Nanotechnology Intervention- Sugarcane Waste to Wealth: A Review

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Abstract
Nanotechnology is nothing but anything smaller than micro technology. Nanoparticles have been widely used because of their incredible properties such as high heat resistance and chemical inertness. They are synthesized using different metals and metalloids such as calcium, titanium, silicon, etc. In the recent years there has been increased interest on synthesis of nanoparticles using organic waste. Sugarcane bagasse is one of the green ways for synthesis of nanoparticles. Various methods can be used to obtain nanocellulose, such as acid hydrolysis, ultrasonic technique and enzymatic hydrolysis etc. This review focuses on the how best we could use sugarcane waste material for production of nanoparticles.

Key words: Bagasse, Nanocellulose, Nanosilica, Nanosilver, Sugarcane.

Today is the era of nanotechnology. Though the technology is new, the nanoparticles (NPs) are not new. They are as old as earth and have history as long as that of earth itself. Nanoparticles (NPs) have been widely used because of their incredible properties like advance thermal conductivity, high surface area etc. NPs can be classified based on the size, morphology, physical and chemical properties as carbon-based nanoparticles, ceramic nanoparticles, metal nanoparticles, semiconductor nanoparticles, polymeric nanoparticles and lipid-based nanoparticles. They are synthesized from pure metals like gold, platinum, silver, titanium, zinc, cerium, iron and thallium or their compounds like oxides, hydroxides, sulfides, phosphates, fluoride and chlorides. But In the recent years there has been increased interest on synthesis of nanoparticles using organic waste (Ghos et al. 2017). Agricultural or biological waste have attracted a great attention of the researchers due to the advantages with availability, low cost, low density, biodegradability and other specific properties over metal oxides. However, there is very few research carried out to convert agricultural waste to high valued product such as nanoparticles. Although chemical and physical methods may successfully produce pure, well deened nanoparticles, these are quite expensive and potentially dangerous to the environment. Use of biological waste material can be one of the alternatives in ecofriendly management of agricultural waste. Sugarcane waste can also be used for bio synthesis of a variety of metal and metal oxide nanoparticles and it can be considered an alternative, eco-friendly, cost effective and viable green chemistry-based route.

Sugarcane produces mainly two types of Biomass. Cane Trash and Bagasse. Cane Trash is the field residue remaining after harvesting of cane. Bagasse is the dry pulpy fibrous residue that remains after sugarcane stalks are crushed to extract their juice. The word bagasse originally meant “rubbish,” “refuse,” or “trash.” It is a heterogeneous material containing around 30-40 percent of pith fiber which is derived from the core of the plant and is mainly parenchyma material. A typical chemical analysis of washed and dried bagasse consists of 45-55 per cent Cellulose, 20-25 per cent hemicellulose, 18-24 per cent lignin, 1-4 per cent ash, Waxes <1 percent (Rainey, Thomas J 2009). Bagasse is the major by-product of sugarcane crop. It was estimated that every three tons of sugarcane crushed will yield about one ton of bagasse. It has been mainly used as fuel in boilers to raise steam from the old ages. This waste is a renewable and sustainable resource, it can be used to produce steam for power generation, bioetanol production, paper industry and feed stock for cattle. But it has some disadvantage also. As it is very stringy, it is unsuitable for paper production. Moreover, the pith cells in bagasse are 30% to 35%, which makes the material fine, thin walled, low cellulose content cells and do not produce paper making fiber.

Cellulose is a naturally obtained renewable, biodegradable polymers. Due to its long chain and high molecular weight (more than 500,000 Da) it is insoluble in water. It has a size range from 10 nm to 350 nm (Wulandari et al. 2016). Nanocellulose obtained from this cellulose can be a promising raw material for new bio based composites due to their high mechanical strength, stiffness, large surface area, low thermal expansion, optical transparency, renewability, biodegradability, low cost and low toxicity (Brinchi et al. 2013).
Various methods can be used to obtained nanocellulose, such as acid hydrolysis, ultrasonic technique and enzymatic hydrolysis. The method that most widely used is acid hydrolysis (Li et al. 2012). In Indonesia, Wulandari et al. (2016) isolated nanocellulose from sugarcane bagasse by using acid hydrolysis.

