Groundnut shell -a beneficial bio-waste

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ABSTRACT

Groundnut shells account for approximately 20% of the dried peanut pod by weight, meaning there is a significant amount of shell residual left after groundnut processing. Increased groundnut production leads to the accumulation of these groundnut shells which is not utilized, thus either burnt or buried. As Groundnut shells are rich in many functional compounds and composed of cellulose, hemicellulose and lignin, it can be utilized in multiple ways. This review highlights potential applications of groundnut shells for commercial and industrial purposes. Groundnut shells can be converted in various bio-products such as biodiesel, bioethanol, nano-sheet and also has applications in enzyme and hydrogen production, dye and heavy metal degradation etc. An efficient management strategy is required to convert this otherwise considered waste into valuable bio-products to achieve zero waste production system.

1. Introduction

Groundnut is a nutritious leguminous crop, grown mainly for seed and oil worldwide. Groundnut shells are the leftover product obtained after the removal of groundnut seed from its pod. This is the abundant agro-industrial waste product which has a very slow degradation rate under natural conditions (Zheng et al., 2013). However, Groundnut shells contain various bioactive and functional components which are beneficial for mankind. Commercially, it is used as a feedstock, food, filler in fertilizer and even in bio-filter carriers. But most of the deserted groundnut shells are burnt or buried resulting in environmental pollution. Thus, new technologies need to be developed in order to attain zero waste production and direct this otherwise waste product into meaningful use in food, feed, paper and bioenergy industries (Sheelendra and Shilpa, 2014; Bishnu et al., 2018; Wilson et al., 2006).

Over the years, various efforts have been made to utilize these shells. Small fractions were integrated into animal feed, especially for cattle (Gary, 2002), while few researchers have experimented on their use as dietary fiber for humans (Collins et al., 1981). Other research trials include its uses in pulp production (Jones et al., 1998), feedstock for bioethanol production (Fang et al., 2014; Iqbal et al., 2013), particle board component (Batalla et al., 2005), mulch and activated charcoal (Wilson et al., 2006). Other applications of groundnut shell include its use in composting wet materials, for wastewater treatment, plastic, wardrobes and also used as insulation board, metal casting, and a medium for pesticides as well as activated carbon. However, the major disadvantage of its use in large scale industrial process is the higher lignin content which is mainly responsible for its resistance to biodegradation under normal environmental conditions and also for its poor digestibility in ruminants.

This review summarizes the wide range of potential applications of groundnut shell biomass in the production of various bio-products (Fig. 1).

2. Usage of groundnut shell

2.1. Biodiesel production

Biodiesel, obtained from vegetable oil or animal fats, is an attractive substitute fuel source and is acquiring attention due to its non-polluted and eco-friendly nature. According to a study by Udeh, (2018), biodiesel can be produced using the fungus *Aspergillus niger* from the lipase catalyzed groundnut shells. Results showed that biodiesel with the viscosity of $2.88 \, cm^2 \, s^{-1}$ was obtained from the groundnut shells, which is slightly higher than the biodiesel derived from the waste sunflower vegetable oil ($2.81 \, cm^2$). Additionally, it has the capacity to
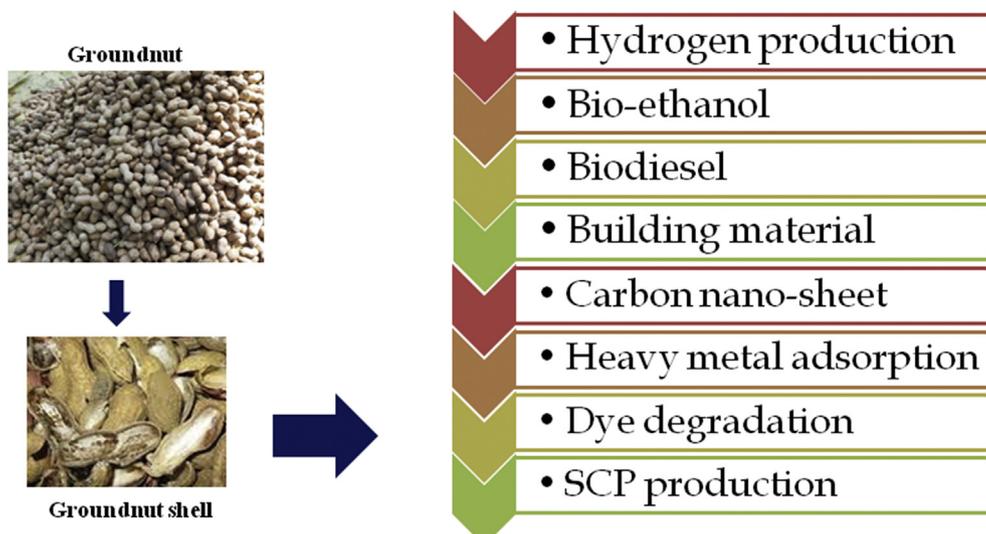
Fig. 1. Applications of groundnut shells in various bio-products production.

