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PROFESSOR DR. MANSOR AHMAD @ AYOB

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Contents

INTRODUCTION

Polymers play a great part in our daily lives and without them around, this world would be very, very different, if not impossible to live in. Nevertheless, most people do not even know what polymers are, or just how prevalent they are around us. Many a time, the term *polymer* is used to refer to plastics, but it actually comprises a larger class of natural and synthetic materials with a wide range of properties and applications. A variety of polymers exist in nature, such as cotton, cellulose, shellac, amber, silk, ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). Synthetic polymers include polyethylene, polypropylene, polystyrene, synthetic rubber, neoprene, nylon, polyvinyl chloride (PVC), Teflon, silicone, polyacrylonitrile, and many others. Monomers are essentially the building blocks of the molecules that make up everything, living and non-living, naturally occurring and man-made. A polymer may contain thousands of monomers, or just a few. Each monomer affects how that polymer looks, tastes, smells and behaves.

Early polymer research was focused on synthesising monomers and polymerising them into polymers and copolymers with better properties compared to natural polymers. Polyisoprene is an example of a polymer initially produced to have properties similar to natural rubber, produced synthetically in 1909 by Bayer Germany. A war-born material, synthetic rubber became one of the most important creations of man when the progress of modern civilisation was still dependent on the volatility of global natural rubber supply. Over the years, synthetic rubbers are produced by the polymerisation of an unsaturated hydrocarbon, a butylene, isoprene, or by the copolymerisation of such hydrocarbons with styrene, butadiene, or the like. The two main types of polymerisation are (i) chain growth polymerisation, where monomer molecules are added to the chain one at a time, and (ii) step growth polymerisation, where monomer molecules bond directly with one another.

Generally, polymers have good characteristics but their applications are often limited by shortcomings in certain properties. Thus, research in polymer modification has gained momentum in the last 50 years as a viable alternative to the synthesis of new polymers. Chemical modification of polymers is a flexible, technologically feasible, and economically viable alternative to the synthesis of new polymers. It frequently involves reactions in a solvent-free environment, for example using reactive extrusion, thus providing environmental benefits, while being economical because of the use of conventional processing equipment. However, chemical modification is a very challenging area of polymer science and technology as it requires the combination of diverse areas of expertise, ranging from the basics of polymer chemistry, reaction kinetics, thermodynamics and rheology, to knowledge of compounding techniques and polymer processing operations. As a typical example, vulcanisation as the most classical and well-known process which allows the transformation of an unusable material into a product with impressive engineering properties, including resistance to heat, light, dimensional stability, mechanical strength, chemical and solvent resistance. The use of synthetic and natural fibre as reinforcing materials is the latest invention in polymer science in order to get higher strength with lower weight composite materials. Polymer composite research has evolved dramatically in the decade when nanomaterials have been shown to possess unique properties. A nanocomposite is a matrix to which nanoparticles have been added to improve a particular property of the material. The properties of nanocomposites have caused researchers and industries to consider using these materials in several fields. Nanocomposite applications include producing batteries with greater power output, speeding up the healing process for broken bones, producing structural components with a high strength-to-weight ratio (carbon nanotubes-polymer composite windmill blades), using graphene to make composites with even higher strength-to-weight ratios and making lightweight sensors with nanocomposites (Paul and Robeson, 2008).

MY RESEARCH JOURNEY

With the brief background on polymers and main research in the field, the manuscript highlights my research journey over the span of 25 years. My first exposure to polymer research was obtained while pursuing doctorate degree at the University of Salford, Manchester UK under the supervision of Prof. Malcolm Huglin. My research was on the preparation and characterisation of copolymeric hydrogels based on n-vinyl-2-pyrrolidone, where several copolymers were prepared by g-irradiation. Hydrogel is a water-swollen, and cross-linked polymeric network material that exhibits the ability to swell and retain a significant fraction of water within its structure, but is insoluble in water. Hydrogels possess a degree of flexibility very similar to natural tissues due to their large water content. The nature of water in copolymeric *N*-vinyl pyrrolidone/methyl methacrylate hydrogels was investigated using dielectric thermal analysis (DETA) and differential scanning calorimetry (DSC). Mixtures of *N*-vinyl-2-pyrrolidone (VP) with methyl methacrylate (MMA) of various compositions in the presence of a fixed concentration of ethylene glycol dimethacrylate (EDMA) were copolymerised to 100% conversion by γ-irradiation. The state of water in the poly(MMA-co-VP) hydrogels, the percentages of free freezing, freezable bound and nonfreezing water were found to vary with the xerogel composition, i.e. the degree of hydration of the hydrogels (Ahmad and Huglin, 1994a,b). At low equilibrium swelling, most of the water exists as a non-freezing type, whereas at higher equilibrium swelling the majority of water exists as free freezing water.

The research on hydrogels was continued in UPM with work on the immobilisation of enzyme on copolymeric hydrogels with Prof. Mahiran Basri. Lipase from *Candida rugosa* was immobilised by entrapment on poly(*N*-vinyl-2-pyrrolidone-co-2-hydroxyethyl methacrylate) (poly(VP-co-HEMA)) hydrogel, cross-linked with ethylene glycol dimethacrylate (Basri *et al.,* 1999a, b). The thermal, solvent, and storage stability of the immobilised preparations were also determined. Increasing the percentage VP from 0 to 90, which corresponded to the increase in the hydrophilicity of the hydrogels, increased the activity of the immobilised enzyme. Lipase immobilised onto VP(%):HEMA(%), 90:10 hydrogel had the highest activity. Increasing the hydrophobicity of the hydrogel (increasing the percentage HEMA) seemed to decrease leaching of the enzyme from the support. Immobilised lipase on 100% HEMA hydrogel indicated highest entrapment and lowest leaching by hexane washing. The lipase immobilised on VP(%):HEMA(%), 50:50 hydrogel showed highest thermal, solvent, and storage stability compared to lipase immobilised on other hydrogel compositions as well as the native lipase.

The effect of water activity on lipase immobilised onto different compositions of poly(hydroxyethyl methacrylate-*co*-methyl methacrylate (poly(HEMA-MMA)) was also studied (Esa *et al.,* 1998). The findings indicated that water plays a key role in the structure and function of enzymes. Some water is necessary for catalytic activity of the enzyme because totally dried enzymes are usually inactive and gain activity upon addition of water. A certain amount of water in the reaction mixture (up to 6%) is favorable for the esterification reaction. Matrices for enzyme immobilisation may be able to hold water and affect the rate of reaction. The presence of water and the ability to hold water by the matrices make immobilised enzymes a choice form of catalysts, at least in research, for reaction in organic solvent environments. The capacity of matrices to retain water as well as the controlled water activity may affect the optimum rate of reaction.

