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Website: www.aarf.asia Email : editor@aarf.asia , editoraarf@gmail.com

SYNTHESIS AND CHARACTERIZATION OF AGRO WASTE NON-WOOD PAPER MODIFIED WITH ANTIMICROBIAL, PHOTOCATALYTIC MATERIALS FOR FOOD PACKAGING AND OTHER APPLICATIONS

Akshay Bisht[1], Dr. P Murli Krishna[2]
[1]National Institute of Food Technology Entrepreneurship and Management (NIFTEM)
[2]Dept of BAS, NIFTEM, Deemed to be University, Autonomous organization under MoFPI, Govt. of India, Kundli-131028, Haryana.

ABSTRACT

Maize or corn produced annually than any other grain crop having 785 million tons production worldwide. Maize is widely used in fodder, chemicals, Bio-fuel and biomass, etc. Agro waste grain less corn cobs (GLCC) holds 50-60% cellulose in fresh can better yield the paper, an alternate to wood pulp in paper industries. This work reports the synthesis paper using grain less corn cob, simultaneously modifying the pulp with Ag (1mmol), natural neem leaf (Azadirachta indica) powder (3g wt) for antimicrobial and TiO_2 (3%) for photocatalytic properties in the paper for various applications. Ag and TiO2 anoparticles prepared by green chemistry method (40-110^{O}C) using orange peel extract as reducing agent. The XRD peak at 2θ= 22.94^{o} of modified paper ascribed to titanium anatase phase (JCPDF no 21-1272) revealing photocataylytic activity. The low crystallinity index, Cr_I = $\{(I_f-I_s)/I_s\}x100$ = 1.545%, (I_f, I_s fundamental and secondary peak intensities at1488 AU,1465AU respectively)) confirming the Ag-TiO_2 binding in cellulose matrix. The TGA trend showed the higher thermal stability due to diffusion of Ag, TiO_2 nanoparticles into the cellulose matrix. From UV -Vis absorption spectra and Mie scattering relation, $\gamma(R) = \gamma_0 + (Av_f)/R$, estimated the Ag nano particle size, R= 40-50 nm, indicating the excitation of surface resonance at visible region in larger particles. The 20g pulp placed under 5-8 Kg resulted light yellow colour paper with size= 5x5cm (apprx), thickness =0.199mm, grammage=0.0081, stiffness (bending) =72-75 Taber (avg) and tearing properties that are comparable commercial recycled packaging paper. The different ratios of modified papers kept under visible light *irradiation and analyzed for Gram-Positive and Gram-Negative bacteria like Bacillus subtilis and E. coli via antibiotic disc diffusion method. The effective microbial control of the modified paper is due to synergistic Ti-Ag nano phase oxidative stress, electrostatic interaction mechanisms and photo-generated TiO_2 reactive radicals. In food packaging test under normal room temperature (25^oC) conditions, the antimicrobial paper showed an enhanced shelf life upto 8 days for the milk based sweet (Burfi) when compared to normal paper. Hence, GLCC will be an alternate to wood, value addition to agro waste. The antimicrobial paper can enhance the shelf life, reduce food waste, medical, regular life applications and environment friendly residue.*

KEYWOEDS: *Antimicrobial Paper, Cellulose, Grain Less Corn Cobs (GLCC), Green Chemistry Synthesis, Silver Nanoparticle, Titanium Nanoparticle*

1. Introduction

Today, 90% of paper pulp is made of wood and Paper production accounts for about 35% of felled trees, (Martin, 2004) and represents 1.2% of the world's total economic output [1]. With increasing deforestation, environmental changes, green house effect, and changes in government polices the demand of non wood agro waste sources for pulp making is increasing. The world is projected to produce 1.01 billion metric tons of corn in 2016. Corn is now America's biggest crop and a staple of the global food supply and used in many ways other than feasting. Grain less corn cobs (GLCC) can be used to make pulp as it is available cheaply and the crop cultivation in India is growing at the rate of 5.5 percent (FICCI, India report 2014), so there is huge potential of grain less cob availability. The proximate analysis of the corn cob shows it has 50% cellulose, which is approximately equal to soft wood (46%) [2-3]. The lignin component is 15% compared to rice husk (18%) and soft wood (31.3%)[4] this clearly shows potential for pulp production to be easily carried out.

Paper is essentially a network of cellulose fibers held together by hydrogen bonds. Natural cellulose is a linear polymer of β-(1→4)-D-glucopyranose possessing abundant surface hydroxyl groups forming plentiful inter and intra-molecular hydrogen bonds. The cellulose chains may be made up of just a few hundred molecules, or several thousand molecules depending on its type. Besides these, the chain lengths, crystallinity and the functional groups distribution along the polymer chains making the cellulose a unique natural polymer (Figure

1) [5]. These hydroxyl groups provide the suitable substrate to incorporate the cellulose surface with metal oxide.