withstand at cold climate conditions which in turn gives smooth and increased engine performance (Amore et al., 2014). Several other reports showed that solid catalyst made from the groundnut shells were used extensively for the production of biodiesel (Yong et al., 2014; Feiling et al., 2015). Results showed the highest catalytic activity for the esterification of waste cooking oil than the solid catalyst produced from $LiCO_3$ modified peanut husk ash for the esterification of soybean oil.

2.2. Bioethanol production

Biofuel can be defined as the solid, liquid or gaseous fuel obtained from biomass. Bioethanol is a type of biofuel produced from various biomass (Nyachaka et al., 2013). Several research studies investigated the production of bioethanol from the groundnut shells using various fermenting microorganisms (Table 1). The process involves extraction of cellulose from biomass and conversion into sugars by cellulolytic action of microorganisms, which is further utilized by microbes to produce ethanol. Fig. 2 represents bioethanol production from groundnut shell. A study investigates the production of bioethanol via simultaneous saccharification and fermentation using combination of bacteria and yeast such as *Bacillus stearothermophilus, Saccharomyces cerevesiae*. Results showed that 16.11 ± 0.49652 (g/L) ethanol was produced after 14 days of incubation (Sheelendra and Shilpa, 2014). *S. cerevesiae* is the most widely used microorganism for bioethanol production. A study showed the highest alcohol yield was attained from 8 g of groundnut shell powder on the fourth day of fermentation (0.5 mg/ml) using *Saccharomyces cerevisiae* (Tejas et al., 2017). From 420 g of groundnut shell powder the ethanol yield obtained after three batch experiments by using *Saccharomyces cerevisiae* and *Aspergillus niger* was
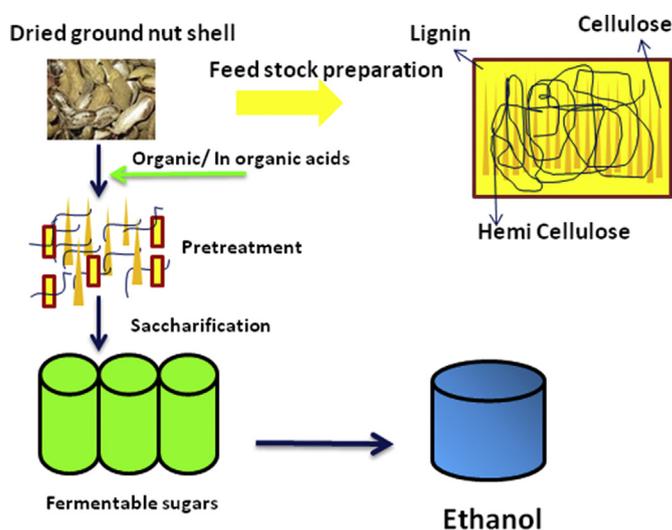

Fig. 2. Schematic diagram of bioethanol production from groundnut shell.

55.8 ml, 45.60 ml, 43.76 ml respectively. The produced ethanol was evaluated based on different parameters such as brake power, torque, brake mean effective pressure and volumetric analysis vs engine speed. The evaluation results showed that this bioethanol can be used in gasoline engine with little or no modifications (Nyachaka et al., 2013).