Moving on, the UPM polymer research group, headed by Prof. Dato' Wan Md. Zin, modified sago starch by grafting in an effort to diversify the use of sago. Lutfor *et al.* (2003) studied on the modification of sago starch by graft copolymerisation: Effect of reaction conditions on grafting parameters. A new chelating ion-exchange resin containing the hydroxamic acid functional group was synthesised from poly(methyl acrylate) (PMA)-grafted sago starch (Lutfor *et al.*, 2000a). The PMA-grafted copolymer was obtained by a free-radical initiating process in which ceric ammonium nitrate was used as an initiator. Conversion of the ester groups of the PMA-grafted copolymer into hydroxamic acid was carried out by treatment of an ester with hydroxylamine in an alkaline solution. The characterisation of the poly(hydroxamic acid) chelating resin was performed using Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) analyses. The binding capacities of copper, iron, chromium, and nickel were excellent and the copper capacity was maximum (3.46 mmol g^{-1}) at pH 6. The rate of exchange of the copper ion was very fast, i.e., $t_{½} < 5$ min. The metal ion-sorption capacities of the resin were pH-dependent and its selectivity toward the metal ions used was found to be in the following order: $Cu^{2+} > Fe^{3+} > Cr^{3+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > As^{3+} > Pb^{2+}$.

The preparation of a chelating ion-exchange resin containing amidoxime functional group was carried out by grafting polyacrylonitrile (PAN) on sago starch (Lutfor *et al.,* 2000b). Conversion of nitrile groups of the grafted copolymer into the amidoxime was carried out by treatment with hydroxylamine under alkaline solution. A significant binding property of metal ions by the chelating resin was observed and the maximum copper capacity was 3.0 mmol g^{-1} at pH 6. The sorption capacities of metal ions by the resin were pH-dependent, and its selectivity towards these metal ions is in the following order: $Cu^{2+} > Fe^{3+} > As^{3+} > Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Cr^{3+} > Pb^{2+}$. The rate of exchange was rapid, i.e. $t_{½} < 9$ min, based on the exchange of copper ion. In another study, sorption behaviour of polystyrene grafted sago starch in various solvents was also studied (Janarthanan *et al.,* 2001). The copolymer for this study was prepared by grafting styrene onto sago starch using ceric ammonium nitrate as a redox initiator. Solvent uptake of the copolymer with respect to time was obtained by soaking the samples in chosen solvents for various time intervals at room temperature. The results obtained from swelling of polystyrene grafted sago starch in polar and non-polar solvents showed that the percentage of swelling at equilibrium and the swelling rate coefficient decreased in the following order: DMSO > water > acetone ≅ cyclohexanone ≅ $CHCl_3$ > toluene ≅ CCl_4. Dimethyl sulfoxide showed the highest percentage of swelling at equilibrium that is 765%. Diffusions of the solvents onto the polymers were found to be of a Fickian only for DMSO.

Graft copolymerisation of acrylonitrile onto sago starch was carried out by a free radical initiating process with ceric ion (Ce^{4+}) an initiator (Lutfor *et al*., 2003). The reaction conditions significantly influenced the graft copolymerisation. The percentage of grafting, grafting efficiency and rate of grafting were all dependent on the concentration of ceric ammonium nitrate (CAN), acrylonitrile (AN), sago starch (AGU, anhydroglucose unit), sulfuric acid (H_2SO_4) and the reaction temperature and period. The optimum yield was obtained when the concentrations of CAN, AN, AGU and H_2SO_4

were used at 9.61×10^{-3}, 0.653, 0.152 and 0.187 mol L^{-1}, respectively. Moving to another natural product, rubberwood was grafted with acrylonitrile using ferrous ion and hydrogen peroxide as initiator. Grafted rubberwood fibre was converted to polyamidoxime ion-exchange resin in order to remove heavy metal ions from aqueous solution (Abuilaiwi *et al.*, 2009). The cation-exchange resin existed predominantly in the *syn*-hydroxyamino form. The water uptake by the resin was ca. 31 g/g dry resin while its hydrogen ion capacity was 3.6 mmol g^{-1}. The adsorption capacity of the resin towards different metal ions from wastewater was determined at different pH values within the range 1–6. FT-IR spectroscopy was used to confirm the conversion of polyacrylonitrile-g-rubberwood fibre to polyamidoxime. The prepared chelating ion-exchanger exhibited the highest adsorption capacity towards Cu^{2+} ions (3.83 mmol g^{-1}), followed by Cd^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+} and Co^{3+} ions, respectively. The results showed that the adsorption capacity was depended on pH of the solution. Polyamidoxime ion-exchange resin was also used to separate Co^{3+} and Ni^{2+} ions from Cu^{2+} ions using a column technique. On passing Cu^{2+}/Ni^{2+} and Cu^{2+}/Co^{3+} ion mixtures through the resin at pH 3, Cu^{2+} ions were adsorbed by the resin but no sorption of Ni^{2+} or Co^{3+} ions was detected. Approximately 98% of the Cu^{2+} ions could be desorbed from the resin.

Instead of using the grafted product as ion exchange resin our group also explored the used of grafted products as a reinforcing filler in polymer composites. Composites are usually composed of two components, i.e. matrix and filler called also reinforcement or more broadly dispersed phase; sometimes also additives are used, mostly compatibilisers. The matrix, as a continuous phase, integrates filler particles and allows products to be shaped appropriately and determines most of physical and chemical properties of material. The dispersed phase is responsible for additional enhancement of selected material properties. Compatibilisers are added mainly to enhance interactions between matrix and filler, but they also influence the material cohesion and homogeneity. Owing to the type of matrix, one can distinguish the various composites: Polymer matrix composites (PMCs), ceramic matrix composites (CMC) or metal matrix composites (MMCs). The first type of composite materials dominates over other in terms of usage and applications. The matrix in PMCs might be made of duroplastic or thermoplastic polymers such as epoxide resins, polyesters and silicons, polyethylene, polypropylene, poly(vinyl chloride), polystyrene and polycarbonates.

The use of rubber wood in furniture and particle board was popular in the early 2000 but the incompatibility between natural fibre and the binder (polymer) deteriorates the properties of the final products. As a polymer chemists, we perceive rubber wood as a polymeric material, which can be modified by grafting and used in composites as a reinforcing fibre. Grafting with hydrophobic polymer such as methyl methacrylate, methyl acrylate, butyl acrylated and so on changes the properties of hydrophylic fibre to hydrophobic, thus make them compatible with the polymer matrix. Methyl methacrylate (MMA) was successfully grafted onto rubber-wood fibre in a free-radical solution polymerisation initiated by ferrous ion and hydrogen peroxide (Abuilaiwi *et al.*, 2003). The effects of the reaction parameters (reaction temperature, reaction period, influence of hydrogen peroxide, ferrous ammonium sulfate, and monomer concentrations) were investigated. The grafting percentage showed dependency on H_2O_2, Fe^{2+}, and monomer concentrations, as well as reaction temperature and reaction period. The optimum reaction temperature was determined to be about 60°C and the reaction period was 60 min. The optimum concentration of H_2O_2 was $0.03M$ and optimum amounts of Fe^{2+} and MMA were 0.26 mmol and 2.36×10^{-2} mol, respectively.

Grafting of different monomers onto oil palm empty fruits bunch fibre (OPEFB) using various initiation methods was also investigated by the polymer group. Examples are the grafting of poly(butyl acrylate) (Ibrahim *et al*., 2003a), methyl methacrylate (Ibrahim *et al*., 2003b) and acrylamide onto OPEFB with methyl acrylate as a comonomer (Ibrahim *et al*., 2005). Results indicated that methyl acrylate facilitated the incorporation of acrylamide monomer onto OPEFB. The highest percentage of grafting obtained was 232% when 25.6 mmol of acrylamide was used under optimum conditions.

