Synthesis and Characterization of Silver/Bentonite/Starch Bionanocomposite by Green Method

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***Abstract*—The aim of this research is to prepare silver nanoparticles (AgNPs) by using green reduction method. Bentonite (BTN), starch (Stc), D(+)-glucose and silver nitrate ($AgNO_3$) were utilized and studied as solid support, stabilizer, green reducing agent and silver precursor respectively. Parameter involved is concentration of 10 mM, 50 mM, 100 mM, 150 mM of silver nitrate. It was found that the best concentration of silver nitrate is at 50 mM to synthesize bionanocomposite as according to UV-Vis result because it is just enough to reduce silver ions. Additional study of properties of bentonite has been made by varying the range of amount such as 1 g, 2 g, 3 g and 4 g of bentonite clay. The study showed that 4 g of bentonite produced the best absorbance peak hence proving that bentonite is a good solid support in bionanocomposite. The synthesized bionanocomposite is characterized by using Ultraviolet visible spectroscopy (UV-Vis), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM).**

Keywords — Bionanocomposite, Green method, Silver Nanoparticles, Bentonite and Characterization.

I. INTRODUCTION

Nanotechnology has been explored over many years and the first researcher who point out scientific explanation of nanoparticles properties is Michael Faraday in his paper called "Experimental Relations of Gold and Other Metals to Light" back in 1857 (Faraday, 1857). Nanoparticles is defined as materials with nano dimension of 1 to 100 nm and have unique properties apart from bulky system. They are extremely small in size and have very large surface area. Silver nanoparticles have attracted the most attention due to inexpensive compared to gold, have antimicrobial effect, unique optical and electronic properties. Subsequently, silver nanoparticles have been commercially available as a drug delivery, water treatment, agricultural and also in biomedical field.

Bionanocomposite is an innovative of nanosized materials. Basically, they have elements of biological source and particles with dimension of 1-100nm. It has likeliness from nanocomposite yet it has differences in method of preparation, biodegradability, biocompatibility, properties, functionalities and application as well. Reinforcement and improvement of the lacking properties are most commonly implemented through addition inorganic fillers. Addition of inorganic additives such as clay minerals and calcium carbonate is a good option because of their reinforcement effects, environmental friendly, easily found and inexpensive (Shchipunov, 2012). In fact, the bionanocomposite films can be used as an ecofriendly material, cost-effective and renewable material for food packaging that has improved antimicrobial effects. Until now, the most frequently research of bionanocomposite that are suitable for packaging application such as starch and cellulose derivatives, polyhydroxybutyrate (PHB), poly- (butylene succinate) (PBS), polylactic acid and poly-caprolactone (PCL) whereas nanoscale fillers are mostly used silicate nanoclays such as kaolinite and montmorillonite (Rhim, Park and Ha, 2013). Bionanocomposite can be an excellent food packaging in which it can have interaction with food by releasing advantageous compounds such as antimicrobial agent, antioxidant agent and also eradicate oxygen and water vapor. Besides that, bionanocomposite has properties of high surface area of nanosized fillers which contribute to large interfacial and boundary area between biopolymer and nanofiller (Azeredo et.al., 2011). Plus, bionanocomposite materials are commonly designed to have the capacity to tolerate mechanical and thermal stress during processing of food, transportation and storage (Rhim et.al., 2013).

There are plenty methods that can be implemented to synthesize nanoparticles such as physical, chemical, green or biological method. Both chemical and physical processes can result in production of toxic by-product, complicated process, costly, inefficient and unsuitable to be used in clinical field. In contrary, green or biological method is environmental friendly due to usage of nontoxic chemicals, less energy and utilize renewable materials. Besides that, the green method also very known as cost-effective, simple and compatible for application in health and pharmaceutical field (Shameli et al., 2012). Some examples of green method including D-glucose (Ortega-Arroyo et al., 2013), microorganism, fungi, algae, plant extract and enzymes (Patra & Baek, 2014). According to Narayanan and Sakthivel, green method is a very significant and suitable alternative route of biocompatibility in synthesis of stable nanoparticles. In fact, the synthesis of nanoparticles using green technology is one of the best way to produce a biocompatible stable nanoparticle.