Pretreatment of biomass plays a vital role in ethanol production. Saccharification of sodium sulfite pretreated groundnut shells provide higher sugar yield (670 mg/g after 50 h of incubation) than the dilute

Table 1
Bioethanol production from ground nut shell using different microorganisms.

S. no	Source material	Bio ethanol Production	Reference
1	Groundnut shell with *Saccharomyces cerevesiae* and *Aspergillus niger*	55.8 ml of ethanol was produced from 420 g of groundnut shell powder.	Nyachaka et al., (2013)
2	Groundnut shell along with *Pichia stipitis*	Maximum ethanol yield (20.45 g/L) obtained on batch fermentation.	Gajula et al., (2011)
3	Groundnut shell along with bacteria & yeast	16.11 ± 0.49652 (g/L) ethanol was produced after 14 days of incubation when *Bacillus stearothermophilus, Saccharomyces cerevesiae* was used for saccharification of groundnut shell.	Sheelendra and Shilpa, (2014)
		Maximum ethanol yield 0.955% was obtained when mixture of *Zymomonas mobilis* & *Saccharomyces* used.	Rabah et al., (2011)
4	Groundnut shell along with maize cobs	3:1 ratio of maize cobs and groundnut shells gave 8.2% ethanol yield.	Akpan et al., (2005)
5	Chemically pretreated Groundnut shell	Maximum 16.4% ethanol was obtained from 25 g of groundnut shell.	Nerissa et al., (2015)
6	Groundnut shell along with *Saccharomyces cerevisiae*	Maximum Ethanol content was found to be 0.5 mg/ml on Day 4.	Kutshik et al., (2016)

acid and alkali treated peanut shells because of delignification (Gajula et al., 2011). Chemically pretreated groundnut shells for cellulose extraction along with *Saccharomyces cerevisiae* and fermentation medium produced the highest ethanol yield (0.5 mg/ml) after fourth day of fermentation. From 8 g, 0.41 g of cellulose per gram of groundnut shell powder was obtained. The study has also analyzed the use of groundnut shell ash as a bio-fertilizer for increasing the crop yield. The results postulated that the groundnut shell ash can efficiently involved in increasing the protein and carbohydrate content of the soil (Tejas et al., 2017).

Some studies focused the comparison between different lingo-cellulosic biomass involved in bio-ethanol production. One of the studies compared the maximum ethanol production between rice husk and groundnut shells. In this research, the rice husk and groundnut shells were enzymatically hydrolyzed using cellulolytic microbes (*Bacillus licheniformis, B. lentus, B. subtilis, Paenibacillus alvei, Yersinia enterocolitica and Salmonella sp*) isolated from rumen content of the ruminants. Then the fermentation of hydrolyzed samples was carried out by *Saccharomyces cerevisiae* and *Zymomonas mobilis* isolated from the palm wine and rotten orange respectively. The study compared the ethanol yield when *S. cerevisiae* and *Z. mobilis* used alone and in combination. The highest yield of reducing sugar of 4.0% was obtained from groundnut shell, whereas 2.9% was obtained from rice husk. Maximum yield of ethanol 0.9% was produced when mixture of *S. cerevisiae* and *Z. mobilis* were used, while the lowest concentration of 0.1% was obtained when *Z. mobilis* was used alone (Rabah et al., 2011).

A research on the production of bioethanol from the rice bran and groundnut shells using simultaneous saccharification and fermentation process postulated that the rice bran gave the highest yield than the groundnut shell (William et al., 2016). When compared to the study on rice husk mentioned above it has been cleared that the rice husk was not efficient in ethanol production than the rice bran (William et al., 2016; Rabah et al., 2011). Another research, which investigated on the utilization of groundnut shells for the ethanol production using *S. cerevisiae* and *Z. mobilis*, found that the maximum yield obtained only when *S. cerevisiae* used alone. This result was contradictory to the results of the study using *S. cerevisiae* and *Z. mobilis* as mentioned previously (Rabah et al., 2011).

Previously, another study performed an investigation on the maximum ethanol production from maize cobs and groundnut shells when mixed at different ratios. The samples were treated with various concentrations at ambient temperature and varying temperature with 4.5M H_2SO_4. Maximum yield attained when 3:1 ratio of maize cobs and groundnut shells were used (8.2% of ethanol produced after 2.5 h) (Akpan et al., 2005).