Preparation and characterisation of polymer composites and polymer blends were actively carried out in UPM polymer group in early 2000s. A comparative study was carried out to investigate the mechanical properties such as tensile strength and modulus of polypropylene/glass fibre composite with polypropylene/OPEFB materials prepared using injection molding and compression molding (Yaacob *et al*., 2004). In the initial stage the samples with 5, 10 and 15 wt.% glass fibre loading were compounded using a single screw extruder before undergoing injection and compression molding process. Results showed that the tensile strength decreased with the increasing of glass fibre loadings which are attributed to the absence of adhesion between polypropylene and electrical type glass (E-glass) due to the difference in polarity between polypropylene and the hydroxyl groups on the fibre surface. Tensile moduli increased with increasing of glass fibre loadings but the maximum value seemed to be very low, i.e. in the order of 500 MPa. In terms of fibre length, the samples prepared by using a 12 mm fibre showed higher tensile modulus and strength particularly at higher fibre loadings compared to samples prepared by using 3 mm or 6 mm fibre length but these results did not reveal anything significant because of the absence of adhesion between fibre surface and polypropylene matrix.

The studies reveal that natural fibres have an outstanding potential as reinforcement in thermoplastics. Studies were carried out to evaluate the suitability of producing composites using coconut coir fibres (Lai *et al*., 2005). Coconut coir composites were prepared using compression technique in which good interfacial adhesion was generated by a combination of fibre modification and matrix methods. Initially the coconut fibres were treated in order to improve resin fibre interfacial bonding. The treatment agents used included alkali, stearic acid, acetone, and potassium permanganate. The various reactions between the modified fibre and polypropylene chains were used improve the interfacial adhesion between the fibre and polymer using the new bond. Generally, composites that contain treated fibre have a higher tensile modulus and greater flexural modulus than do untreated fibre composites.

Over the years, polymer research has been done on materials of different length-scales (macro, micro and nano) as related to obtaining a deeper understanding of the structure-property relationships of polymeric materials. They are related to the morphological, interfacial, processing response, physical and thermophysical properties of multiphase polymers and polymer composite systems: from macro to nano length-scales. Much of the research done in the early part my career was on the macro scale; polymers, hydrogels and composites. However in the last eight years attention was focused on the nano scale, i.e. nanoparticles and nanocomposites, especially with the green chemistry and processes. These are discussed in the subsequent sections.

GREEN SYNTHESIS OF NANOPARTICLES

Nanoparticles can be defined as particles with at least one of their three dimensional sizes in the range of less than 100 nm. They are between the size of atoms or molecules and bulk materials but they have different physical and chemical properties due to their large surface to volume ratio and size-dependent properties. Within this size range, they consist of between 100 and 10,000 atoms. Over the past few years considerable interest has been focused on metal nanoparticles due to their potential application in different fields, including catalysis, biomedical, sensor. Nanoparticles are categorised into two main classes, organic and inorganic nanoparticles. Carbon nanoparticles are considered as the organic nanoparticles. Metal nanoparticles (Cu, Ag, Au, Pd and Pt), metal oxide nanoparticles (ZnO, CeO_2 and TiO_2) and semiconductor nanoparticles (ZnS, CdS, CdSe and ZnSe) are called inorganic nanoparticles. Nanoparticles are of great interest due to their extremely small size and large surface to volume ratio, which lead to both chemical and physical differences in their properties (*e.g.* mechanical properties, biological and sterical properties, catalytic activity, thermal and electrical conductivity, optical absorption and melting point) compared to bulk of the same chemical composition. Therefore, design and production of materials with novel applications can be achieved by controlling shape and size at nanometre scale.

Metallic nanoparticles synthesis is an important area in nanoscience and nanotechnology due to variety and wide range of potential applications from the electronic to biological fields. The numerous preparation routes of nanoparticles can be grouped into two main different strategies: Top-Down (physical methods); from large to small dimensions and Bottom-Up (wet chemical methods); from molecular scale to nanoscale (Figure 1). The Top-Down route involves preparing of particles in nanometer size from breaking of bulk materials such as photolithography, laser-beam processing, and mechanical techniques (Manikam *et al.,* 2011). This method is normally easy but the cost of fabrication is high. This approach is suitable for scale up to large scale fabrications but the crystalline morphology and size distribution of particles obtained is highly broad.

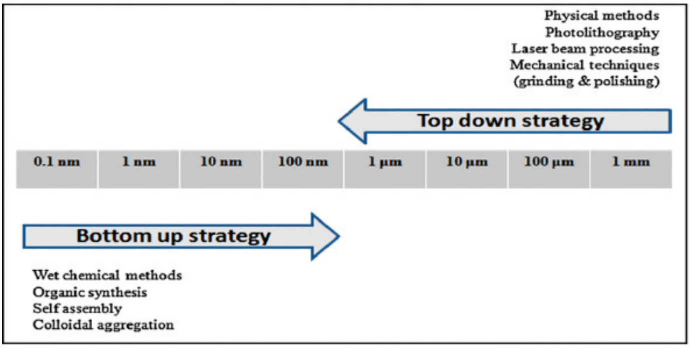


Figure 1 Strategies for synthesising nanoparticles (Manikam *et al.,* 2011)

The bottom-up approach involves synthesis of a large variety of nanometric particles via the assembly of atoms into nanocrystals such as organic synthesis, self-assembly and colloidal aggregation. For example in preparing of metallic and metal oxides nanoparticles the precursor should be dissolve in an aqueous or non-aqueous liquid phase. Metallic clusters can be produced through reduction of metallic ions using reducing agents or controlled decomposition of organometallic compounds. The stabilisers are normally used to inhabitation of aggregation and growth of nanoparticles. During the past decades, different synthetic routes of metal nanoparticles have been developed such as chemical reduction (Musa *et al.,* 2016), physical irradiation, photochemical and thermal method.

The development of efficient green chemistry methods for synthesis of metal nanoparticles has become a major focus of researchers in order to find an eco-friendly technique for production of well-characterised nanoparticles. Nanoparticles produced by plants are more stable and the rate of synthesis is faster than in the case of microorganisms. The advantages of using plant and plant-derived materials for biosynthesis of metal nanoparticles have attracted researchers to investigate mechanisms of metal ions uptake and bioreduction by plants, and to understand the possible mechanism of metal nanoparticle formation in plants. Greener environmentally friendly processes in chemistry are becoming increasingly popular and numerous 'green chemistry' books have been published describing green processes in general and their specialised aspects. These include ultrasound, microwaves, and other methods in synthesis, green analytical chemistry, green tribology, green polymerisation, green engineering and manufacturing, food, textiles, particle technology, biofuels, biomass and biocomposites, and other 'green chemistry' areas. The definition of green chemistry proposed by Anastas and Warner (1998) is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products. The 12 principles of green chemistry have now become a standard guide for chemists and chemical technologists worldwide in developing less hazardous chemical syntheses.