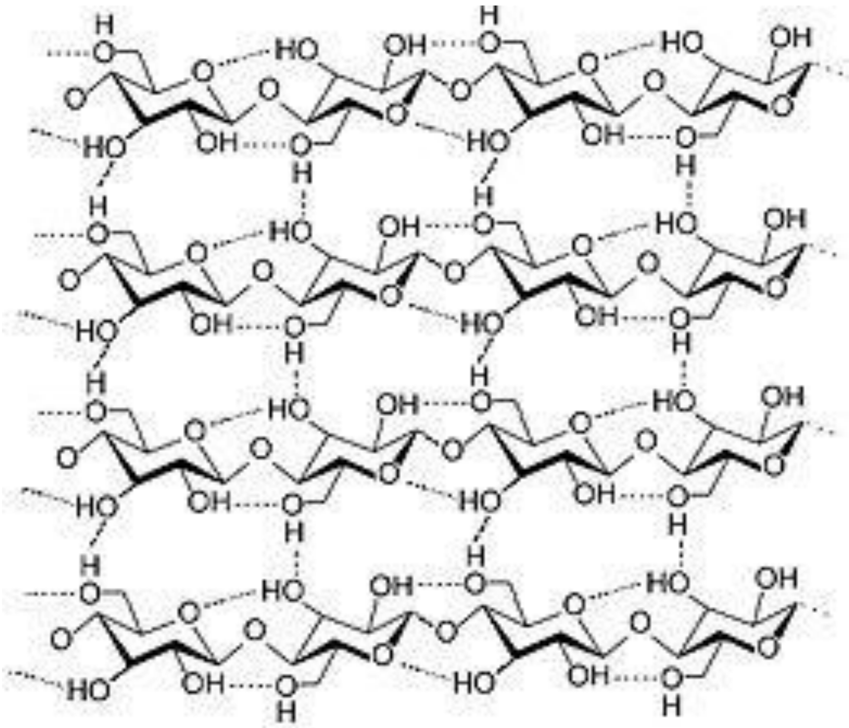


Figure 1: Cellulose strand

The antimicrobial and photocatalytic properties will be introduced into the paper by simultaneous modification with various natural and inorganic amterials like Titanium nanoparticle, Silver nanoparticle and neem leaf extract *(Azadirachta indica)*,etc. Incorporation of Ag,TiO_2 to polymer casting solution greatly affected the morphologies and properties of the resulting composite. Physicochemical Characterization of Mercerized Cellulose/TiO_2 Nano-Composite reported by Sherif et.al [6].

Biopolymers antibacterial activity of two cellulose matrices (vegetable and bacterial) comprising copper nanofillers with morphological distinct copper particulates (nanoparticles and nanowires) matrices prepared by *in situ* and *ex situ* methods were studied on pathogen microorganisms (*Staphylococcus aureus* and *Klebsiella pneumonia)* with an increase in the antibacterial activity with increasing copper content in the composites reported by Ricardo J. B. Pinto et.al [7].

Ag-doped semiconductor nanoparticles received much interest in photocatalysis leading to new applications such as antibacterial, degradation of organic pollutants, textiles, hydrogen production, CO2 photoreduction, disinfection, aqueous plants, food preparation surfaces, air conditioning filters and coated sanitary wares, etc. The photo catalytic properties of TiO_2 was discovered in 1972 [5] and has been studied as an environmental friendly photocatalyst due to its low cost, low toxicity, high chemical stability and excellent photocatalytic activity [8–11]. Silver has been known to be an excellent broad-spectrum antibacterial agent as Ag deactivates bacteria by combing with the –SH groups on its protein. Silver has also been used to enhance the photocatalytic properties of TiO_2, by enhancing the electron–hole separation and interfacial charge transfer. Jiang et al. [12] fabricated a visible-light-driven photocatalyst by uniformly covering the surfaces of TiO_2 nanopillar with Ag nanoparticles [13]. The doping will improve the photoconversion yield and allow the extension of band gap to absorb visible light range due to localized surface plasmon resonance.

It is known that, excited electrons from conduction band (CB) of titanium dioxide trapped by Ag nano phase particles by leaving holes in VB, good charge carrier separation irradiated by visible wavelength photon and causing the enhanced photocatalytic and antimicrobial properties as explained in later discussion. Also, the photoactivity is due to Ag^0/Ag_2O deposited on TiO2. But, the enhanced photocatalytic activity responsible proposed by the photoexcitation of Ag_2O active sites rather than Ag^0 might contribute to the stability [14]. The reaction of silver nitrate with sodium hydroxide produces silver hydroxide via the following mechanism:

$$AgNO_3 + NaOH \rightarrow AgOH + Na^+ + NO_3^-$$

The intermediate AgOH is thermodynamically unstable, and ultimately produces Ag_2O through the following recombination process:

$$2AgOH \rightarrow Ag2O + H2O \ (pK = 2.875)$$

Azadirachta indica, has attracted worldwide prominence in recent years, owing to its wide range of medicinal properties. Neem leaf and its constituents have been demonstrated to exhibit immunomodulatory,anti-inflammatory, ntihyperglycaemic, antiulcer, antimalarial, antifungal, antibacterial, antiviral, antioxidant, antimutagenic and anticarcinogenic properties [15].

In this study the antimicrobial paper was fabricated by using GLCC pulp, Titanium nanoparticle, Silver nanoparticle and neem leaf extract *(Azadirachta indica)* and was compared with existing packaging paper. The Ag and TiO2 nanoparticals synthesis preferred environmental friendly green chemistry method i.e., orange peel extract as the reducing and stabilizing agent. It finds huge application as writing paper or in packaging industry for increasing the shelf life of food products. Non wood fibres can be used in every grade of paper and board, fibreboard (Hurter, 1998; Ververis et al., 2004) and composite materials (Sain and Panthapulakkal, 2006).

2. Experimental

Green chemistry synthesis of Titanium and Silver nanoparticals was done by using orange peel extract to reduce TiO_2 and $AgNO_3$ respectively. The fresh orange peel was washed in warm water to remove dirt, grinded into small pieces, added to distilled water in 1:2 ratio and heated at 70^{O}C for 30min, filtered by using Whitman filter paper 1. 5ml of extract was mixed to 95ml distilled water and this solution (pH=4.51) was used in synthesis of nanoparticals. 0.5Mm, 1mM concentration $AgNO_3$ (SRL, Grade –AR) solution were made by mixing in the ratio of 10:1 to orange peel extract solution, stirred on magnetic stirrer (IKA RH basic model –RH B1522) at 60^{o}C for 5-8min. For synthesis of Ti nanoparticals 1%, 3% TiO_2 (SRL, Grade –AR) solution was prepared and subjected to stirring at temperature of 45^{O}C, equal volume of orange peel extract solution was added to reaction medium with the feed rate of 0.42mL/min. The stirring was continued for 2hrs and temperature of 45^{O}C till the end of reaction [16].