Starch is one of the most encouraging substance among any other natural polymers especially in terms of biodegradability and biocompatibility. It can be easily found and available at cheap price (Shameli et al., 2011). It also can be easily form dispersion in water hence it is suitable as a protecting agent (Yakout & Mostafa, 2015). According to Raveendran et al., research has been conducted using starch as a stabilizer of metal nanoparticles and β-D-glucose as the green reducing agent. It was found that the nanocomposite is highly stable, monodisperse, uniform, can serve as capping agent and storage of suspension can be up to two months (Raveendran et al., 2003). Furthermore, this thermoplastic starch matrix can also be filled by nanofiller of layer silicates. Among many types of layer silicates, kaolinite and montmorillonite are some of the remarkable types of clay that can

function as solid support in bionanocomposite.

Bentonite also very well-known as a good solid support in nanoparticles technology. The geologist defined term “bentonite” as a rock created of highly colloidal and plastic clays composed mostly of montmorillonite structure in which it is a type of clay mineral of the smectite group and is formed by in situ devitrification of volcanic ash. Fundamentally, the revolution of ash to bentonite actually occur only in water such as seawater, alkaline lakes, and other fresh water during or after deposition process (Grim ,1968; Patterson and Murray, 1975). Particularly in India and Malaysia, bentonite manufacturers are a dominant contributor to the economic welfare of their communities (Murray, 2002). Bentonite contain montmorillonite, feldspar, biotite, kaolinite, illite, cristobalite, pyroxene, zircon, and crystalline quartz (Parkes, 1982).

In fact, bentonites have outstanding rheological, high ionic exchange capacity and good absorbent properties. Especially when added to water, sodium bentonite has a high swelling capacity, and gel-like masses is created. Meanwhile, calcium bentonite has lower swelling capacity than sodium bentonite. Nevertheless, treatment with soda ash can efficiently help in creating sodium exchanged bentonite. Usually this sodium swapped bentonites have less swelling capacity as compared to natural sodium bentonites (Murray, 2002). Application of bentonite are wide such as pet waste absorbents, drilling mud, iron ore pelletizing, foundry sand binding and in waterproofing and sealing process. Besides that, bentonite also well known in helping as a stabilizer, filler, or extender in adhesives, paints, cosmetics, and in medicines. As in cosmetics application, bentonite is used as paste masks, skin care and cleansing preparations, eyeliners, foundations, and many more. In addition, bentonite also can act as a carrier in pesticides and fertilizers, as an attaching agent in animal feeds, purifying vegetable oil, wastewater and wine (Patterson & Murray, 1983).

Bentonite is one of the most common clays that is being utilized as a good solid support in nanoparticles field. For an instance, bentonite has been used as stabilizer in preparation of silver/organo clay nanocomposite research done by Pessanha et al., 2014. It was found that bentonite effectively reduce the aggregation of nanoparticles hence can maintain the nanosized. Other than that, Shahwan et al., 2010 also used bentonite in their synthesis with iron nanoparticles. Numerous applications that are significantly utilized by well-known company proved that bentonite can be a good component in bionanocomposite with many improved properties. This showed that bentonite has high capability to become a good packaging material in future.

As for the conclusion, synthesis and characterization of silver / bentonite / starch bionanocomposite by using the green method is critically important in order to develop, maximize and combine all advantages possessed by each material used and compare type of solid support clay that are being used. In fact, synthesis and characterization bionanocomposite is essential before the product is to be commercially produce at another level. Bionanocomposite has increasingly grab the attention of recent researchers and as for this project, combination of many powerful properties of silver nanoparticles stabilized by starch and utilization of bentonite as an additional solid support. The green method also has been critically implemented by many researchers lately due to usage of environmental friendly substance and replacement for the conventional method to synthesize bionanocomposite.

II. METHODOLOGY

A. Materials

The materials involved such as silver nitrate Chem AR ($AgNO_3$) powder (Systerm, Malaysia), bentonite (BTN) (Sigma Aldrich, Darmstadt, Germany), starch (Stc) from potato soluble C.P (Bendosen, Malaysia), D(+)-glucose- anhydrous from (Systerm, Malaysia) and double distilled water (DDW).

B. Synthesis of Silver/Bentonite/Starch Bionanocomposite.

Initially, soluble starch solution was prepared which is 1 wt. % in 100 mL of double distilled water (DDW). At that point the soluble starch solution was heated to 60 ºC using heating plate. The starch solution is then vigorously stir for 1 hour at 700 rpm. For the time being, the silver nitrate solution (10 mM $AgNO_3$) was stirred under constant stirring rate which is 700 rpm for preparation of mixture of starch and silver nitrate solution. In the meantime, bentonite solution was weighed 1 g and dispersed it in 200 mL DDW. Bentonite solution was stirred vigorously for 1 hour at 700 rpm.