The synthesis of metallic nanoparticles (MNPs) using environmentally friendly and biocompatible components could lower the toxicity of the resulting materials and the environmental impact of the byproducts. Non-toxic solvents, closed reactors, green techniques without contacting reaction media and air and low temperatures, can be used to achieve the goal. The techniques for obtaining nanoparticles using naturally occurring reagents such as plant extracts, sugars, biodegradable polymers, and microorganisms as reductants and capping agents could be considered attractive for nanotechnology (Darroudi *et al.*, 2009). These syntheses have led to the fabrication of limited number of inorganic nanoparticles. Among the reagents mentioned above, plant based materials seem to be the best candidates and they are suitable for large-scale biosynthesis of nanoparticles. Overall, biological materials provide an environmentally friendly or greener chemical method to produce invaluable materials because the biomaterial based routes eliminate the need to use toxic chemicals. Mechanisms of these bioreductive transformations, as well as catalytic properties of materials obtained via these routes have been well-accepted.

The green synthesis of MNPs should involve three main steps based on green chemistry perspectives, the selection of (i) a biocompatible and nontoxic solvent medium, (ii) environmentally benign reducing agents, and (iii) non-toxic substances for stabilisation of the nanoparticles. Green nanotechnology targets the application of green chemistry principles in designing nanoscale products, and the development of nanomaterial fabrication methods with reduced hazardous waste and safer applications. Biochemical process can occur at low temperatures, because of the high specificity of the biocatalysts. Several green methods have been developed by our research group to synthesis silver nanoparticles (Ag-NPs).

Synthesis of Ag-NPs in Montmorillonite by UV Irradiation

We have successfully developed a simple method for preparing silver nanoparticles (Ag-NPs) using UV irradiation of $AgNO_3$ in the interlamellar space of a montmorillonite (MMT) without any reducing agent or heat treatment (Darroudi *et al.*, 2009). The properties of Ag/MMT nanocomposites were studied as a function of the UV irradiation period. UV irradiation disintegrated the Ag-NPs into smaller size until a relatively stable size and size distribution were achieved. The results from UV–vis spectroscopy showed that particles size of Ag-NPs decreased with the increase of irradiation period. The crystalline structure of Ag-NPs was determined by X-ray diffraction (XRD). Transmission electron microscopy (TEM) images and their corresponding size distributions shown when the MMT/$AgNO_3$ suspension was irradiated under UV for 3 h, photoreduced Ag-NPs were formed with a broad size distribution and mean particle size of about 30.53 nm and when the irradiation period was increased to 48 h, the mean particles size of Ag-NPs was decreased considerably to 6.01 nm. It can be seen that the larger Ag-NPs were obtained under shorter irradiation period and it were disintegrated under the further irradiation of UV light.

Synthesis of Ag-NPs in Gelatin by UV Irradiation

Ag-NPs were successfully synthesised using the UV irradiation of aqueous solutions containing $AgNO_3$ and gelatin as a silver source and stabiliser, respectively (Darroudi *et al.,* 2011a). The UV irradiation times influence the Ag-NPs diameter, as evidenced from surface Plasmon resonance (SPR) bands and TEM images. When the UV irradiation time was increased, the mean size of particles continuously decreased as a result of photo-induced Ag-NPs fragmentation. Based on XRD, the UV-irradiated Ag-NPs were a face-centered cubic (fcc) single crystal without any impurity. This study reveals that the UV irradiation-mediated method is a green chemistry and promising route for the synthesis of stable Ag-NPs for various applications. The fabricated Ag-NPs are very stable over a long period of time (e.g., 3 months) in an aqueous solution without any sign of agglomeration or precipitants. The results suggest that photoreduction methods such as UV irradiation can maintain Ag-NPs in the presence of green stabilisers (e.g., gelatin at ambient temperature). The important advantages of this method are that it is cheap, easy, and free of toxic materials.

Preparation of colloidal Ag-NPs using a nanosecond pulsed Nd:YAG laser, λ= 532 nm, with laser fluence of approximately about 0.6 J/pulse was done in an aqueous gelatin solution. The size and optical absorption properties of samples were studied as a function of the laser repetition rates. The results from the UV–vis spectroscopy demonstrated that the mean diameter of Ag-NPs increased (from about 9 to 15 nm) as the laser repetition rate was increased (from 10 to 40 Hz). This work provides important advantages namely, simplicity, speed, and cleanness. This approach is general and may be extended to other noble metals such as Au, Pd and Pt.

Colloidal Ag-NPs were also successfully prepared using a nanosecond pulsed Nd:YAG laser, λ=1064 nm, with laser fluence of approximately about 360 mJ/pulse, in an aqueous gelatin solution (Darroudi *et al.,* 2011d). Gelatin was used as a stabiliser, and the size and optical absorption properties of samples were studied as a function of the laser ablation times. The results from the UV-visible (UV-Vis) spectroscopy demonstrated that the mean diameter of Ag-NPs decrease as the laser ablation time increases (Table 1). The Ag-NPs have mean diameters ranging from approximately 10 nm to 16 nm. Compared with other preparation methods, this work is clean, rapid, and simple to use.

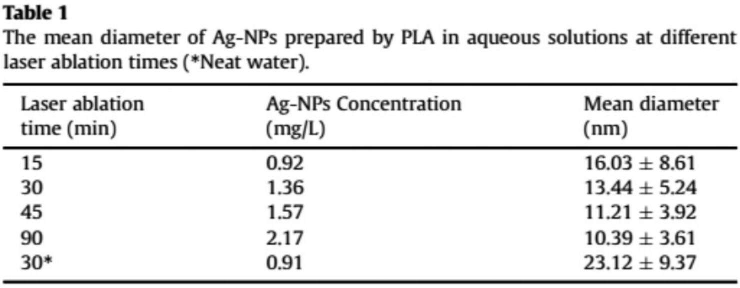


Table 1
The mean diameter of Ag-NPs prepared by PLA in aqueous solutions at different laser ablation times (*Neat water).

Laser ablation time (min)	Ag-NPs Concentration (mg/L)	Mean diameter (nm)
15	0.92	16.03 ± 8.61
30	1.36	13.44 ± 5.24
45	1.57	11.21 ± 3.92
90	2.17	10.39 ± 3.61
30*	0.91	23.12 ± 9.37

In the preparation of Ag-NPs by γ-irradiation method (Darroudi *et al.,* 2013), the absorbed dose of γ-irradiation was found to influence the particles diameter of the Ag-NPs, as evidenced from SPR and TEM images. When the γ-irradiation dose was increased (from 5 to 50 kGy), the mean size of particles was decreased (from 20.4 to 16.4 nm) continuously as a result of γ-induced Ag-NPs fragmentation. The XRD pattern also displays the fcc geometry for obtained Ag-NPs. These fabricated Ag-NPs were very stable over a long period of time in aqueous solution without any sign of agglomeration or precipitants. This approach reveals that γ-irradiation-mediated method is a promising route for the synthesis of stable Ag-NPs for different applications and can potentially be used for other metal salts, e.g. Au and Pd.

