed oil and castor oil were not good at dissolving but had low volatility and phytotoxicity, but had high viscosity. Several SULV formulations were developed for insecticides.

Similar studies in West Africa (Cadou, 1959) enabled this system to be adopted in Francophone Africa from 1975 and continued until 1995, when the availability of the UL formulation was withdrawn by the agrochemical industry. Farmers continued to use a sprayer with a rotary atomiser, but they applied sprays in about 11-10 litres of water per hectare. Another ULV sprayer developed was the Electrodyn (Coffee, 1979, 1981; Matthews, 1981), which was used successfully in several countries before it was withdrawn by the ICI.

Looking back at these developments in an era that is much more concerned about climate change, raises the question why are pesticides formulated to mix with water? This goes way back to the dilution of copper sulphate in water pre 1900 to spray on vines to deter children stealing the grapes, that led to the introduction of Bordeaux Mixture, an efficient fungicide to protect the vineyards. Today we need to recognise that the spray deposit obtained on sprayed foliage is susceptible to being washed off by rain. This has undoubtedly resulted in pesticides being washed off leaf surfaces and enter the soil. The rain ultimately moves the "run-off" of the spray into the soil or down to a ditch or stream and then to rivers. More recently concern has been expressed about detection of pesticides in rivers and the impact they have on fish and other aquatic organisms. Studies have shown that fish health may be impaired at environmental concentrations. Sensitive fish species, whose early life stages are present when highest pesticide concentrations occur, are likely to be most vulnerable (Werner et al., 2021).

Fig 1a. ULV spraying trial in Malawi

Fig. 1b Rotary atomiser ULV sprayer used in Cameroon.

Fig 2 Electrodyn Sprayer being used in Brazil

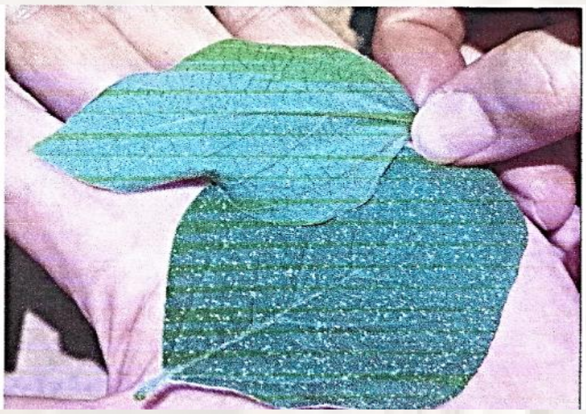

Fig 3. Close up of an aerial spray at 5l/ha.[Photo Credit : Alan McCracken]

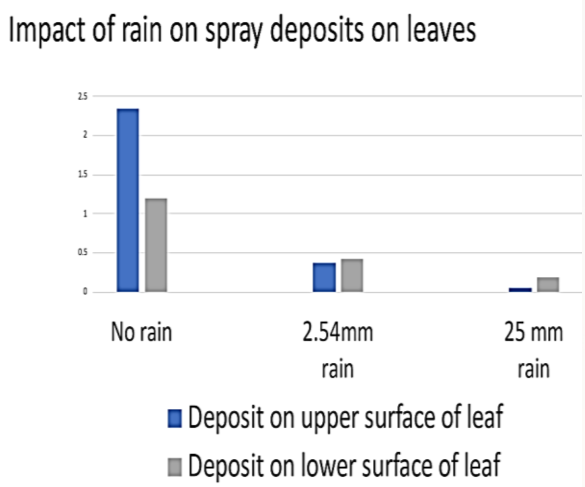

Fig 4. Results of spraying a cotton plant with most of the spray on the upper surface of leaves and more exposed to the impact of rain. (Matthews, 2022).