Next, the mixture of starch and silver nitrate solution were mixed together with bentonite suspension. The silver/starch/bentonite mixture was vigorously stirred for more than 3 hours at room temperature of 37ºC so that $[Ag(BTN/Stc)]^+$ was created. Preparation of D(+)-glucose powder 1.0M in 150ml aliquot was done. The D(+)-glucose solution was mixed together to silver/starch/bentonite nanocomposite with 37ºC heat and left to be sustained at this temperature for 24 hours. Observation on alteration of solution color was done after 3 hours of constant mixing bionanocomposite. Subsequently, separation method by centrifugation at 14,000 rpm speed in 15 minutes for preparation of characterization of instrument that needed in powder form. The bionanocomposite then washed using DDW twice and dried under overnight.

Experiment were repeated with 50 mM, 100 mM and 150 mM. In addition, study of different amount of bentonite was done such as 1 g, 2 g, 3 g and finally 4 g to see whether there are noteworthy changes to the bionanocomposite properties. Therefore, all the procedures were repeated for these types of manipulated variable. Control variable for this research was preparation of bentonite solution only. Samples are not direct to any heating as a control. Experiment was done in dark room because silver nitrate can easily oxidize when exposed to light.

C. Characterizations of Bionanocomposite.

Profound understanding in characterization of the synthesized bionanocomposite is also very essential especially for study in potential use in countless drug delivery and biomedical application. Some characterization that will be highlighted in this research is Ultraviolet visible spectroscopy (UV-Vis), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) which are to study the surface plasmon resonance (SPR), crystalline structure, functional groups available and morphology of silver nanoparticles in bionanocomposite respectively.

The UV-Vis spectrum is using range of 300 to 700 nm with UV-Vis spectrophotometer Agilent Technologies Cary 60. This is the preliminary step or confirmation step of any sign of nanoparticles present in bionanocomposite. Any sign of nanoparticles will cause the peak to increase at certain range of wavelength.

The X-ray diffraction (XRD) brand used is Rigaku D/max-2200/PC (Japan). Particle size is determine using Scherrer

equation (Scholes et al., 1999). Angle used is from 5º to 80º. Used 40 kV voltage, with current of 6 mA.

Fourier transform infrared spectroscopy (FTIR) is to analyze MIR spectra whereas acetone as solvent to clean the apparatus.

Scanning electron microscopy (SEM) is to study the morphology of bionanocomposite. SEM was performed using Hitachi SU3500 with 1.50 kV and magnification of 100X, 300X, 500X, 1000X and 2000X.

III. RESULTS AND DISCUSSION

A. Characterization of Ag/BTN/Stc Bionanocomposite

As for the preliminary evaluation of detecting presence of silver nanoparticles, the observation of colour changes of samples has been done. Theoretically, colour changes can occur due to excitation of Surface Plasmon Resonance (SPR) vibrations by the nanoparticles (Ahmed et al., 2016). Silver nanoparticles are extraordinarily efficient at absorbing and scattering light and, unlike many dyes and pigments, have a color that depends upon the size and the shape of the particle. Basically, brown color indicated the formation of silver nanoparticles in the suspension. As clearly shown in Fig. 1, colour changes did happen from cloudy suspension into very dark brown colour in which indicated that silver nanoparticles successfully being synthesized. The brown colour becomes more darken by increasing concentration from 10 mM until 150 mM of silver nitrate. The colour changes shown complementary to other research conducted such as done by Yakout and Mostafa, (2015). This shown that the synthesis bionanocomposite has been successfully done because the preliminary evaluation showed positive result. Further characterization has been made in order to confirmed the presence of silver nanoparticles.

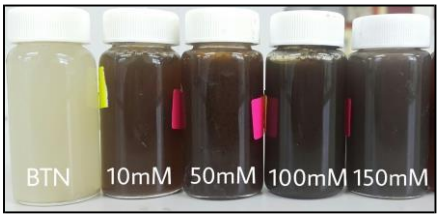

Fig. 1: Result of Colour Changes of Ag/BTN/Stc Bionanocomposite.

Further investigation has been done using UV-Vis. As according to Fig. 2, increasing concentration of silver nitrate showed increasing in absorbance at wavelength between 400-450nm. Firstly, there were peaks being observed around 400-450nm which signified the presence of silver nanoparticles. The absorbance increased from 10 mM until 50 mM concentration of silver nitrate. However, at concentration of 100mM and 150mM silver nitrate, the absorbance started to decrease significantly. The amount of concentration from 10 mM until 50 mM silver nitrate were just enough for the conversion of the Ag^+ to Ag^0 (El-Sheikh, 2014). It can be concluded that 50 mM concentration of silver nitrate in which the highest absorbance peak has been observed was considered the best concentration for silver/bentonite/starch bionanocomposite. In fact, a broad peak around 400 nm is the characteristic SPR absorption of spherical silver nanoparticles (de Faria et al., 2014). In addition, the broadness of the band is because of the extensive sizes of the nanoparticles.