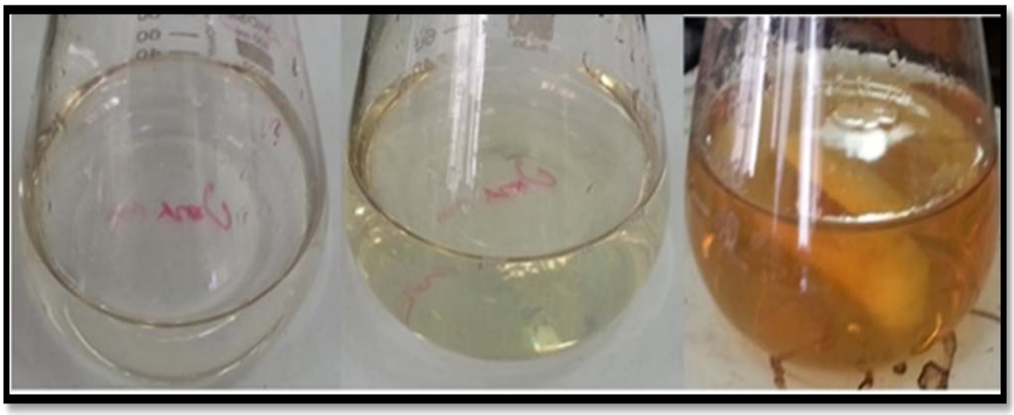


Figure 2: After 5 minutes colour changed to light yellow, then after 8 min to dark yellow which indicates that silver nanoparticles are formed

Freshly collected neem leaves were dried in hot air oven at 28^{0} **C** for 24hours and grinded. The 10 gm of obtained powder was dissolved in 100ml water for 12 hours to obtain neem leaves extract [15, 17].

Grain less corn cobs (GLCC) was chopped into small pieces (1-2 cm), added with 6% NaOH solution (SRL, Grade –AR) in the ratio of (1:6) i.e. one part dry GLCC and six part sodium hydroxide solution to degrade the lignin. 1M H_2SO_4 was used to adjust the pH (8.5) of the pulp. The complete mixer was kept at room temperature for 45 hours for soaking then cooked at temperature of 90-110^{o}C for 80-100 minutes using coil heater till gel like structure form, followed by cooling to room temperature , washing with tap water and filtered using muslin cloth to wash off the lignin. Filler was prepared from waste paper to employ with pulp to increase strength of paper. The paper was soaked in water for 24 hours and mixed in mixer to make paste.

Three different combinations of Ag and Ti nanoparticals was prepared, 0.5m molar Ag and 1% Ti; 1m molar Ag and 1% Ti; 1m molar Ag and 3% Ti. The volume of pulp was mixed with 10% of filler and 20% Silver nanoparticles solution and 20% Titanium nanoparticles solution and stirred for 5-6 hours on magnetic stirrer for uniform mixing and then poured in tray which holds only pulp. Pressing was done by keeping 5-8 kg weight for 8 hrs and paper was dried at 35^{0}C for 5-6 hours while keeping paper in between board, to avoid shrinkage. Best results were obtained with 1m molar Ag and 3% Ti and results are discussed for the same.

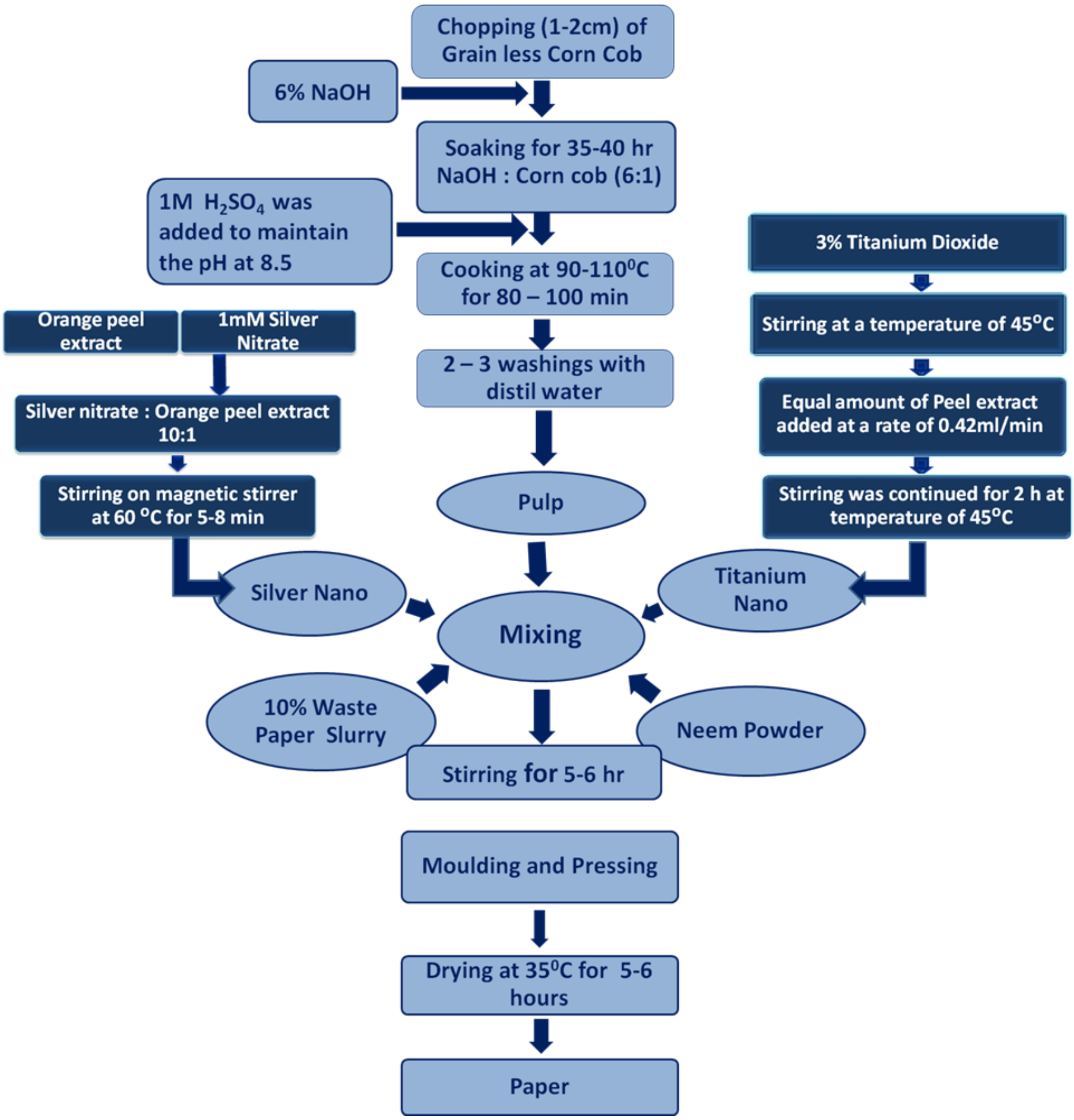


Figure 3: Flow Chart for synthesis of silver and titanium nanoparticles, pulp and paper fabrication