Another reason to move away from applying water-based sprays is that when hydraulic nozzles are used, there is inevitably a wide spectrum of droplets produced. The movement of these droplets between the nozzle and the target surface in a crop will be related to their initial size and their subsequent change in size depending on not only the air temperature, but also the relative humidity of air and wind speed. Water in the droplets evaporates especially if the temperature is high and the humidity is low, so the smaller droplets can shrink in size and are liable to travel over longer distances in relation to wind speed. Thus, spray drift downwind can be over longer distances. The larger droplets will tend to move downwards and depending on the leaf size and extent to which the leaf surface is hydrophobic, the liquid may spread on the surface or bounce off. Some crops, such as peas, deposition is better using small droplets and lowering surface tension, by adding a surfactant to the spray (Brunskill, 1956).

The need for ULV sprays is also due to increasing use of drones to apply pesticides. The initial introduction of automated drones to spray began in Japan, as the farm labour for spray operations was limited and the work very arduous in rice fields. Lower spray volumes are required for drone operations to avoid frequent refills and improve productivity.

Figure 5 A drone spraying cotton in China. [Photo Credit: Professor Xiongkui He.]

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Plant Host Resistance in Cotton

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Cotton plants with improved host plant resistance (HPR) mechanisms against a range of insect pests could benefit growers by giving them varieties that maintain stable yields under increased insect pressure. Ideally, the grower could then decrease the amount of pesticide applied, providing significant cost savings and protecting beneficial non-target organisms. Improving a plant's endogenous defenses against pests is not a new concept, and it can be accomplished by avoidance, tolerance or resistance.

The emphasis here is not on the absolute yield pattern but on the proportional decrease in yield among the cultivars in the presence of insect vis-a-vis the yield obtained in its absence. It means that a cultivar may yield poor but carries the genes for resistance and, on the contrary, a cultivar may yield good without having any genes for resistance. Moreover, it is not always true that resistance is manifested only in the form of greater yield because there can be stage or age specific characteristics imparting resistance.

Cotton (*Gossypium hirsutum* L.) as a major crop has a 1.0% share in GDP and 5.5% in agriculture value addition in Pakistan. During 2017–2018, the cotton crop in Pakistan was cultivated on 2.699 Mha. The production stood at 11.935 million bales (One bale = 170 kg), which is 15% off the target of 14.04 million bales (Government of Pakistan 2017–2018). A decline in production has several reasons in which the sucking insect pests played a major role. Sucking insect/pest complex especially whitefly, jassid and thrips have caused severe damages to genetically modified cotton systems in Pakistan. Notable yield losses have occurred in previous years and these are expected in the future due to lack of resistant cultivars, increased insect pressure and pesticide resistance.

Genetic modification (GM) permitted the incorporation of toxins from bacteria (*Bacillus thuringenesis*, *Bt*) into cotton to control key *Lepidopteron* pests. However, sucking insect pest complex (whitefly, jassid and thrips) which is not controlled by *Bt* cotton has emerged as a new problem. This sucking complex causes significant loss in yield and fiber quality, and their management is also a key challenge for cotton growers. Losses up to 40% are reported due to sucking pest complex. Significant losses > 12% were estimated even after taking control measures. Current control measures include the use of different chemicals as pesticides, which is associated with high cost, pesticide resistance and environmental risks. Alternative methods should be opted for the control of these sucking insects. Host plant resistance (HPR) offers an opportunity for effective control of sucking insect pests as an economically and environmentally safe strategy in the GM cotton system. The role of some morphological plant traits against sucking insect pest complex observed of cotton. The negative response of whitefly to gossypol glands on leaf lamina, midrib and vein. The biochemical HPR basis of insect resistance in cotton, and found that the resistant varieties showed more phenolics and tannin as compared with the susceptible varieties; the negative correlations were witnessed between total phenols and the insect attack.