In a separate study by Venkatachalam et al. (2014), agricultural wastes such as sugarcane bagasse, sweet sorghum, maize stover, groundnut shell, paddy straw and forestry waste, wood chips were pretreated using *P. florida* and were used as the sources for bioethanol production by solid state fermentation. This study showed that the groundnut shells are not efficient in ethanol production when compared to sweet sorghum because of its high sugar content.

Apart from all the complex biological processes of the bioethanol production a simple extraction method was carried out by using sulphuric acid and CaO lime for the pretreatment of groundnut shells (Nerissa et al., 2015). Various chemicals such as Ammonium sulphate, Magnesium sulphate and Sodium phosphates were used as nutrients in fermentation process and also yeast and water were used for the enhancement of fermentation process. After one week the colourless and flammable ethanol (16.4%) was extracted from 25 g of groundnut shells.

2.3. Carbon nano-sheet formation

Production of Carbon nano-structured materials, such as nano-sheets, from natural waste, involve carbonization and activation. In a study by Kanokon et al. (2018), researchers produced the carbon nano-sheets from the groundnut shells based on the influence of KOH. This study investigated the effect of the state of KOH (solid or solute) treated groundnut shells on carbon nano sheet's microstructure. Carbon nano-sheets produced from the activation of groundnut shells by solute KOH showed flat and thin surface (< 50 nm) than the solid KOH treated groundnut shells. The outcome of the study postulated that the KOH treatment is more effective for the production of carbon nano-sheet from groundnut shells.

2.4. Enzyme production

A research study investigates the production of cellulolytic enzymes from the groundnut shells by solid state and submerged liquid fermentation process using individual and synergistic consortia of fungal cultures comprising *Pycnoporus sanguineus* (PS) in combination with *Aspergillus oryzae* (AO) and *Trichoderma harzianum* (TH) (Thota et al., 2018). The Mandel and Reese medium was used for enzyme production and the contents were analyzed for filter paper activity (FPU/gds), CMCase (IU/gds) and β -glucosidase (IU/gds). Under ternary combination of cultures, cellulase production was highest at 123.0 ± 1 FPU/gds; β -glucosidase production at 875.6 ± 26.4 IU/g dry substrate (gds); and CMCase at 474.95 ± 45.5 IU/gds. β -glucosidase production was highest on the 2nd day at 987.03 ± 64.2 IU/gds while CMCase peaked at 514.97 ± 21.4 IU/gds on 2nd day for PS, maximum cellulase enzyme production was observed on the 6th day at 192.2 ± 0.96 FPU/gds (AO + PS). The results concluded that the synergistic combination of fungal cultures showed balanced enzyme activities to saccharify biomass which can then be fermented to produce various bio-products.

Lipase is an enzyme involved in various industrial applications and was produced by different species of microbes in nature. Isolation of extracellular Lipase from groundnut shells were performed under submerged fermentation process (Sarika and Aradhana, 2016). Lipolytic bacteria was isolated from the soil and subjected to grow on various agro-waste materials such as wheat bran, ground nut, potato peel extract, and banana peel extract at 1% concentration. Among all of them groundnut shells showed the maximum lipase activity (0.0055 μg/ml/min) followed by 0.0050 μg/ml/min with wheat bran and 0.0049 μg/ml/min with Banana peel extract and 0.0046 μg/ml/min with Potato peal extract. The results found that the groundnut shells can be a good source for the lipase production.

2.5. Dye degradation

Micro crystalline cellulose (MCC) is a white, odourless, crystaline powder isolated from groundnut shell pulp and was investigated for the degradation of crystal violet and methylene blue dyes (Zakariyya and Saifullahi, 2018). The solutions of methylene blue and crystal violet were subjected to MCC and the removal of dye was determined by UV Visible spectrophotometer. Dye adsorption was determined according to different parameters like pH, adsorbent dosage, stirring rate. Regeneration and reusability of adsorbents were also tested. Their result showed that 100% removal of crystal violet and methylene blue dye at alkaline pH. Groundnut shell MCC showed maximum removal up to 6 cycles with 62% and 84% removals for crystal violet and methylene blue respectively when it is re-used. As such MCC obtained from groundnut shell is considered to be effective adsorbent for the removal of environmentally pollutant dyes.