In another study, silver nanoparticles were prepared with simple and green synthesis method by reducing Ag^+ ions in aqueous gelatin media with and in the absence of glucose as a reducing agent (Darroudi *et al.,* 2011b). Gelatin is the protein from collagen and has a three-chain helical structure in which individual helical chains are stranded in a super-helix about the common molecular axis. Gelatin was used for the first time as a reducing and stabilising agent. It was found that with increasing temperature the size of nanoparticles is decreased. The TEM results indicate that the samples obtained in gelatin and gelatin–glucose solutions retained a narrower particle size distribution. Particle size of Ag-NPs obtained in gelatin solutions was smaller than in the gelatin-glucose solutions, which can be related to rate of reduction reaction. The average size of all prepared Ag-NPs was less than 15 nm, and a smaller average size (about 3.7 nm) was obtained for reaction without glucose at 60 °C. The use of eco-friendly reagents, such as gelatin and glucose, provides green and economic attributes to this work.

The work on eco-friendly chemistry goes on for preparing Ag-NPs in natural polymeric media was successfully developed by Darroudi *et al.* (2011c). The colloidal Ag-NPs were synthesised in an aqueous solution using silver nitrate, gelatin, and glucose as a silver precursor, stabiliser, and reducing agent, respectively (Figure 2). The properties of synthesised colloidal Ag-NPs were studied at different reaction times. The UV-Vis spectra were in excellent agreement with the obtained nanostructure studies performed by TEM and their size distributions. The TEM results indicate that the samples obtained over a longer time period retained a narrower particle size distribution; the average size of all prepared Ag-NPs was 20 nm; and a smaller average size (about 5 nm) was obtained in absence of glucose. The prepared samples were also characterised by XRD and AFM. The value determined by the AFM was close to the TEM determined, and the films of gelatin containing Ag-NPs displayed a densely uniform packed structure. Thus, the Ag-NPs–gelatin films could provide a biocompatible and rough surface for special biological applications, such as cell immobilisation.

Figure 2 An illustration of colloidal silver nanoparticles synthesised in aqueous gelatin solution

Ag-NPs were successfully synthesised in the natural polymeric matrix. Silver nitrate, gelatin, glucose, and sodium hydroxide have been used as silver precursor, stabiliser, reducing agent, and accelerator reagent, respectively (Darroudi *et al.,* 2010). This study investigated the role of NaOH as the accelerator. The colloidal sols of Ag-NPs obtained at different volumes of NaOH show strong and different surface Plasmon resonance (SPR) peaks, which can be explained from the TEM images of Ag-NPs and their particle size distribution. Nanoparticle agglomeration was controlled with the addition of gelatin as a stabilising agent. XRD and TEM measurements displayed that the resultant nanoparticles were faced centered cubic (fcc) structures smaller than 20 nm in diameter. Compared with other synthetic methods, this work is green, rapid, and simple to use. The newly prepared Ag-NPs may have many potential applications in chemical and biological industries.

The influence of different stirring times on antibacterial activity of silver nanoparticles in polyethylene glycol (PEG) suspension under moderate temperature at different stirring times was also investigated (Shameli *et al.,* 2012). Silver nitrate ($AgNO_3$) was used as the metal precursor while PEG was applied as the solid support and polymeric stabiliser. The antibacterial activity of different sizes of nanosilver was investigated against Gram–positive [Staphylococcus aureus] and Gram–negative bacteria [Salmonella typhimurium SL1344] by the disk diffusion method using Müeller–Hinton Agar.

Formation of Ag-NPs was determined by UV–vis spectroscopy where surface plasmon absorption maxima can be observed at 412–437 nm from the UV–Vis spectrum. TEM analysis revealed that Ag-NPs synthesised were in spherical shape. The optimum stirring time to synthesise smallest particle size was 6 hours with mean diameter of 11.23 nm. Zeta potential results indicated that the stability of the Ag-NPs increased at the 6 h stirring time of reaction. FT-IR spectra revealed that there was complexation existing between PEG and Ag-NPs. The Ag-NPs in PEG were effective against all bacteria tested, with higher antibacterial activity was observed for Ag-NPs with smaller size. These suggest that Ag-NPs can be employed as an effective bacteria inhibitor and can be applied in medical field. Ag-NPs were successfully synthesised in PEG suspension under moderate temperature at different stirring times. The study clearly showed that the Ag-NPs with different stirring times exhibit inhibition towards the tested gram-positive and gram-negative bacteria (Figure 3).

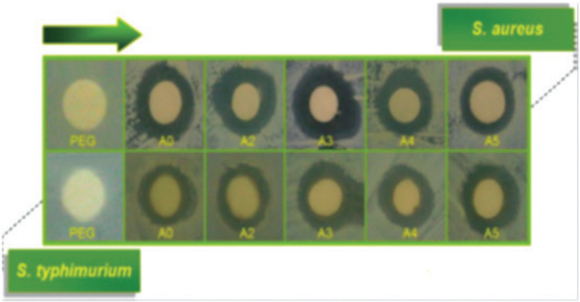


Figure 3 Comparison of the inhibition zone test between Gram-positive and Gram-negative bacteria [*S. aureus and S. typhimurium*] for PEG, [Ag (PEG)]$^+$ (A0) and [Ag (PEG)] suspension at different stirring times [A2–A5 (3, 6, 24 and 48 h)].

In the antibacterial activity tests, inhibition zone values were obtained for PEG, [Ag (PEG)] $^+$(A0) and [Ag (PEG)] suspension at the different stirring times, i.e. 3 (A2), 6 (A3), 24 (A4) and 48 h (A5) and tested against *S. aureus* and *S. typhimurium*. The results and images of inhibition zones are presented as the average values in Figure 3 and Table 2, respectively. Table 2 show that the AgNO3 and Ag-NPs in PEG suspension gives high and similar antibacterial activity against Gram-negative and Gram-positive bacteria. This is due to their size, Ag-NPs can easily reach the nuclear content of bacteria and they present the large and impressive surface area; thus, the contacts with bacteria were the greatest. In the polymeric matrix systems, silver ions released from the surface of Ag-NPs are assumed responsible for their antibacterial activity (Morones *et al.,* 2005).

In the aqueous phase systems, the results show that the antibacterial activity of Ag-NPs at 3 and 6 h stirring times in *S.aureus* is higher than that of the Ag$^+$ ions. Similarly, the antibacterial activity of Ag-NPs in *S. typhimurium* is generally higher than that of the Ag+ ions. With the exception of the Ag- NPs at 3 h stirring time, the activity decreased with an increase in the stirring time (6, 24 and 48 h). The high activity at the 6 h stirring time Ag-NPs is assumed for large surface area of the nanoparticles (Jeong *et al.,* 2005). The solution of PEG (10 mg/ml) does not show any antibacterial activity. The $[Ag(PEG)]^+$ (A0) suspension for all tested bacteria shows high antibacterial activity and interestingly these effects in the [Ag (PEG)] (A2–A5) were increased with the decreasing size of Ag-NPs. However, a higher Ag-NPs loading do not improve the antibacterial activity (Jeong *et al.,* 2005).

Table 2 Average inhibition zone and standard deviation for PEG, $[Ag (PEG)]^+$ (A0) and [Ag(PEG)] suspension (A2-A5) at different stirring times; 3, 6, 24 & 48 h, respectively.