Therefore, the deployment of morphological and biochemical HPR traits as a cotton plant defense mechanism provides an alternative management strategy and controls these insect pests. Cotton cultivars having HPR against these insects would entail fewer pesticide applications, reducing costs and risks associated with pesticide resistance and beneficial the insect populations. How each of the traits reduces insect predation and/or damage varies depending on the trait. Often the trait has multiple effects that interact to produce. For example, nectariless cotton not only makes the plants less attractive by eliminating an important food source, it also has a reported antibiosis effect. While plants with smooth leaves (glabrous) are more susceptible to some insects, plants with semi-smooth leaves have sufficient trichomes to physically decrease the ability of insect females to lay eggs. The okra leaf trait has been identified as a spontaneous mutation in a number of different genotypes. The effect of okra leaf on insect predation is not clear, with some reports attributing earlier maturity (insect avoidance) or decreased attractiveness to bollworms and budworms to this trait.

Plant breeders have actively cooperated with entomologists for several years to identify strains of cotton with antibiosis against the bollworm/tobacco budworm. Numerous obsolete cultivars, wild race accessions and special genetic stocks have been identified. Techniques are now available which allow the breeder to select resistant plants from segregating progeny or progeny rows following crosses between resistant and susceptible lines. Most of the resistant lines were found originally in non-adapted cottons. Techniques have been developed for infesting plots with eggs; however, these were not considered to be as useful as those using first instar larvae.

The appearance of early-maturing, rapid fruiting cultivars in the past several years signals the beginning of a concerted effort to breed cotton plants that evade pests and thus have effective field resistance to pests. In the next few years, new cultivars with resistance to bollworm/tobacco budworm, plant bugs and pink bollworm should appear on the market. Also, significant progress should be made in identifying resistant germplasm and management strategies that will help reduce problems from other major cotton pests. In fact, the new cultivars and resistant germplasms will form the foundation for even more successful methods of pest control. Control of cotton insects may not be possible without the continued use of insecticides to supplement other control methods. On the other hand, quantities of insecticides used with be reduced significantly as resistant germplasm and other alternative control methods are integrated into production systems.

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Nano-fertilizers: A smart way to improve nutrient use efficiency and cotton nutrition

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Abstract

Cotton is one of the most important fiber/cash crop and plays a dominant role in the country's industrial and agricultural economy. The main fertilizers used in cotton production are nitrogen (N), phosphorous (P), and potassium (K). Generally, the need for cotton fertilization is met with synthetic NPK fertilizers. However, excessive use of synthetic fertilizers causes financial burden, increasing soil, water and atmospheric pollution. Recently, Nano-fertilizers have shown great potential for their sustainable uses in soil fertility, crop production with minimum environmental risk. Nano-fertilizers are of microscopic sizes, have a large surface area to volume ratio, can encapsulate nutrients, and have greater mobility hence they may increase plant nutrient access and crop yield. Due to these properties, nano-fertilizers can play a vital role in improving cotton plant nutrition and increasing cotton yield.

Introduction

Fertilizers play a vital role in improving the productivity of agricultural crops. However, the nutrient use efficiencies of conventional fertilizers in cotton production hardly exceed 30–35 %, 18–20%, and 50% for N, P, and K, respectively in arid climate. Nano-fertilizers tend to improve the nutrient use efficiencies by exploiting unique properties of nanoparticles. The nano-fertilizers are synthesized by fortifying nutrients singly or in combinations onto the adsorbents with nano-dimension. Nano-fertilizers are known to release nutrients slowly and steadily for more than 30 days which may assist in improving the nutrient use efficiency without any harmful effects. Since the nano-fertilizers are designed to deliver slowly over a longer period, the loss of nutrients is substantially reduced and thus ensuring environmental safety.