In this process sugarcane bagasse was dried in sunlight and then cut into small pieces. The cut bagasse was milled to become powder. The powder of bagasse was bleached with 250 ml of 0.735% (w/v) sodium hypochlorite for 6 hours with constant stirring at 45°C to remove the lignin. The residue was washed with distilled water until a neutral pH is obtained. The neutral residue was refluxed with 150 ml of 17.5% sodium hydroxide for 3 hours with constant stirring at 45°C to remove hemicellulose. The residue of this process was also washed until reach a neutral pH and it was dried at room temperature for 2-3 days. Isolated cellulose from sugarcane bagasse was hydrolyzed with sulfuric acid with a ratio of cellulose to sulfuric acid 1:25. Thus, a colloidal suspension was produced and was centrifuged at 6500 rpm for 30 minutes.

Then, it was dialyzed for 5 days to neutralize and eliminate the sulfate ions. The neutral colloidal suspension was sonicated for 10 minutes to homogenize the generated nano-cellulose. Thus produce nanocellulose with particle size of 10 nm until 4000 nm.

He also tried with two different concentration of sulphuric acid with two different duration. Firstly in 60% of sulfuric acid at 40 °C for 5 minutes (nano-cellulose A) and 50% of sulfuric acid at 40 °C for 10 minutes (nano-cellulose B). It was observed that nanocellulose B has the smaller size than nanocellulose A, due to the longer hydrolysis time (10 minutes) to produce nano-cellulose B than nano-cellulose A (5 minutes) so that the chain of cellulose B was more hydrolyzed than cellulose A and generates a smaller particles size.

But more interestingly acid concentration does not significantly influence in particle size of nano-cellulose. It was reflected in prostate-specific antigen (PSA) that indicates acid concentration does not significantly influence in particle size of nano-cellulose. This is evidenced by the particle size of nanocellulose A has an average diameter of 196.7 nm with the maximum distribution of 148.4 nm. However, the maximum diameter of nanocellulose B is 111 nm and the maximum distribution in 95.9 nm, whereas the acid concentration to produce nano-cellulose A was higher than nano-cellulose B (60% of sulfuric acid for nano-cellulose A and 50% for nano-cellulose B).

But Brinch et al. (2013) reported that higher of acid concentration used during hydrolysis process produces the nano-cellulose with the lower crystallinity index.

Li et al. (2012) reported the isolation of nanocellulose with diameter range of 10–20 nm from sugarcane bagasse by high pressure (80 MPa for 30 cycles) homogenization in homogenous ionic liquid 1-butyl-3-methylimidazolium chloride media with 90% recovery under optimum refining condition.

Maddahy et al. (2012) reported the extraction of nanocrystalline cellulose from sugarcane bagasse based cellulose by alkaline hydrolysis (50% NaOH) at 40 °C and acid hydrolysis (50%) at 40, 60 and 80 °C. The results showed that crystallinity and degree of polymerization of cellulose increased as the temperature increased from 40 to 60 °C and then decreased at 80 °C lower than the value at 40 °C.

Quantum Dots (QD) are tiny carbon nanoparticles, which are about four nanometers across. Because they emit light and are non-toxic, carbon quantum dots can serve as biosensors, in light-emitting diodes and even to deliver drugs around the human body. Thambiraj and Ravi Shankaran (2016) successfully synthesized carbon quantum dots from sugarcane bagasse. They first cut the sugarcane bagasse into small pieces and sun-dried it for six days. After burning the dry bagasse, they chemically oxidized and exfoliated it. The morphological and topographical study of QDs produced was done by High-Resolution Transmission Electron Microscopy (HR-TEM) and Atomic Force Microscope (AFM) and was observed that the average size is 4.1 ± 0.17 nm and surface thickness is 5 nm with a face centered cubic crystal structure.