Groundnut shells were also used for the activated carbon production which can be utilized for the industrial effluent treatment process (Kamaraj and Umamaheswari, 2017). Groundnut shells activated carbon (GSAC) used for the removal of methylene blue dye from the aqueous solutions that accompanied with moderate micro biostatic activity. Groundnut shell activated carbon prepared (56.60%) was analyzed for different parameters like pore size, porosity, moisture

content, BET(Brunauer-Emmett-Teller) surface area and langmuir surface area. The dye adsorption was checked based on pH, dosage, contact time and initial concentration. GSAC showed high methylene blue adsorption efficiency on Batch and column mode; moderate micro biostatic activity against different microbial strains. Thus the GSAC can efficiently be used for dye effluent treatment processes for the removal of dyes.

In another study, activated carbon prepared from the groundnut shell (GSC) and Indian almond shell (IASC) were subjected to the remove Azure A (AA) dye from the aqueous solutions by batch mode experiments (Meenakshi Sundaram and Shivakumar, 2012). The removal of dye was determined based on varying dye concentration, particle size, dosage, contact time, pH. The results revealed that GSC has the more adsorption capacity (Qo = 142.85) than IASC (Qo = 55.55).

2.6. Use of groundnut shells as building material

Groundnut shell ash can be used as binder in sandcrete blocks (1:8 ratio) as for cement replacement. The silt content, specific gravity, the slump and compressive strength of groundnut shell ash and were tested. The groundnut shell ash can be used as a partial replacement of cement in sandcrete block to achieve a satisfactory compressive strength at about 20 percentage of the binder quantity (Mahmoud et al., 2012). Groundnut shell constituent material was used in concrete for the partial replacement of fine aggregate (river sand). Physical properties of cement, groundnut shell and aggregates were determined. It was found that groundnut shells can be used to replace fine aggregates at 0–75%. The workability of fresh concrete was determined based on the effect of groundnut shells by slump and compacting factor value test and the compressive strength and density values of the cubes also estimated. The results concluded that the groundnut shell can be efficiently used for the production of light weight concrete (Sadaa et al., 2013).

Chemical composition of groundnut shell ash (GSA) and ordinary Portland cement (OPC) was determined and particle size, density, specific gravity, compressive strength were also analyzed of GSA and OPC. Final result of their study proposed that the compressive strength value of the GSA/OPC concrete ranged from 29% at 40% replacement level to about 70% at 10% replacement level of the compressive strength of the control (0% GSA replacement) at the 28th day. Thus it was concluded that 10% is suggested for the mass concrete construction (Nwofor and Sule, 2012).

2.7. Growth media

Investigation was done for the use of groundnut shell as a composite for the replacement of peat for growth of the ornamental plant (Violet) (Jalal et al., 2017). The test was carried out at randomized design of five experiments with various concentration of peat and groundnut shell to determine their ability to induce the better plant growth. Final result of the study indicates that the use of groundnut shell as a composite for the growth media for the plant increases the no. of flowers, plant height, dry-weight of canopy when compared to control and 50% of the Peanut shells compost showed the greatest effect on violet plant growth.

2.8. Groundnut shells in hydrogen production

Production of hydrogen gas from the groundnut shell biomass was assessed in one study where it is achieved by pyrolysis process (Evans et al., 2002). Pelletized groundnut shells are used as a feed material in fluid bed pyrolysis reactor for the production of activated carbon by two stage process. The vapour by-products from the first stage pyrolysis were used for the steam generation. This steam was allowed through the catalytic steam reforming reactor for the conversion of whole biomass pyrolysis vapours to hydrogen. Pyrolysis vapours of the first step

were tested in phase two then the hydrogen produced were purified by converting residual CO to H2 over a shift catalyst and separating hydrogen from CO2 using pressure swing adsorption. The purified hydrogen can be mixed with natural gas and used for the transportation.