Figure 4: Fabricated Paper

3. Characterization and Measurement

The surface morphologies of antimicrobial paper modified with synthesised Ti and Ag nanoparticles examined using field emission scanning electron microscope (FESEM, JEOL JSM–6700). The microstructure and phase identification of were carried out using transmission electron microscopy (JEOL JEM–3010). Fourier transform infrared spectroscopic (FTIR) measurements were conducted using a FTIR 7600 spectrophotometer (Lambda Scientific Systems, Inc). The spectra were recorded in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} as KBr pellets.

The pulp obtained was used to plot Stress-Strain Rheometer (MCR52 SN81388592). The fabricated paper was characterization by using SEM, XRD from 5^{O} to 45^{O}, TGA (NETZSCH TG 209F1 Libra). Mechanical properties like tearing strength [Tearing Strength Tester (Emeldorf Type) (Techno (India), Model- TI/TS/ED/126)], grammage (density), thickness [Digimatic Micrometer (Mitutoyo Corporation, Model-293-821)], stiffness [Stiffness Tester (Taber Type) (Techno India, Roorkee, U.K., Model-TI/TS/ED/126)] were measured for fabricated agro waste antimicrobial paper. The antibacterial properties were studied using antibiotic disc diffusion method. The gram positive and gram negative bacteria i.e. *Bacillus subtilis* and E. *coli* respectively were used and studied in presence and absence of visible light to check the photocatylitic activity of Ti nanoparticles. Further milk based sweet: Burfi was used to study the shelf life at $25^{O}C$ for 8 days.

4. Result and Discussions

A. SEM-Scanning Electron Microscopy

Fabricated paper scanning electron microscope (SEM) images shown in figure 5. The SEM revealing the proper synthesis steps, temperature and keeping under weight for fabrication resulted burly strands indicating the cellulose occupied fibered with nano composites inside the paper. The fibers in the handmade paper are longer and more intact. This usually interprets into the good strength and durability of the paper. The dispersed spherical Ag nanoparticles were successfully positioned around the edge of the cellulose fiber as a clear evidence of the immobilization of the metal nanoparticles on the modified cellulose. The noble metal Ag have a relatively high electronegativity and a large ionic radius, are classified into soft acid. Soft acids tend to bind covalently with soft bases having a low electronegativity and a radius (e.g., oxides, sulfides, and phosphorus compounds). Hence, the TiO_2 may act like a functional groups in the modified cellulose microsctrucre are anticipated to provide the cellulose with a strong driving force, i.e., covalent bonding, for the immobilization of the metal nanoparticles.

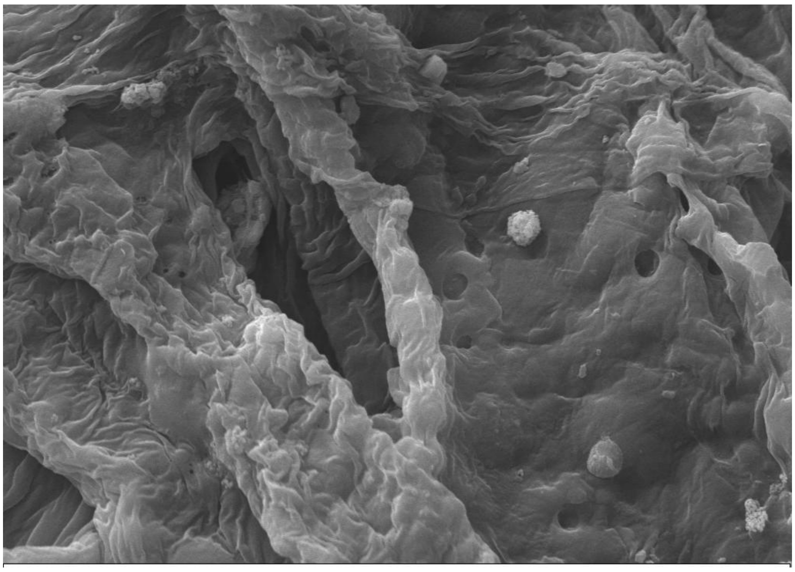


Figure 5: SEM hand made paper showing nanoparticals

B. XRD –X Ray Diffraction

The XRD pattern of fabricated paper is shown in figure 6. The pattern show the diffraction peak $2\theta=16.59^{o}$ characteristic for Cellulose I crystals [18], at 22.94 ^{o}, 36.08 ^{o}, 43.60 ^{o} indicates that Titanium is in anatase phase (JCPDF no 21-1272) with more photocataylytic properties absence of amorphous phase, and less Ag [19]. The crystallinity index (CrI) is calculated using the relation [20], CrI = { $(I_f-I_s)/I_s$}x100 = 1.545% where (I_f =1488 AU,I_s =1465AU of the fundamental and secondary peak intensities) are the peak intensity of the fundamental and secondary bands respectively. The low crystallinity index indicates that structural changes occurred in the polymer matrix as the nano-TiO2, Ag diffused. Also, the nano-Ag, TiO2 concentration plays a dominant role in both morphological and microstructural change in the polvmer matrix which is observed from TGA analysis discussed in later section[21].