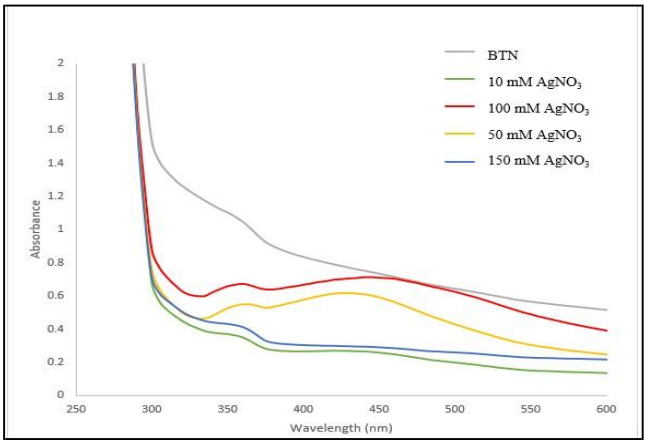

Fig. 2: Result of UV-Vis on Effect of Different Concentration Silver Nitrate in Ag/BTN/Stc Bionanocomposite.

Additional study of synthesis bionanocomposite by using different concentration of bentonite has been made. Concentration of silver nitrate. As clearly shown in Fig. 3, colour changes did happen from brown suspension into very dark and intense brown colour in which showed that silver nanoparticles successfully being synthesized. The brown colour turned into darker by increasing concentration bentonite from 1 g until 4 g. Evaluation of different concentration of clay has been done in order to see whether bentonite can appear to be a good solid support as mentioned by Patterson and Murray, (1983). The sample of 4 g showed the highest dark brown intensity colour which indicating that 4 g bentonite produced high concentration of silver nanoparticles.

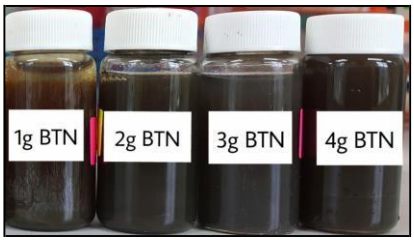

Fig. 3: Result of Colour Changes of Different Amount of Bentonite in Ag/BTN/Stc Bionanocomposite.

Referring to Fig. 4, increasing concentration of bentonite showed increasing in absorbance at wavelength between 400-450nm which shows presence of silver nanoparticles. The absorbance increased from 1 g until 4 g of bentonite. In addition, it can be seen that the absorbance peak becomes narrower as increasing the bentonite amount. It shows that the silver nanoparticles become more stable and reflecting a good characteristic of solid support especially at 4 g of bentonite. It can be concluded that 50 mM concentration of silver nitrate in which the highest absorbance peak has been observed was considered the best concentration for silver/bentonite/starch bionanocomposite. In addition, the broadness of the band is because of the extensive sizes of the nanoparticles.

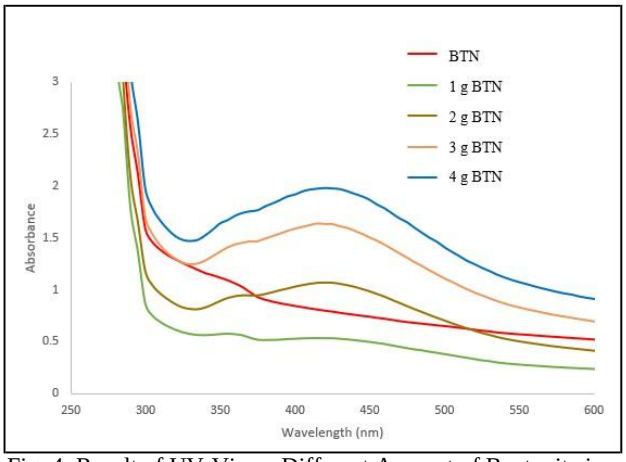

Fig. 4: Result of UV-Vis on Different Amount of Bentonite in Ag/BTN/Stc Bionanocomposite.