2.9. Groundnut shells in nanofiber preparation

The preparation of polylactide nano-fibre by reinforcing the mechanical characteristics of groundnut shell particles was done by Samson et al., 2016. The quality of the produced nanofiber was checked according to different parameters like Ultimate tensile strength (UTS), Ductility, Stress at break, Energy at break, etc. Result showed that most of the GSP-PLA nanofibres produced showed poor Modulus of Elasticity and PLA reinforced with 5 wt % untreated GSP indicated best blend of properties such as hardness, stiffness, UTS, energy and stress at break but fair in ductility. Thus the GSP-PLA fibers produced have potential applications in packaging, tissue engineering, and drug delivery.

2.10. SCP production

Comparative study on utilizing agricultural biomass such as sugarcane bagasse and groundnut shell was carried out for the production of single cell protein using *Saccharomyces cerevisiae* (Kutshik et al., 2016). The pH, moisture content, reducing and non-reducing sugar, and crude protein content of fermented sugar bagasse and groundnut shell were determined. When compared to sugarcane baggasse, the highest SCP production with increased protein content was found with *S. cerevisiae* at 9.3 mg per 2 g of substrate on groundnut shells. Thus, it was found that the groundnut shell can efficiently be used for the SCP production.

2.11. Paper production

Groundnut shells can also be used in the paper production as reported by Upendra et al. (2018). In this study, groundnut shells were crushed and subjected to kraft's pulping and soda pulping using different chemicals. After that, the pulp was washed, bleached, dried and compressed to produce paper. This study concluded that paper produced from kraft's process was of better quality as compared to soda pulping process. Thus, this study showed that groundnut shell can be used for paper production.

2.12. Groundnut shells in heavy metal adsorption

Groundnut shells act as a good biosorbent for the adsorption of heavy metals from the industrial effluents. In a study be Shruthi et al., efficacy of groundnut shells was examined for the removal of heavy metals from wastewater. Efficacy was tested using several parameters such as effect of pH, contact time and dosage of groundnut shell at standard temperature conditions. Removal efficiency for Cu and Pb was 68.2% and 77.8% respectively (Shruthi and Pavithra, 2018). Similarly, groundnut shells are proved to be effective in removing toxic metals from the zinc and chromium plated water. The ability to remove toxic metals from the zinc and chromium plated water was achieved using groundnut shells. Finally the initial concentration of zinc (285) and chromium (136) were reduced to 0.75 and 0.85 respectively (Aarti Sowmya et al., 2018).

Rice husk and groundnut shells were also examined for the adsorption of copper metal ions from the aqueous solution by batch experiments based on different parameters such as effect of pH, contact time, initial concentration of metal ion and dosage (Prabha and Udayashankara, 2014). Efficient removal of copper (96.72%) was attained at pH 8 by rice husk which is slightly higher than the groundnut shell (93.90%). The maximum adsorption of Cu by groundnut shells (93.90%) was achieved at pH 6 which was greater than the Cu adsorption (68.2%) done by Shruthi et al., (Shruthi and Pavithra, 2018;

Prabha and Udayashankara, 2014). In a separate study, Groundnut shell activated carbon for the adsorption of metal ions such as copper (II), zinc (II), nickel (II) and chromium (IV) from the aqueous solution was compared based on the pH and metal ion concentration of the aqueous solution. The result indicated that the groundnut shell activated carbon showed the highest adsorption of the Chromium (IV) ions than the other metal ions (Romero et al., 2004).

3. Conclusion

Groundnut shell is generally considered as agro-industrial waste and every year million tons of its quantity is left in environment. Rich in lignin, these shells undergo slow degradation in natural environment. However, groundnut shell biomass has wide range of applications. This waste can be converted to a valuable bio-product in order to achieve zero waste production. The present review highlights results of several scientific studies illustrating potential industrial applications of groundnut shells. Through simple bio chemical treatments, this can be transformed into a large number of bio-products having commercial applications such as biofuels, building material, paper production, heavy metal adsorption, dye degradation etc. A more environmental friendly approach and concerted efforts are needed to implement this habit of converting this waste into useful product.

Conflicts of interest

The authors have declared that no competing interests exist.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bcab.2019.101206.

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