Bagasse can also be used for synthesis of silica nanoparticles. There are still few studies about the use of sugarcane bagasse and ash as raw materials for the production of silica nanoparticles. Silica nanoparticles can be used in paints, batteries, as biopolymers, catalyst, adsorbent, membranes for fuel cell etc. Rovani et al. (2018).

Ash from sugarcane residues contains more than 70% silica by mass. But the sugarcane ash contains lots of impurities like salt and carbon species, organic compounds and low solubility elements etc. They were separated through washing and sieving with a size of more than 0.6 mm. Kalapathy et al. (2000). Silicon was extracted from sugarcane waste ash by reaction with sodium hydroxide under heating at 400 °C by following the method of Alves et al. (2017). At 400 °C, sodium hydroxide is melted, which increases silicon extraction. This procedure helps to increase silicon purity, liberating elements which can be in the structure of ash, making them more soluble. This procedure of extraction generates silicon in the form of silicate and after extraction, this silicate was solubilized in deionized water, ulered and saved for the preparation of silica nanoparticles (SiO\textsubscript{2}NPs).

SiO\textsubscript{2}NPs can be prepared by a wide variety of methods, including the sol/gel method, hydrothermal synthesis, üame synthesis and the reverse microemulsion technique etc. Rovani et al. (2018). They have used sodium silicate solution to prepare SiO\textsubscript{2}NPs. By hydrolysis and condensation (formation of siloxane) reaction using sulfuric acid in a biphasic medium in the presence of cetyl trimethyl ammonium bromide (CTAB) Sharma et al.(2015), Wang et al. (2004)

CTAB helps to control the size of nanoparticles, to prevent agglomeration and to modify their surface. This way,
the co-condensation procedure using sulfuric acid generates a white solid with low dispersion in both media and easily removed by centrifugation. With the help of ICP-OES, an analytical technique capable of detecting traces metals and elements, the content of SiO₂ determined in sugarcane ash was 88.68 ± 0.87 wt % and in the prepared SiO₂NPs was 99.08 ± 0.99 wt % (Rovani et al. 2018). These results demonstrate a significant purification of sample that generates high pure SiO₂NPs.

Sivakumar et al. (2013) synthesized nano silica by using thermo chemical method. Sugarcane bagasse ash was cleaned, dried and calcined through a heating rate of 300°C per hour and then held at 650°C for 2 hour. At 500°C the organic compounds decomposed off and at 650°C a large amount of ash with high silica (72%) content was obtained (Amutha et al. 2010). Sivakumar and his team took 10 g of treated bagasse ash (BGA) and were dissolved in 80 ml of 2.5 N sodium hydroxide solution under constant stirring. Then boiled at 100°C for 3 hour. After boiling the solution was filtered in a silica crucible. Then they obtained a colourless, transparent, denser sodium silicate solution and were allowed to cool at room temperature. After filtration process the sodium silicate solution was titrated with HCl. Under constant stirring, 5N HCl was added drop by drop in the sodium silicate solution then a white silica gel was formed. The pH of the silica gel was found to be 2 i.e. acidic in nature that proves complete precipitation of silica gel. To break the silica gel bond and to settle down pure silica particles constant stirring at a temperature in the range of 90°C - 100°C for 5 hour changes the pH to 10. Then the silica particles were washed by demonized water for neutrality and then dried at 70°C for 17 hour. In this way pure silica was found and was used to synthesize nanosilica through reflux method.