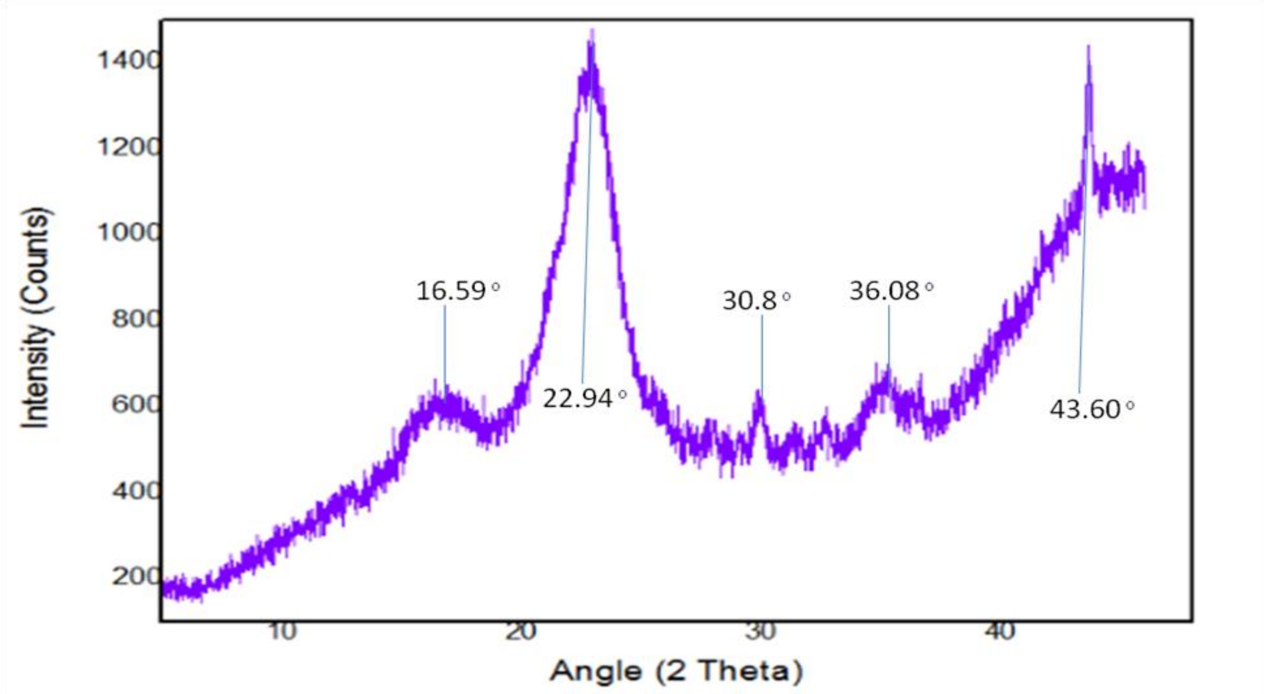


Figure 6: XRD of fabricated paper

C. UV-Vis Spectroscopy

The peaks between 405-420nm and 360-380nm shows the formation of Titanium and Silver nanoparticals respectively as shown in figure 7 (a and b). The UV-Vis spectra and Mie relation between resonance broadening γ(R) and the nanoparticle sizes R is given by, $\gamma(R) = \gamma_0 + (Av_f)/R$, [22] where, γ_0 is velocity of bulk scattering (for silver $5\times10^{12}s^{-1}$), v_f is the Fermi velocity (for silver 1.39×10^{6} m/s), and A= ¾ for silver scattering process used to calculate, R= 40-50 nm for Ag, indicating that, the excitation of the surface resonance exhibits in visible light region for larger particles.

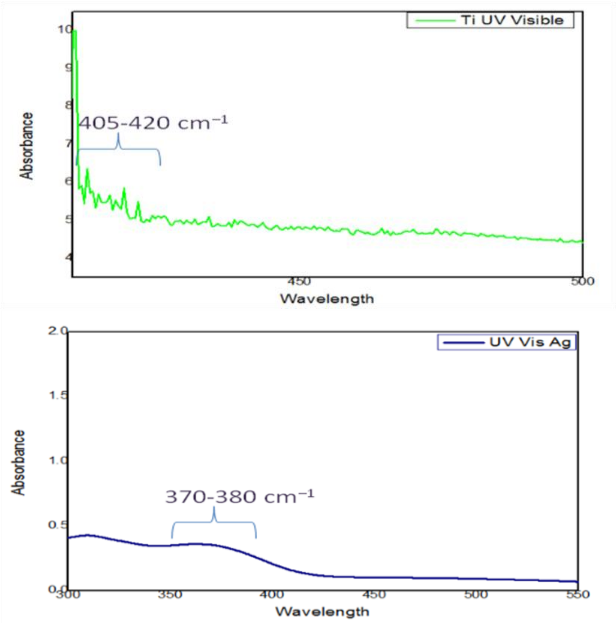


Figure 7: UV-Vis spectra of Ti and Ag nanoparticals

D. FTIR- Fourier Transform Infrared Spectroscopy

The broad peaks in figure 8 at 1632; 2128; 3442 cm^{-1} and 3433 1630 cm^{-1} confirms the formation of silver and titanium nanaoparticals corresponding to the stretching of OH group and H-O-H bending [23].

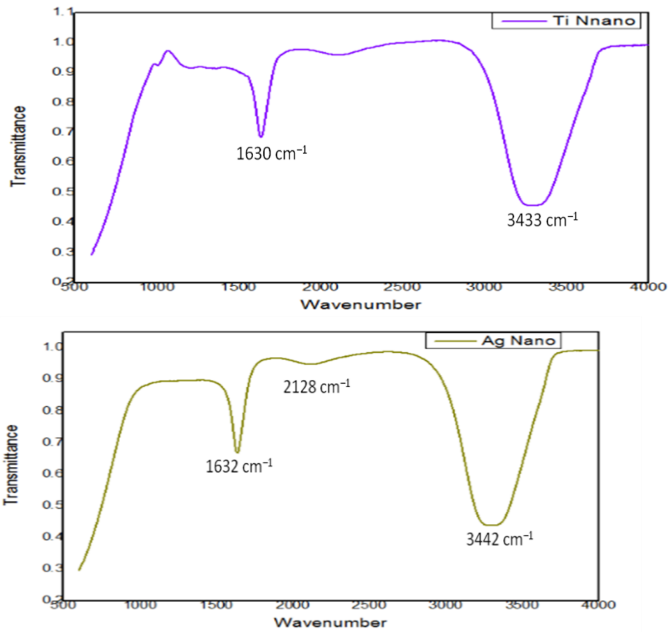


Figure 8: FTIR spectra of Ti and Ag nanoparticals

E. Rheological properties

The pulp after filtration was used to plot the stress-strain curve as shown in figure 9. PP attachment was used. 100 data points after every 2 sec was obtained. Pulp behaves as a

Plastic/ Bingham fluid with yield value of 70 Pa and will behave as a Newtonian fluid i.e. viscosity will remain constant thereafter as a result mixing time of 5-6 hrs can be set without change in viscosity.