The morphology of the synthesized silver/bentonite/starch bionanocomposite was observed by SEM analysis. It can be clearly seen that the morphology of 50 mM of bionanocomposite were irregular in shape as observed from Fig 5 (a) until (e). In fact, the synthesized of silver nanoparticles were strongly attached on the surface of starch/bentonite as shown in Fig. 6. From data of UV-Vis analysis, the broad peak indicated wide size of nanoparticles and it is confirmed by SEM analysis. As according to Shameli et al., (2011), the SEM result of montmorillonite demonstrated a layered surface with some large flakes, which is the typical structure for montmorillonite. This is almost similar to this case where the bentonite which comprises largely from montmorillonite have large flakes. As mentioned by Wang et al., (2017), it was mentioned that many polysaccharides-based metal nanoparticles (PMNPs) are irregular in shape and thus hard to define. Other findings such as Ghasemzadeh et al., (2016) also found that the morphology of silver nanoparticles is irregular.

Furthermore, the morphology of the synthesized silver/bentonite/starch bionanocomposite of 4 g bentonite of 50 mM of bionanocomposite was also majoring in irregular shape. It can be seen that the synthesized of silver nanoparticles were strongly bound on the surface of starch/bentonite as shown in Fig. 6. It can be seen that increasing concentration of bentonite have better size control of bionanocomposite. As confirmed by UV-Vis analysis, the broad peak indicated wide size of nanoparticles.

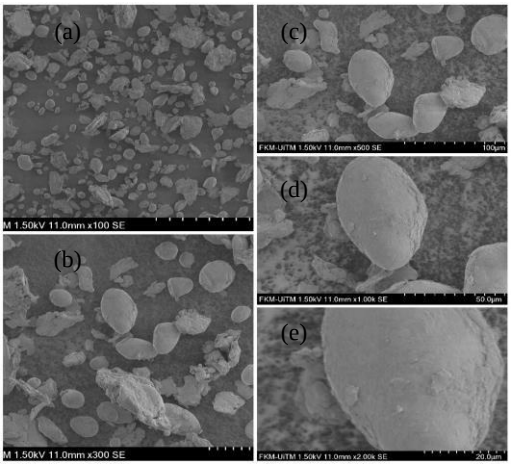

Fig. 5: Result of SEM of 50mM of silver nitrate in Ag/BTN/Stc Bionanocomposite. Fig (a) shows 100X magnification, (b) shows 300X magnification, (c) shows 500X magnification, (d) shows 1000X magnification and (e) shows 2000X magnification.

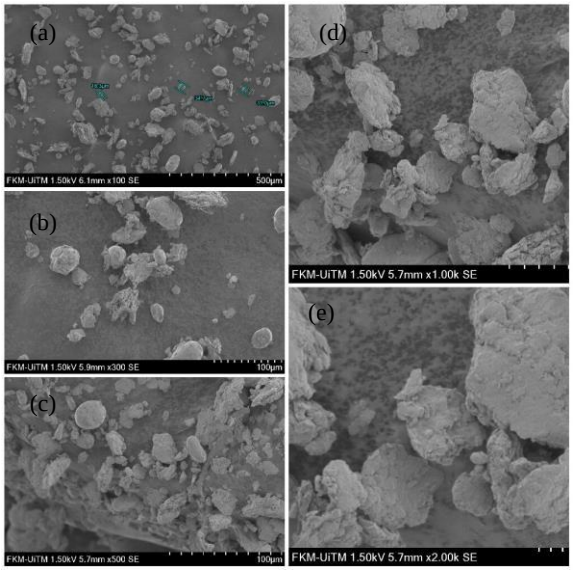

Fig. 6: Result of SEM of 4g Bentonite of 50mM Ag/BTN/Stc Bionanocomposite. Fig (a) shows 100X magnification, (b) shows 300X magnification, (c) shows 500X magnification, (d) shows 1000X magnification and (e) shows 2000X magnification.

For XRD analysis, it actually verified the crystalline structure of silver nanoparticles in bionanocomposite. The diffracted intensities were recorded from 20º to 80º. As according to Fig. 7, it can be clearly observed there were four strong Bragg reflections that displayed presence of silver nanoparticles which at 38.32º, 44.48º, 62.30º and 77.60º. The values corresponded to the planes of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) respectively which can be indicated based to the facets of face centered cubic crystal structure of silver as mentioned by Prakash et al., (2013). Besides that, the presence of bentonite also can be found at Bragg reflection at 62.30º which indicated montmorillonite crystalline structure as it contained the highest composition in bentonite. It shows that it produced significant impact as a stable substrate as mentioned by Shameli et al., (2011).