Pure silica with 6N HCl solution was subjected to continuous refluxing the temperature at 80 - 90°C for 8 hour. After refluxing the sample was washed with more amount of warm distilled water to become alkali free and then hot air oven dried. Afterwards 80 ml of 2.5 N sodium hydroxide was added to the silica powder under constant stirring for 9 hour. Then concentrated HCl was added to the solution until a white precipitate was formed. The precipitate was washed thoroughly by warm triple distilled water for neutrality. The synthesized nanosilica was dried in a hot air oven at 110°C for 24 hour. The results of SEM with EDS suggested prismatic particles consist mainly of silica only. The spherical ones contain silica as well as Na, K, Al, Fe, Mg and Ca. The percentage of silica in the ash is 72% with some metallic impurities. SEM micrograph of nanosilica shows that the particles are almost spherical, homogeneous and agglomerated form. SEM-EDS report the silica particle is 90 nm in size and of 99% purity. Kaur et al. (2013) reported that silver nanoparticles have possible applications in diverse areas such as electronics, cosmetics, coatings, packaging and biomedical applications like antimicrobial and anticancer agents. The synthesis of silver nanoparticles using various sugars has been reported by Nadagouda et al. (2011). Nanosilver was successfully synthesized by Mishra and Sardar (2013) using sugarcane bagasse with the help of only microwave oven and silver nitrate (AgNO₃). They have synthesized nanosilica using sugarcane bagasse by microwave irradiation. This is a fast, simple and energy efficient and low cost technique. In this process, they first boiled 5 gm of washed bagasse in 100 ml of distilled water for 10 minutes. The suspension was cooled and filtered. Then they mixed 90 ml of the filtrate with 10 ml of aqueous solution of AgNO₃ (10⁻³M) to synthesis silver nanoparticles. This mixture was treated with microwave irradiation (800 W) in a domestic microwave oven operated in a cycling mode (on 10 sec, off 5 sec). The synthesis starts within one minute and the reaction completes in 4 minutes. The characteristic surface Plasmon band (SPR) was observed at 435 nm. But when the bagasse alone was microwave treated no spectra was observed up to 4 minutes. This shows the sugars present in extract are responsible for the synthesis of silver nanoparticles. The silver nanoparticles formed were purified by following the method of Mishra and Sardar (2013). The formed silver nanoparticles were characterized by TEM that depicts particle size ranges from 50–150 nm and spherical in size. But the major drawback of biosynthetic processes is that the synthesis of nanoparticles is at a much slower rate to compete with the chemical processes.

Brazil is the one of the dominant country in sugarcane production. Besides production of ethanol and sugar, carbon nanomaterials are also developed from sugarcane bagasse. It was Joner Alves et al. (2012) who reported production of carbon nanotube or nanomaterial using gases generated during the pyrolysis of sugarcane bagasse. With the help of Transmission Electron Microscopy and Scanning Electron Microscopy it was found that the generated nanotube is 50 micro meter long and diameter is about 20-50 nanometer with straight, tubular in structure with smooth wall and axially-uniform diameter which are also the characters of carbon nanotube.

Nanomaterials obtained from sugarcane bagasse can also be used for treating chromium polluted water. Fathy et al. (2020) successfully used carbon nanostructures as absorbent in removing toxic chromium ion. Carbon nanostructures were prepared by catalyzing sugarcane bagasse with hydrothermal process or carbonization of sugarcane bagasse. The carbon nanostructures thus obtained was oxidized with HNO₃/H2O2 and immediately followed by coating with diethylenetriamine. TEM and SEM prove that the resultant carbon nanostructures are made up of carbon nanotube and graphene sheets. The absorption of chromium by HNO₃/H2O2 is 56 miligram per gram and diethylenetriamine is 44 miligram per gram.

**CONCLUSION**

Sugarcane bagasse- the agro-industrial-waste has high potential for the value-added products. Though, it has
already been utilized for many potential applications such as paper, newspaper, textiles fibres, paper board, construction and very recently butane-an alternative to air turbine fuel (ATF) etc. but there is still a wide possibility of this lignocellulosic biomaterial to be exploited for production of various nanomaterials to be used in industrial and biomedical sectors. This small review of the extraction of various nanomaterials from this agrowaste may provide the insight for further research.