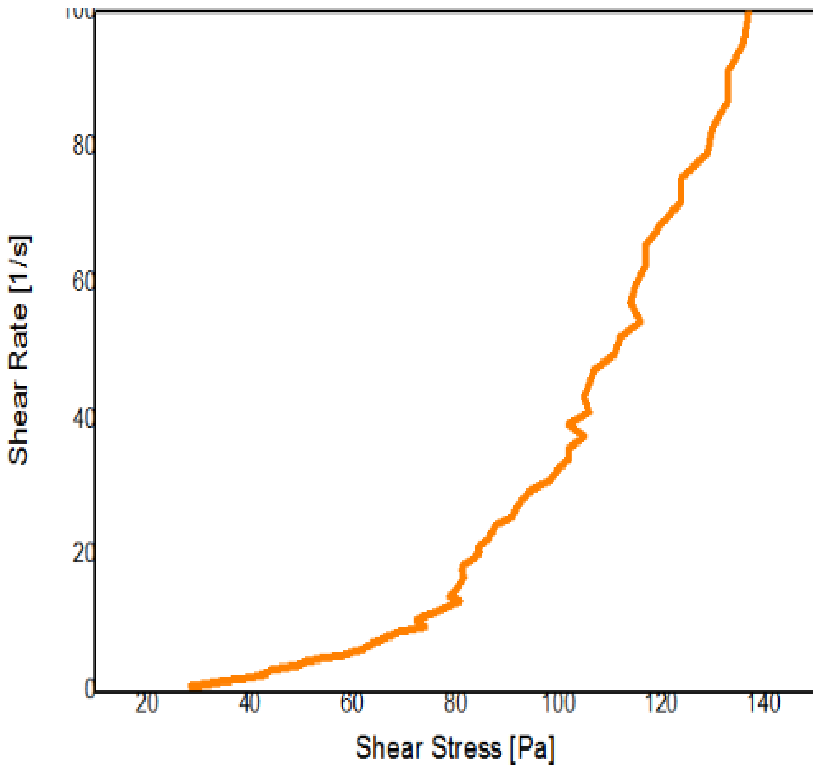


Figure 9: Stress-Strain curve for pulp

F. TGA- Thermo-gravimetric analysis

Thermal stability of fabricated paper was investigated by thermo-gravimetric analysis using Al_2O_3 crucible in N_2 atmosphere from 25^{O}C to 500^{O}C, was carried out as shown in the figure 10.

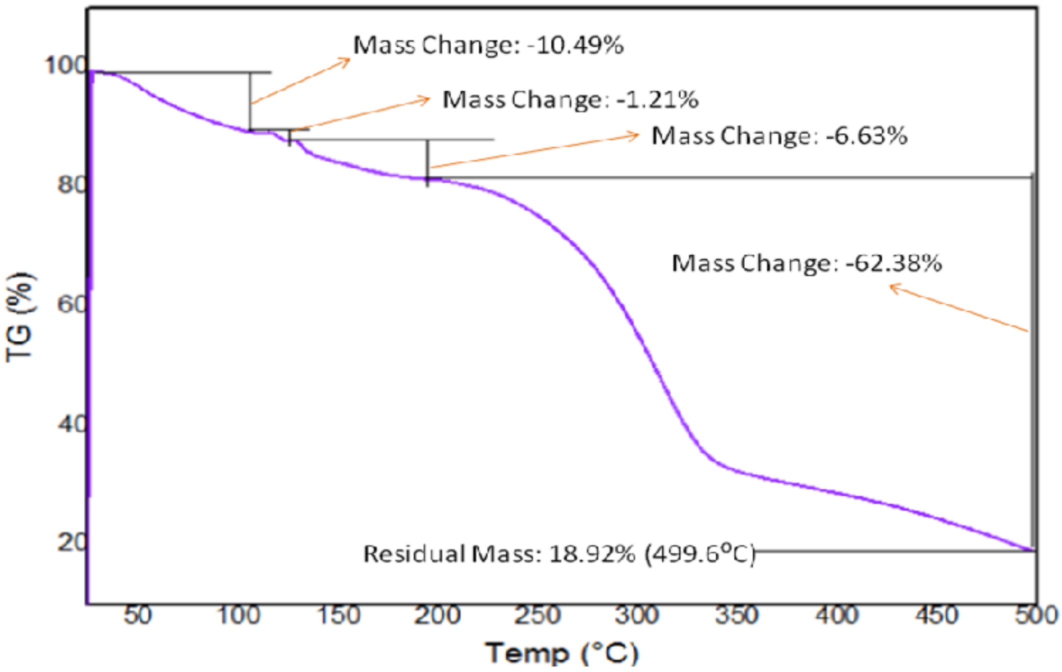


Figure 10: TGA of fabricated paper

Thermo-gravimetric analysis determines the effect of the synthesized cellulose TiO_2-Ag hetero structure nanoparticles. The higher thermal stability of nanocomposite can be attributed to the presence of inorganic Ag, TiO2 nanoparticles into the cellulose matrix. The cellulose thermal decomposition include depolymerisation, dehydration, and decomposition of glycosyl units, followed by the formation of a charred residue. The two major exothermic peaks by 100^0C is considered as initial H_2O desorption at polymer associated with a weight decrease (~11.60%). The second stage at about 170^0C is due to removal of protonic acids, organic compositions. Cellulose, lignin and hemicelluloses are stable and their degradation occurs at much high temperature and over a very wide range i.e. 200^{O}C-500^{O}C [24], revealing the complicated molecular and crystalline structure induced in cellulose mixing with nano-TiO_2 powder plays a dominant role in both morphological and microstructural change in the polymer matrix. Next stage (~290^0C), indicates the polymerchain break which lead to production of gases. After combustion of the organic part, a residual mass of ~18.92% by weight is still present at the end of 499.6^{O}C showing the more of char, silver and titanium nanoparticals at the end.