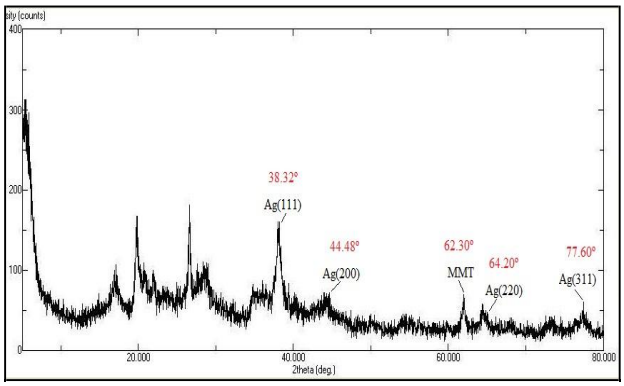

Fig. 7: Result of XRD of 50mM Silver Nitrate in Ag/BTN/Stc Bionanocomposite.

Based on Table 1, there is absorption at 3620cm^{-1} which is accredited to stretching vibration of OH groups in the Si-OH and Al-OH groups respectively of bentonite component (Abdullahi and Audu, 2017). Meanwhile the bending frequency is at frequency of 915 cm^{-1}. Both bands can be considered as characteristic of dioctahedral clay (Van der Marel and Beutelspacher, 1976). Besides that, absorption of band at 1637.35 cm^{-1} denotes that C = O stretching of ketones and aldehydes. According to Paulkumar et al., (2017), the functional

group of aldehyde and ketone showed the presence of reducing sugar compounds which is glucose in the bionanocomposite. Plus, the redox reaction of reducing sugar compounds triggered the reduction of Ag^{+} to Ag^{0}.

The spectrum of starch demonstrates the O–H group stretching bands, the band at 3344.00 cm^{-1} indicated the (O–H) bending of water (Mano et al., 2003). The absorption bands at 2187.00 cm^{-1} parallel to the C-H bending whereas at 1663.00 cm^{-1} in the fingerprint region parallel to –C–O–C– stretching vibration in glucose bonds (Fang et al., 2004).

The spectrum of the BTN/Stc displays the combination of characteristic absorptions due to the bentonite and C-H stretching and bending groups of starch. The peaks of C-H groups in starch are shifted 2163.00 cm^{-1} in the BTN/Stc corresponding to the deformation vibration of C-H group of starch. Plus, there was no significant changes in the spectra of BTN/Stc and Ag/BTN/Stc bionanocomposite.

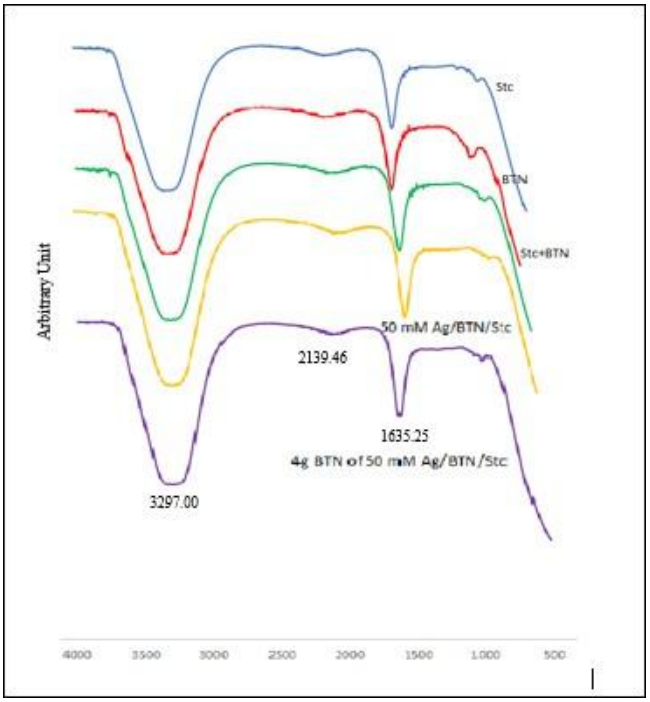

Fig. 8: Result of FTIR of Starch (Stc) only, Bentonite (BTN) only, Starch and Bentonite, 50 mM Silver/Bentonite/Starch Bionanocomposite and 4 g of 50 mM Silver/Bentonite/Starch Bionanocomposite.

Table 1: Result of Functional Group present in samples.