Bacteria	**Inhibition zone (mm)**					**Control -**	**Control +**	
	A0	A2	A3	A4	A5	(mm) PEG	(mm) CTX	(mm) C
S.aureus	11.65 ± 0.56	12.78 ± 0.12	13.64 ± 0.29	11.56 ± 0.36	9.71 ± 0.14	NA	18.45	17.45
S. typhimurium	9.67 ± 0.33	9.44 ± 0.36	11.51 ± 0.43	10.64 0.39	10.62 ± 0.36	NA	18.75	16.58

Abbreviation: NA; Not Appear; CTX, Chloramphenical; C, Cefotaxime

Synthesis of Gold Nanoparticles from Marine Macroalgae Sargassum Muticum

Gold nanoparticles (Au-NPs) were synthesised using brown marine algae Sargassum (*S. muticum)* aqueous extract as both a reductant and a capping agent (Namvar *et al*., 2015). The treatment of aqueous solution of gold precursors with *S. muticum* algae extract resulted in rapid formation of stable nanoparticles for gold. The growth of nanoparticles is monitored by UV–Vis spectrophotometer and complemented with characterisation using TEM, XRD and zeta potential. The formation of Au-NPs was confirmed through the presence of an absorption peak at 550 nm using a UV–Vis spectrophotometer. TEM images revealed that the particles are spherical in shape with a mean size of 5.42 ± 1.18 nm. The capping of anionic bio-compounds on the surface of nanoparticles was confirmed by zeta potential measurement (-35.8 mV) and is responsible for the electrostatic stability.

The reduction of the Au^+ ions during the exposure to *S. muticum* aqueous extract could easily be followed by visual assessment and UV–Vis spectroscopy (Figure 4). The gold colloids after 15 min reaction have an SPR peak around 520 nm, which corresponds to the uniform colloids. However, at longer reaction time, the SPR peaks are red shifted to 550 nm, indicating an aggregation process in accordance with absorbance tail in the longer wavelengths and dark purple color of solution.

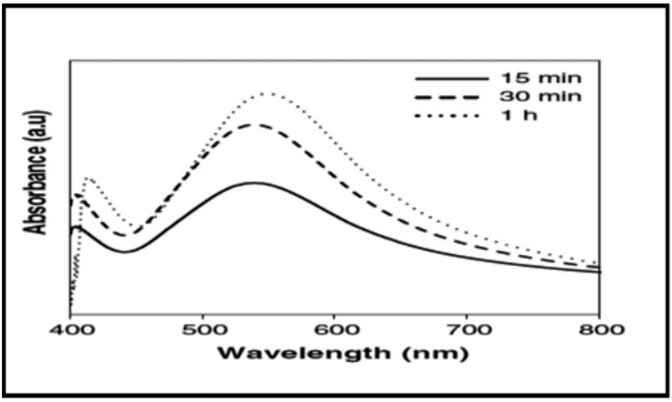


Figure 4 UV–Vis spectra of biosynthesized gold nanoparticles solution at different time of reaction

This absorption gradually increases in intensity as a function of time of reaction indicating an increase in the number of formed Au-NPs in the solution. The metal particles were observed to be stable in solution even 6 months after synthesis. On the other hand, in the pH range of 3–9, the biosynthesised Au-NPs, except for in the pH = 3 due to the agglomeration of nanoparticles in high protonic solution, showed no significant visible change in the intensity or position of the absorbance at 550 nm (Figure 5). This shows that Au-NPs are stable in the pH range of 5–9. A very important requirement for nanoparticle biosynthesis for medical applications is aggregation resistance in different pH or in an ionic environment.

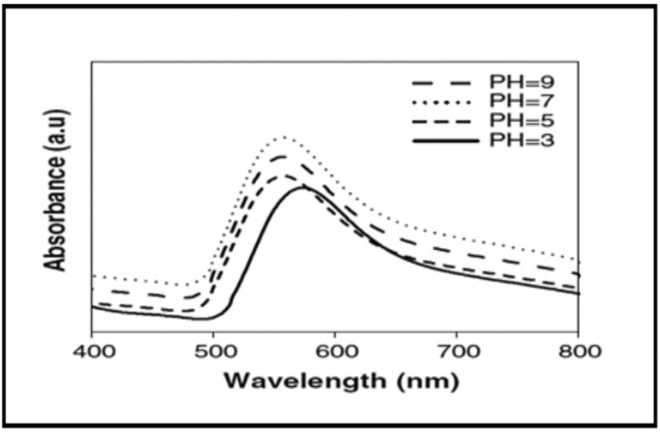


Figure 5 UV–Vis spectra of biosynthesised gold nanoparticles solution in the pH range of 2–10

The TEM images (Figures 6a and b) and particle-size distribution graph (Figure 6c) show the Au-NPs formed have spherical structures with some agglomeration and a mean size of 5.42 ± 1.18 nm.

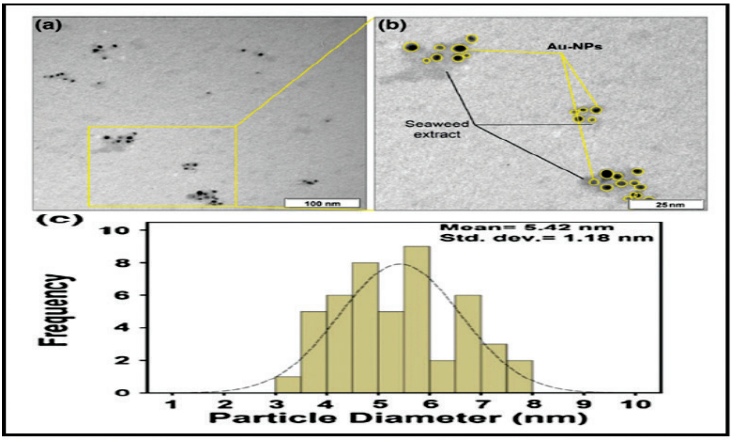


Figure 6 TEM images (a, b) and corresponding size distribution graph (c) of biosynthesised Au-NPs

Metallic Au-NPs are also detected by XRD analysis of biosynthesised Au-NPs (Figure 7). The Au-NPs formed on the surface of *S. muticum* have revealed clear peaks of face-centered cubic phases (JCPDS No. 03-0921) at 38.25 (1 1 1), 44.46 (2 0 0), 64.64 (2 2 0), and 77.20 (3 1 1). The slight move in the peak positions may be owing to the presence of some strain in the crystal structure, which is a characteristic of nanocrystallites synthesised through bio-method. On the other hand, the sharp peaks indicate some bio-organic compounds/proteins in the nanoparticle during the synthesis (Gardea-Torresdey *et al.,* 2003). The XRD results provide strong evidence supporting UV–Vis spectra and TEM images for the presence of gold particles.