G. Physical Parameters

Mechanical properties like grammage, tearing strength, stiffness were measured and compared with already existing recycled packaging paper as shown in the table 1. Fabricated paper was more thicker (0.199±0.001mm) with more fiber per sq meter (0.0081±0.002) and more tearing strength (MD 40±0.1,CD 41±0.1) but showed easy bending (72-75 Taber (avg)). The unbleached paper was yellowish in appearance with less smooth surface.

Table 1: Comparison of physical parameters for fabricated paper and recycled paper

S.No.	PARAMETERS	RECYCLED PAPER	FABRICATED PAPER
1	Thickness	0.111±0.001 mm	0.199±0.001mm
2	Grammage	0.0078±0.001	0.0081±0.002
3	Tearing Strength	MD 38±0.05 , CD 40±0.05	MD 40±0.1 ,CD 41±0.1
4	Stiffness (bending)	75-80 Taber (avg)	72-75 Taber (avg)
5	Appearance	Brownish	Yellowish
6	Bleaching	No	No
7	Smoothness	Smooth	Less smooth

H. Antibacterial Properties

Titanium oxide (TiO_2) is one of the promising photocatalytic, microbiocidal effects under UV light due to wide band gap material (3.2 eV). On the other hand, silver nanoparticles doping to TiO2 tune the band gap upto 2.7 eV can absorb visible light due to localized surface plasmon resonance [25], extending their wavelength response toward the visible region, trap the excited electrons from TiO_2 and leave the holes for the degradation yield and the enhancement of antimicrobial properties leading to new applications such as antibacterial and photo catalytical effects useful for food packaging paper and coated sanitary wares [26].

The better photocatalytic activity shown by Ag-TiO_2 over the prepared TiO2 can be explained on the basis of silver being an acceptor impurity in doping of TiO_2, it acts as an electron trap and prevents the electron hole recombination, which is important factor in determining the photocatalytic activity as represented in Figure 11 [25, 26]. The photocatalytic deposition is carried out in the presence of metal ions, semiconductor support and hole scavengers. After irradiation, the photogenerated electrons reduce the surface-adsorbed metal ions forming metal clusters, and then, Ag nanoparticles via a repeated reduction process [27,28].

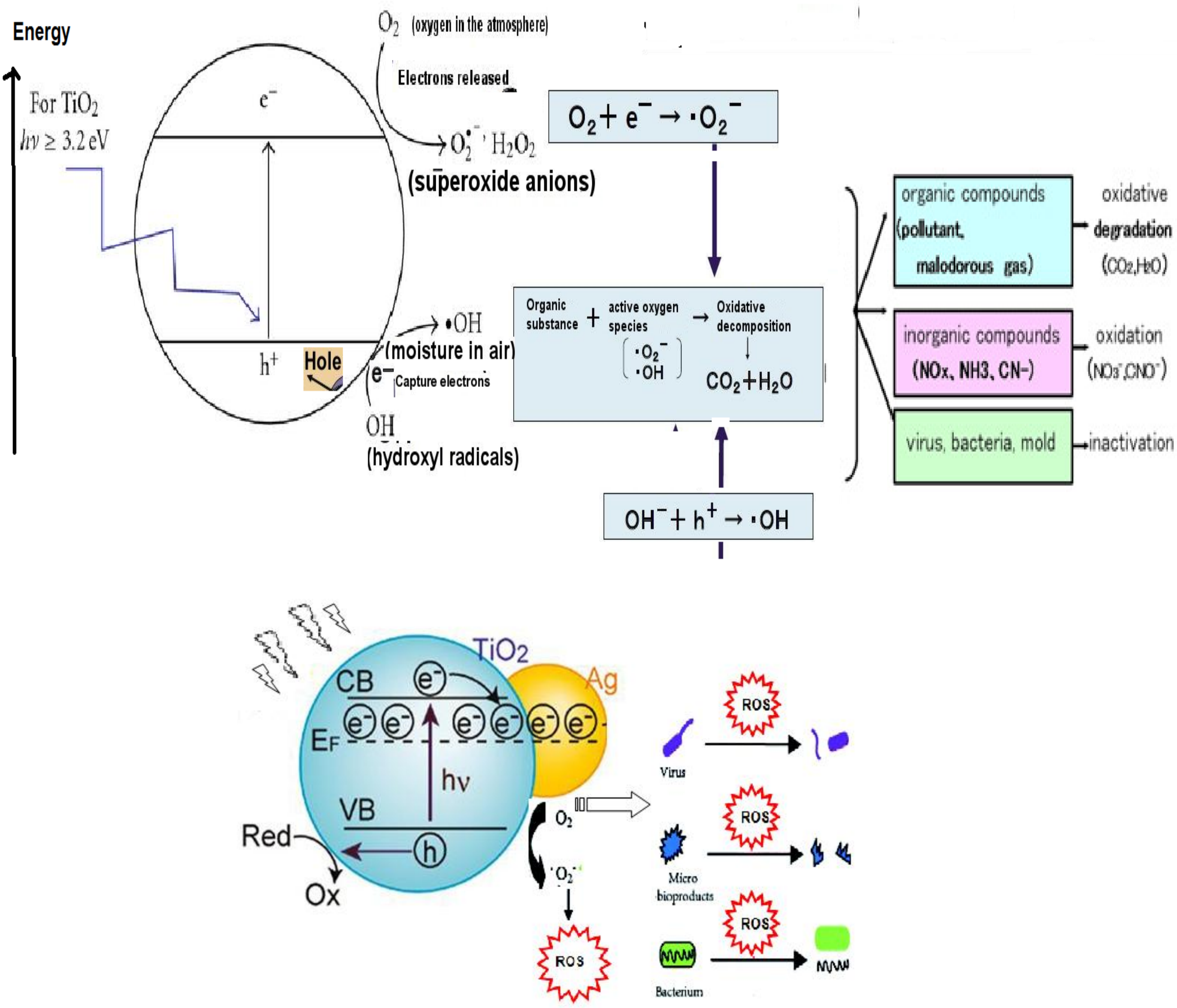


Figure 11: Mechanism of photocatalytic degradation in presence of visible radiation