Functional Groups	Absorbance bands (cm^{-1})				
	STC	BTN	STC+BTN	50mM Ag/BTN/STC	4g of 50mM Ag/BTN/STC
O-H stretch	3344.00	3373.00	3302.00	3302.84	3297.00
C-H stretch	2187.00	2025.00	2163.00	2158.73	2139.46
C = O	1663.00	1606.00	1629.00	1637.15	1635.25
Si-O stretch	1016.00	1009.00	1011.00	1011.00	1009.00
(Al-Mg)-OH vibration	919.00	909.00	913.00	915.00	997.00

IV. Conclusion

As a conclusion, the synthesis of silver/bentonite/starch bionanocomposite was successful. This is in accordance to the positive result of characterization such as colour changes, UV-Vis, SEM, XRD and FTIR. The suspension of bionanocomposite turned into very dark brown as we increased the concentration of silver nitrate from 10 mM, 50 mM, 100 mM and 150 mM. Result of UV-Vis for this synthesis produced peak at 400-450nm which indicated the presence of silver nanoparticles. Among four parameters of concentration silver nitrate being considered, it has been observed that 50 mM silver nitrate produce the highest spectrum of UV-Vis. Besides that, the peak of UV-Vis also became narrower and increased as we increased the amount of bentonite from 1 g until 4 g of bentonite. It indicated that as we increased the amount of bentonite, the silver becomes more stable and it proved that bentonite is a good solid support of bionanocomposite.

Other characterization confirmation is SEM. The morphology of bionanocomposite is irregular in shape. The XRD analysis confirmed the presence of silver nanoparticles in bionanocomposite. It can be clearly shown that the crystalline structure of silver nanoparticles that corresponded to the planes of (1 1 1), (2 0 0), (2 2 0) and (3 1 1) in which it is actually the facets of face centered cubic crystal structure of silver. As for FTIR, functional groups present such as Si-O stretch and (Al-Mg)-OH vibration in bentonite, stretching vibration of OH groups and C-H stretching in starch and bentonite meanwhile C = O stretching of ketones and aldehydes due to presence of glucose.

It is recommended to perform this research in dark room where the silver nanoparticles can have no interaction with light in order to prevent agglomeration to occur. From the result obtained in SEM, the morphology of silver nanoparticles is irregular and many agglomerations occurred. Besides that, it is recommended to perform characterization instantly because time also influenced the agglomeration of silver nanoparticles.

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References

[1] Abdullahi, S. L., & Audu, A. A. (2017). Comparative analysis on chemical composition of bentonite clays obtained from Ashaka and tango deposits in Gombe State, Nigeria. *ChemSearch Journal*, *8*(2), 35-40.

[2] Ahmed, S., Ahmad, M., Swami, B. L., & Ikram, S. (2016). Green synthesis of silver nanoparticles using Azadirachta indica aqueous leaf extract. *Journal of Radiation Research and Applied Sciences*, *9*(1), 1-7.

[3] Azeredo, H.M.C.D., Mattoso, L.H.C., McHugh, T.H., 2011. Nanocomposites in Food Packaging – A Review, in *"Advances in Diverse Industrial Applications of Nanocomposites"*. In: Reddy, B. (Ed.), InTech. Available from: http://www.intechopen.com/books/advances-in-diverseindustrial-applications-of-nanocomposites/nanocomposites-in-food-packaging-a-review

[4] Cabal, B., Torrecillas, R., Malpartida, F., & Moya, J. S. (2010). Heterogeneous precipitation of silver nanoparticles on kaolinite plates. *Nanotechnology*, *21*(47), 475705.

[5] de Faria, A. F., Martinez, D. S. T., Meira, S. M. M., de Moraes, A. C. M., Brandelli, A., Souza Filho, A. G., & Alves, O. L. (2014). Anti-adhesion and antibacterial activity of silver nanoparticles supported on graphene oxide sheets. *Colloids and Surfaces B: Biointerfaces*, *113*, 115-124.

[6] El-Sheikh, M. A. (2014). A novel photosynthesis of carboxymethyl starch-stabilized silver nanoparticles. *The Scientific World Journal*, *2014*.

[7] Fang, J. M., Fowler, P. A., Sayers, C., & Williams, P. A. (2004). The chemical modification of a range of starches under aqueous reaction conditions. *Carbohydrate polymers*, *55*(3), 283-289.

[8] Faraday, M. (1857). LIX. Experimental relations of gold (and other metals) to light. —The bakerian lecture. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, *14*(96), 512-53.

[9] Grim R.E (1968). Clay mineralogy, 2nd ed. New York, McGraw-Hill, 596 pp.

[10] Ma, X., Bruckard, W.J. (2010). The effect of pH and ionic strength on starch–kaolinite interactions. Int J Miner Process 94:111–114.

[11] Mano, J. F., Koniarova, D., & Reis, R. L. (2003). Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability. *Journal of Materials Science: Materials in Medicine*, *14*(2), 127-135.