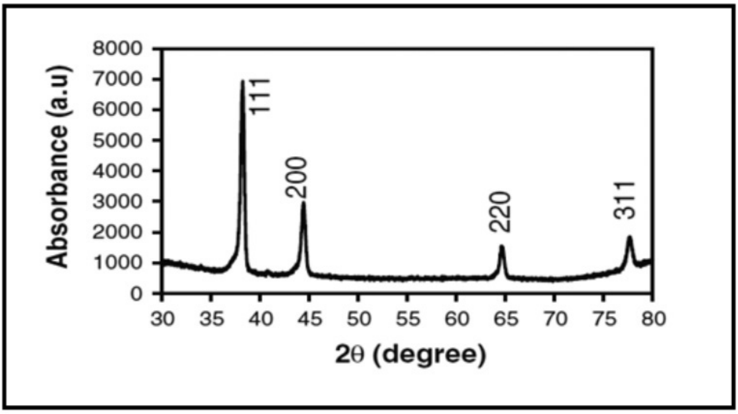


Figure 7 X-ray diffraction pattern of biosynthesised Au-NPs

Zeta potential (ZP) of the bio-synthesised Au-NPs was -35.8 mV. From the average ZP values, it is suggested that the bio-synthesised Au- NPs were stable and warped with anionic compounds and responsible for electrostatic stabilization. This may be attained by means of the high repulsive and attractive forces happening between each nanoparticle.

Preparation of Fe_3O_4 Nanoparticles

Iron oxide nanoparticles (Fe_3O_4-NPs) were prepared by adding 0.1 M $FeCl_3$ solution to the Brown seaweed (BS) extract in a 1:1 volume ratio (Figure 8). Fe_3O_4-NPs were immediately obtained with the reduction process (Mahdavi *et al.,* 2013a). The mixture was stirred for 60 min and then allowed to stand at room temperature for another 30 min. The obtained colloidal suspensions were then centrifuged and washed several times with ethanol and then dried at 40 °C under vacuum to obtain the Fe_3O_4-NPs. FT-IR spectroscopy was used to identify the functional groups of the active components based on the peak value in the region of infrared radiation. After complete bioreduction of iron ions, the BS extract was centrifuged for 2 min to isolate the Fe_3O_4-NPs from the compounds present in the solution.

Figure 8 Brown seaweed (*Sargassum muticum*) (A), Brown seaweed (*Sargassum muticum*) powder (B)

The FESEM image and EDXRF spectra for the Fe_3O_4-NPs are shown in Figure 9. The FESEM image (Figure 9A) confirms that the Fe_3O_4-NPs are cubic in shape (Mahdavi *et al.*, 2013b). In the EDXRF spectrum (Figure 9B), the peaks around 0.8, 6.2, and 6.9 keV are related to the binding energies of Fe. Therefore, the EDXRF spectra for the Fe_3O_4/seaweed extract confirmed the presence of Fe_3O_4-NPs in the BS aqueous extract without any impurity.

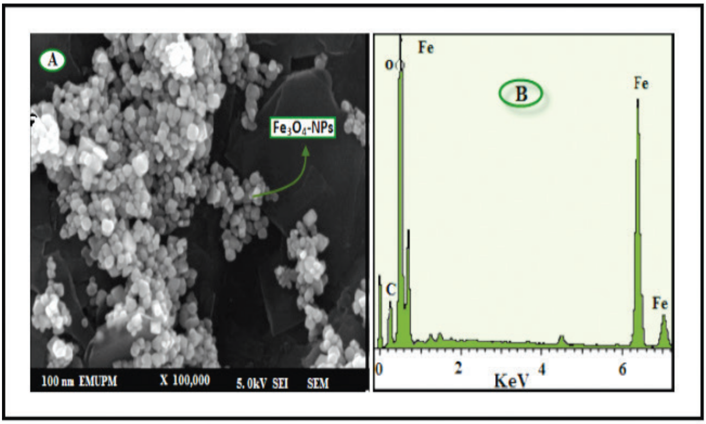


Figure 9 FESEM image (A) and energy-dispersive X-ray fluorescence spectrometry spectra of Fe_3O_4-NPs synthesised using BS extract (B).

For TEM, a drop of the Fe_3O_4-NPs solution synthesised by treating ferric chloride solution with BS extract was deposited onto a TEM copper grid. After drying, the grid was imaged using TEM. The TEM image and the size distribution are shown in Figures 10A and 10B. Sizes of Fe_3O_4-NPs are almost uniform, and all of the particles are cubic in shape. As shown in Figure 11B, the particle size distribution curve of Fe_3O_4-NPs indicated that mean diameter size of this nanoparticle was found to be 18 ± 4 nm. The XRD pattern suggested that the unassigned peaks may indicate the crystallisation of bio-organic phase present in the extract which was also observed from TEM micrographs. The good correlation between particle sizes obtained from Scherrer equation and TEM supports the crystalline structure of the iron nanoparticles.

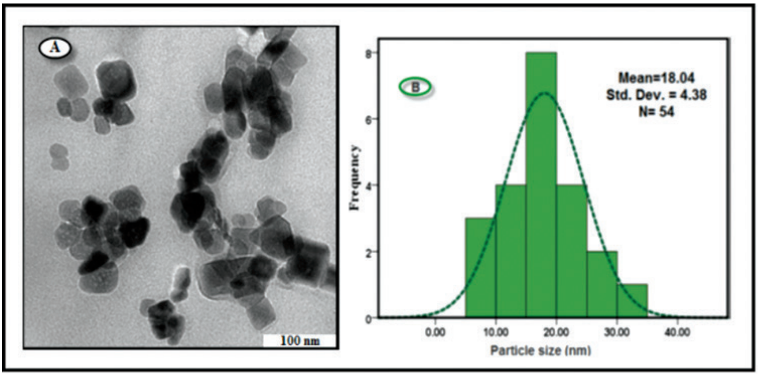


Figure 10 TEM image (A), and corresponding size distribution of Fe$_3$O$_4$-NPs synthesised using BS extract (B)

Effect of *Curcuma longa* Tuber Powder Extract on the size of silver nanoparticles

The biosynthetic method using plant extracts has received more attention than chemical and physical methods and even than the use of microbes. The method is suitable for nanoscale metal synthesis due to the absence of any requirement to maintain an aseptic environment (Shameli *et al.,* 2010a). The possibility of using plant materials for the synthesis of nanoscale metals was reported initially by (Gardea-Torresdey *et al.,* 2002; Gardea-Torresdey *et al.,* 2003). Later, the bioreduction of various metals to nanosize materials of various shapes, capable of meeting the requirements of diverse industrial applications, was extensively studied (Shankar *et al.,* 2004). In continuation, we have demonstrated the prospect of using *VitexNegundo* L. leaf and *Callicarpa manigayi* stem bark methanolic extracts for the synthesis of the Ag-NPs at ambient conditions, without any additive protecting nanoparticles from aggregating, template-shaping nanoparticles or accelerants (Zargar *et al.,* 2011; Shameli *et al.,* 2012).

An environmentally friendly, ultrafast, one-step, cost efficient green method for producing Ag/C. *longa* has been developed. The Ag-NPs were prepared using silver nitrate as silver precursor and *C. longa* tuber powder water extract as reducing agent and stabiliser. Also, the effect of different volumes of *C. longa* tuber powder water extract was investigated on controlling the size of Ag-NPs. The *C. longa* tubers are shown in Figure 11a. The tubers were cut into small pieces, powdered in a mixer, and then sieved using a 20-mesh sieve to get a uniform size range (Figure 11b). For the production of the extract, 0.1 g of *C. longa* tuber powder was added to a 100 mL Erlenmeyer flask with 20 mL sterile distilled water and then mixed for 4 h in room temperature.