Fabricated paper confirms the antibacterial properties, by showing the zone of inhibition for both Gram positive and Gram negative i.e. *Bacillus subtilis* and E. *coli* respectively. Paper was more sensitive towards E. *coli* then *Bacillus subtilis* in both presence and absence of visible light. Titanium nanoparticals are known to show photocatylitic properties in presence of UV range but doping with Silver nanoparticals enhance this property even in visible range also [28]. The enhanced antimicrobial ability proposed from the synergistic activities of Ti-Ag components in nano phase, revealing the electrostatic interaction mechanisms by the released Ag species and oxidative stress caused by photo-generated reactive radicals contained in the paper as shown in figure 12 [19]. The neem based paper didn't show any antibacterial properties but rather showed denser growth as shown in figure 13; hence further studies were no conducted for this paper. It is expected initially that robust covalent linkage between the nanoparticles and the cellulose leads to a remarkable suppression of the release of metal nanoparticles from the paper. But, the release and collection metal nanoparticles residues on food sample from the paper will be determined by inductive couple plasma mass spectroscopy (ICPMS) is under progress.

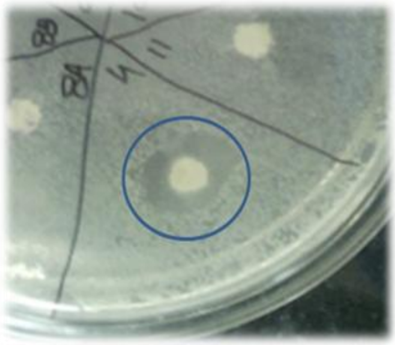
Comment	Absence of visible light	Presence of visible light
a) E. coli More broader inhibition in presence of visible light		
b) Bacillus subtilis Inhibition in both the cases, but less than *E. coli*		

Figure 12: Antibacterial activity of fabricated paper in presence and absence of visible light for

(a) E. coli (b) Bacillus subtilis by antibiotic disc diffusion method

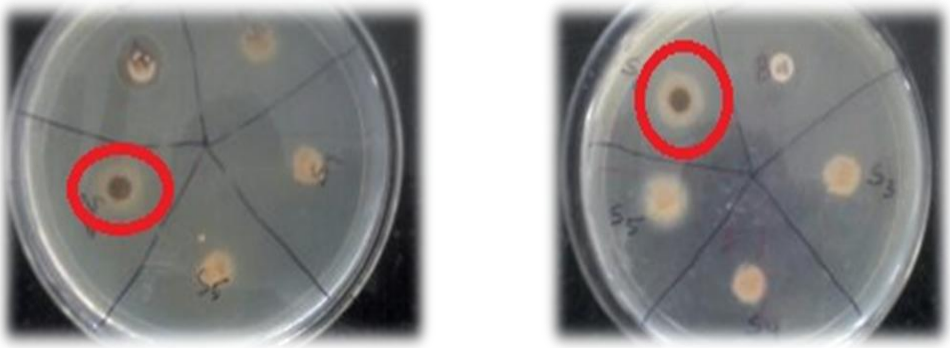


Figure 13: No growth inhibition by neem leave fabricated paper in both E. coli (right) and

Bacillus subtilis (left)

I. Shelf Life study on Burfi

The Burfi sample packed in recycled packaging paper and antimicrobial fabricated paper at 25^{O}C for 8 days was studied and microbial load was compared using TPC method. The fabricated paper was found to be more resistant and increased the shelf life of burfi by 8 days as shown in the graph in figure 14.

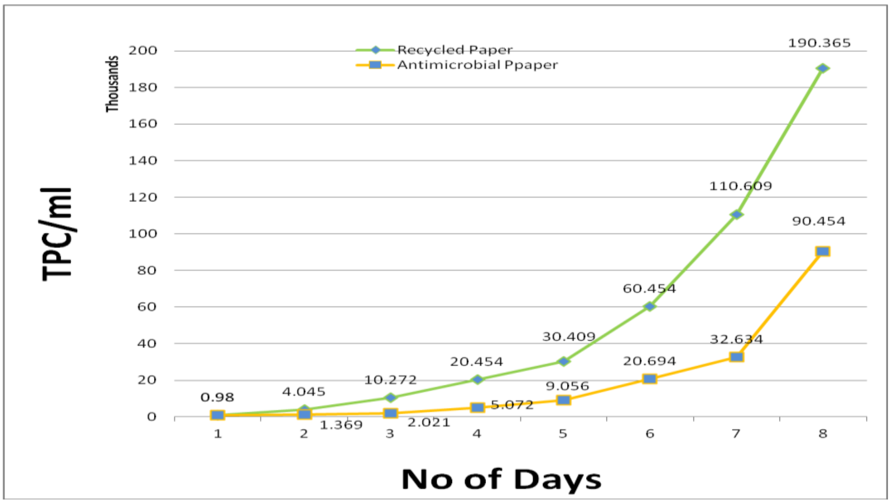


Figure 14: Graphical representation of shelf life of burfi by TPC method

5. Conclusion

Silver and Titanium nanoparticals were synthesised using green chemistry method and were used to introduce antibacterial properties in the yellowish fabricated paper, from the GLCC using cold alkali method. It showed better grammage, tearing strength, stiffness and less microbial load when compared with recycled packaging paper. Hence, the antimicrobial paper using GLCC, opening the scope for an alternate to wood, value addition to agro waste, additional income to the farmers, encourage the rural entrepreneurs, reduce the food spoilage and environment friendly residue.

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