[12] Mansor, A., Kamyar, S., Majid, D., Wan, M., Nor, A. I., Azizah, A. H., & Mohsen, Z. (2009). Synthesis and antibacterial activity of silver/montmorillonite nanocomposites. *Research Journal of Biological Sciences*, *4*(9), 1032-1036.

[13] Murray, H. (2002). Industrial clays case study. *Mining, Minerals and Sustainable Development*, *64*, 1-9.

[14] Murray, H. H. (2007). Applied clay mineralogy. Developments in clay science, 2. *Elsevier*, *2*.

[15] Park, K., Seo, D., & Lee, J. (2008). Conductivity of silver paste prepared from nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *313*, 351-354.

[16] Parkes, W.R. (1982). Occupational Lung Disorders. Butterworths, London, pp. 310–318.

[17] Patra, J. K., & Baek, K. H. (2014). Green nanobiotechnology: factors affecting synthesis and characterization techniques. *Journal of Nanomaterials*, *2014*, 219.

[18] Patterson SH & Murray HH (1975) Clays. In: Lefond SI ed. Industrial minerals and rocks, 4th ed. New York, American Institute of Mining, Metallurgical, and Petroleum Engineers, pp 519–595.

[19] Paulkumar, K., Gnanajobitha, G., Vanaja, M., Pavunraj, M., & Annadurai, G. (2017). Green synthesis of silver nanoparticle and silver based chitosan bionanocomposite using stem extract of Saccharum officinarum and assessment of its antibacterial activity. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, *8*(3), 035019.

[20] Pessanha, N. F. N., Kawase, K. Y. F., & Coelho, G. L. V. (2014). Preparation and characterization of silver/organo-clay nanocomposites. Chemical and Materials Engineering, 2(8), 173-178.

[21] Prakash, P., Gnanaprakasam, P., Emmanuel, R., Arokiyaraj, S., & Saravanan, M. (2013). Green synthesis of silver nanoparticles from leaf extract of Mimusops elengi, Linn. for enhanced antibacterial activity against multi drug resistant clinical isolates. *Colloids and Surfaces B: Biointerfaces*, *108*, 255-259.

[22] Raveendran, P., Fu, J., & Wallen, S. L. (2003). Completely “green” synthesis and stabilization of metal nanoparticles. Journal of the American Chemical Society, 125(46), 13940-13941.

[23] Rhim, J. W. (2007). Potential use of biopolymer-based nanocomposite films in food packaging applications. *Food Science and Biotechnology*, *16*(5), 691-709.

[24] Rhim, J.-W., Park, H.-M., & Ha, C.-S. (2013). Bio-nanocomposites for food packaging applications. *Progress in Polymer Science*, *38*(10–11), 1629–1652. https://doi.org/10.1016/j.progpolymsci.2013.05.008.

[25] Shahwan, T., Üzüm, Ç., Eroğlu, A. E., & Lieberwirth, I. (2010). Synthesis and characterization of bentonite/iron nanoparticles and their application as adsorbent of cobalt ions. Applied Clay Science, 47(3-4), 257-262.

[26] Shameli, K., Ahmad, M. B., Zamanian, A., Sangpour, P., Shabanzadeh, P., Abdollahi, Y., & Zargar, M. (2012). Green biosynthesis of silver nanoparticles using Curcuma longa tuber powder. *International journal of nanomedicine*, *7*, 5603.

[27] Shameli, K., Ahmad, M. B., Zargar, M., Yunus, W. M. Z. W., Ibrahim, N. A., Shabanzadeh, P., & Moghaddam, M. G. (2011). Synthesis and characterization of silver/montmorillonite/chitosan bionanocomposites by chemical reduction method and their antibacterial activity. *International journal of nanomedicine*, *6*, 271.

[28] Shchipunov, Y. (2012). Bionanocomposites: Green sustainable materials for the near future. *Pure and Applied Chemistry*, *84*(12), 1. https://doi.org/10.1351/PAC-CON-12-05-04

[29] Wang, C., Gao, X., Chen, Z., Chen, Y., & Chen, H. (2017). Preparation, Characterization and Application of Polysaccharide-Based Metallic Nanoparticles: A Review. Polymers, 9(12), 689.

[30] Yakout, S. M., & Mostafa, A. A. (2015). A novel green synthesis of silver nanoparticles using soluble starch and its antibacterial activity. *International journal of clinical and experimental medicine*, *8*(3), 3538.

[31] Yusoff, M., Muslim, M., Foo, C. T., & Murshidi, J. A. (2006). High Purity Alumina and Zeolite from Local Low Grade Kaolin.