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REFERENCES
Alves, J., Jorge, A.S.T., Zhuo, C. and Levendis, Y. (2012). Characterization of Nanomaterials Produced from Sugarcane Bagasse. Journal of Materials Research and Technology. 26(1). DOI: 10.1016/S2238-7854(12)70007-8
Alves, R.H., Reis, T.V. d.S., Rovani, S., Fungaro, D. (2017). A green synthesis and characterization of biosilica produced from sugarcane waste ash. Journal of Chemistry: 1-9.
Amutha, K., Ravibaskar, R. and Sivakumar, G., (2010). Extraction, synthesis and characterization of Nanosilica from rice husk ash. International Journal of Nanotechnology and Applications. 4 (1): 61- 66.
Brinchi, L., Cotana, F., Fortunati, E. and Kenny, J. M. (2013). Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. Carbohydrate Polymer. 94: 154-169
Ghos, R.P., Fawcett, D., Sharma, S.B., Shashi, B., Gerrard, E.J. (2017). Poinem production of high-value nanoparticles via biogenic processes using aquacultural and horticultural food waste. Materials (Basel). 10(8): 852.
Kalapathy, U., Proctor, A., Shultz, J. (2000) A simple method for production of pure silica from rice hull ash. Bioresource Technology, 73: 257-262.
Kaur, H., Kaur, S., Singh, M. (2013). Biosynthesis of silver nanoparticles by natural precursor from clove and their antimicrobial activity. Biologia, 68(6). DOI: 10.2478/s11756-013-0276-1.
Li, W., Yue, J. and Liu, S. (2012). Preparation of Nanocrystalline Cellulose via Ultrasound and Its Reinforcement Capability for Poly (vinyl Alcohol) Composites, Ultrasonics Sonochemistry. 19: 479-485.
Maddahy, N.K., Ramezany, O., Kermanian, H. (2012). Production of nanocrystalline cellulose from sugarcane bagasse. Proceedings of the 4th International Conference on Nanostructures (ICNS4): Kish Island, I.R. Iran.
Mishra, A. and Sardar, M. (2013). Rapid biosynthesis of silver nanoparticles using sugarcane bagasse-an industrial waste. Journal of Nanoengineering and Nanomanufacturing. 3: 154. doi:10.1166/jnan.2013.1135
Nadagouda, M.N., Speth, T.F. and Varma, R.S. (2011). Microwave-assisted green synthesis of silver nanostructure. Accounts of Chemical Research. 44(7): 469-478.
Nady, A., Fathy, Sahar, M. El-Khoul and Ola, I., El-Shafey (2020). Modified carbon nanostructures obtained from sugarcane bagasse hydrochar for treating chromium-polluted water. Current Analytical Chemistry. 16: 1.
Rainey, Thomas, J. (2009). A study of the permeability and compressibility properties of bagasse pulp. Faculty of Built Environment and Engineering Thesis, Brisbane: Queensland University of Technology.
Rovani, S., Jonnatan, J. Santos, Paola Corio and Denise A. Fungaro (2018). Highly pure silica nanoparticles with high adsorption capacity obtained from sugarcane bagasse ash. ACS Omega: 3: 2618-2627.
Sharma, R.K., Sharma, S., Dutta S., Zboril, R. Gawande, M.B. (2015). Silica-nanosphere-based organic-inorganic hybrid nanomaterials: synthesis, functionalization and applications in catalysis. Green Chemistry. 17: 3207-3220.
Sivakumar, G. and Haritharan, V. (2013). Studied on synthesized nanosilica obtained from bagasse ash. International Journal of Chemtech Research. 5(3): 1263-6.
Wang, X. Li., Zhu, W.G., Qiu, S., Zhao, D., Zhong, B. (2004). Effects of ammonia/silica molar ratio on the synthesis and structure of bimodal mesopore silica xerogel. Mesoporous Mater. 71: 87-97.
Wulandari, T., Rochladi, A. and Arcana, I.M. (2016). Nanocellulose prepared by acid hydrolysis of isolated cellulose from sugarcane bagasse. IOP Conf. Ser.: Material Science and Engineering. 107: 012045.