Nano-fertilizers

Nano-fertilizers are nutrient carriers of nano-dimensions ranging from 30 to 40 nm (10^{-9} m or one-billionth of a meter) and capable of holding plenty of nutrient ions due to their high surface area and release it slowly and steadily to meet the crop demand. Nano-fertilizers can be used to control the release of nutrients from the fertilizer granules so as to improve the NUE while preventing the nutrient ions from either getting fixed or lost in the environment. Nano-fertilizers have high use efficiency and can be delivered in a timely manner to a rhizospheric target. The nano-clay-based fertilizer formulations (zeolite and montmorillonite with a dimension of 30–40 nm) are capable of releasing the nutrients particularly N for up to >1,000 hours than the conventional fertilizers having <500 hours release time. Clay particles are adsorptive sites carrying reservoir of nutrient ions. Major portion of nutrient fixation occurs in the broken edges of the clay particles. Zero valence nanoparticles are adsorbed onto the clay lattice, thereby preventing fixation of nutrient ions. Further, nanoparticles prevent the freely mobile nutrient ions in soil system that would otherwise get precipitated. These two processes assist in promoting the labile pool of nutrients that can be readily utilized by plants. Fertilizer particles can be coated with nano-membranes that facilitate in slow and steady release of nutrients. This process helps to reduce loss of nutrients while improving fertilizer use efficiency of crops.

Nano-particles entry into the plant

Plant cell wall acts as a barrier for easy entry of any external agents including nanoparticles into the plant cells. The sieving properties are determined by pore diameter of cell wall that ranges from 5 to 20 nm. Hence, only nanoparticles with diameter less than the pore diameter of the cell wall can easily pass through and reach the plasma membrane. There is also a chance for enlargement of pores or induction of new cell wall pores upon interaction with engineered nanoparticles, which in turn enhance nanoparticle uptake. Further internalization occurs during endocytosis with the help of a cavity-like structure that forms around the nanoparticles by plasma membrane. They may also cross the membrane using embedded transport carrier proteins or through ion channels. In the cytoplasm, the nanoparticles are applied on leaf surfaces; they enter through the stomatal openings or through the base of the trichomes and then translocated to various tissues. However, accumulation of nanoparticles on photosynthetic surface causes foliar heating which results in alterations of gas exchange due to stomatal obstructions that produce changes in various physiological and cellular functions of plants.

Nanocomposites

Nanocomposites have been developed in order to supply wide range of nutrients with desirable properties. These compounds are capable of regulating the inputs depending on the conditions of soil or requirement of crops. Zinc–aluminum layered double-hydroxide nanocomposites have been used for the controlled release of nutrients that regulate plant growth. In soil, nano-materials are porous and hydrated, and as such they control moisture retention, permeability, solute transport, and availability of plant nutrients in soils. These nano-materials also control exchange reactions of dissolved inorganic and organic species between the soil solution and colloidal surfaces. The physicochemical properties on the surface of nanocomposites provide much of reactivity to soil biological and abiotic processes. The organic agent and clays form nanocomposites through hydrogen bond combination.

Effect of Nanocomposites on Crop Growth

The addition of nanocomposites benefits the soil and raises the utilized efficiency of fertilizer because of its excellent characteristics. The physical adsorption and chemical combination occurs between nutrient elements and nanocomposites due to surface reaction and small sized promoted reaction of nanocomposites. They form the efficient multifunctional fertilizer, which increases the adsorption of nutrient elements by plants, lowers the leaching in soil, and the fixation of fertilizer in the soil. The nanocomposites affect and control the structure and penetrability of the soil, increase the organic mineral granule of the soil, improve fertilizer storage and water holding capability in the soil, promote action of microorganisms, regulate the ratio of C/N and enhance the fertility of the soil.

Conclusion

In the scenario of everyday increasing cost of inputs, nano-fertilizers can play a vital role in enhancing cotton yield through regulated and sustained release of nutrients and thus improving the nutrient use efficiencies. Though nutrient release is regulated through physical and chemical processes, the biological significance of nutrient release is yet to be clearly understood. More research is needed to address the nutrient interactions at the physiological and molecular levels, antagonistic and synergistic interactions among nutrients, and biosafety of nano-fertilizers besides long-term impact of nano-fertilizers on physical, chemical, and biological properties of soils is yet to be determined.