Briefly, aqueous extract of tubers *C. longa* (0.25 g) was added to distilled deionised water (50 mL) with vigorous stirring for 4 h. Forty milliliters of $AgN0_3$ (1×10^{-3} M) were then added to 1, 2.5, 10, and 20 ml. of *C. longa* extract at different five cuvettes and mixed at room temperature (25 °C) for 24 h, respectively. Ag-NPs were gradually obtained during the incubation period. Throughout the reduction process, all solutions were kept at a room temperature in the dark to avoid any photochemical reactions. All solution components were purged with nitrogen gas prior to use. Subsequently, reduction proceeded in the presence of nitrogen to eliminate oxygen. The obtained colloidal suspensions of [Ag (C. *longa)*] were then centrifuged at 15,000 rpm for 20 min and washed four times to remove silver ion residue. The precipitate nanoparticles were then dried overnight at 30 °C under vacuum overnight to obtain the [Ag (C. *longa)].*

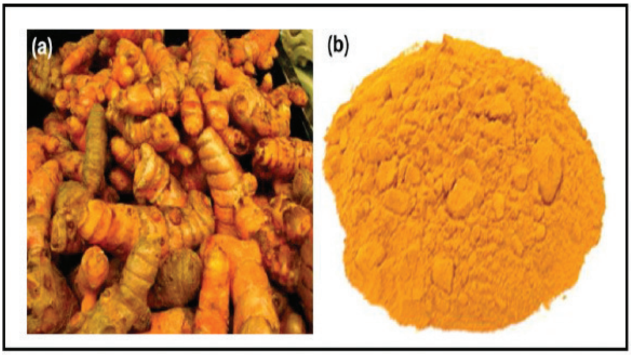


Figure 11 *C. longa* tubers plant (a) and powder of C. longa (b)

Reduction of Ag^+ into Ag-NPs during exposure to water extract of C. longa tuber powder could be followed by the color change. The fresh suspension of C. longa was yellow in color (Figure 12a). However, after addition of $AgNO_3$ and stirring for 24 h at room temperature, the emulsion turned to light brown, brown, and dark brown, respectively (Figure 12). The colour changes in aqueous solutions are due to the surface plasmon resonance phenomenon. The result obtained in this investigation is found to be interesting because it can serve as a foundation in terms of identification of potential forest plants for synthesising Ag-NPs.

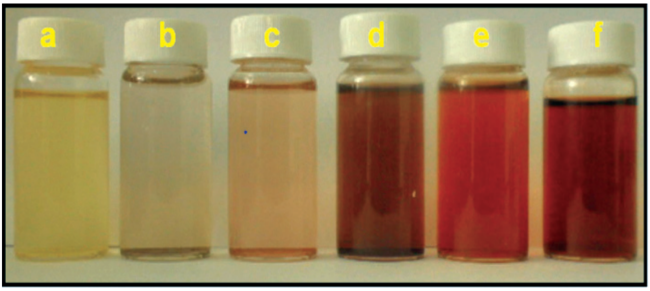


Figure 12 Aqueous extract of *C. longa* (a) and Ag/C. longa emulsions (b–f)

The formation of Ag-NPs was followed by measuring the surface plasmon resonance (SPR) of the C. longa and Ag/C. longa emulsions over the wavelength range from 300 to 800 nm. The preparation of Ag-NPs was studied by UV-Vis spectroscopy, which has proven to be a useful spectroscopic method for the detection of prepared metallic nanoparticles. Figure 13a shows that Ag-NPs started forming when [Ag (*C. longa*)]$^+$ reacted directly at room temperature. In UV-Vis spectra, the spherical Ag-NPs must display a SPR band at around 400 nm (Kelly *et al.,* 2003). The shift to the left or right (blue or red shifts) in the λ_{max} of the SPR peaks could be related to obtaining Ag-NPs at various shapes, sizes, or solvent dependencies of formed Ag-NPs. From this research the SPR band characteristics of Ag-NPs were detected around 415-457 nm (Figure 13a, b) which strongly suggests that the Ag-NPs were spherical in shape which has been confirmed by the TEM results of this study (Shameli *et al.,* 2012).

The intensity of the SPR peak increased as the volume of *C. longa* extract increased, which indicated the continued reduction of 1he silver ions, and the increase of the absorbance indicates that the concentration of Ag-NPs increases (Figure 13c). There is no characteristic UV-Vis absorption of Ag-NPs in *C. longa* emulsions. The SPR peak at 457 nm indicates the formation of Ag-NPs in 1mL *C. longa* extract. Gradually, with the increase in the volume of *C. longa* extract from 2 to 5 and 10 mL, the corresponding peak intensities increased, with concomitant blue shifts in wavelength from 455 to 450 and 417 nm, respectively.

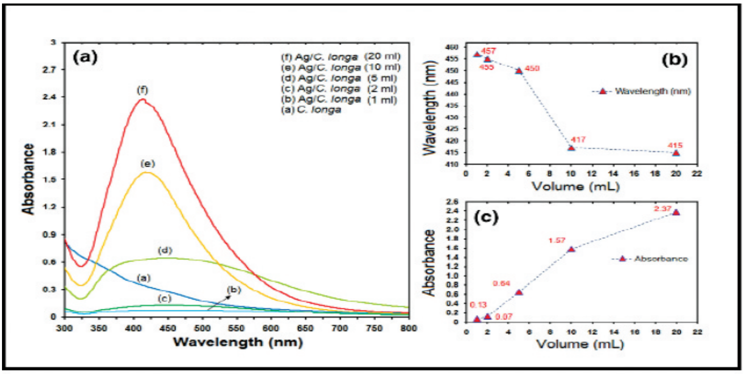


Figure 13 UV–Vis absorption spectra of C. longa (a) and Ag/C. longa emulsion prepared at 1, 2, 5, 10, and 20 mL of C. longa, respectively (a–c)

Also, with the increase again in the volume of *C. longa* extract to 20 mL, the matching peak intensities increase once more, with attendant blue shifts in wavelength to 415 nm. Therefore, colloidal Ag-NPs prepared at these absorption bands were assumed to correspond to the Ag-NPs extra fine and homogeneous distribution with relatively small size (less than 5 nm). Thus, there is a normal case in this situation for the SPR absorption band for the particles, which agreed with the TEM results, whereby blue shifts were observed as the size decreased with the increase of the volume of the C. longa extract to 1, 2, 5, 10, and 20 mL respectively (Ahmad *et al.,* 2011a & 2011b). This phenomenon could be due to the fact that the *C. longa* extract as stabiliser and reducing agent was able to control the nanoparticles size effectively, which resulted in the very small size.

The XRD patterns of Ag/*C. longa* indicated that the structure of Ag-NPs is face-centered cubic (fcc) (Shameli *et al.,* 2012). In addition, all the Ag-NPs had a similar diffraction profile, and XRD peaks at 2θ of 38.18, 44.25, 64.72 and 77.40 could be attributed to the 111, 200, 220 and 311 crystallographic planes of the fcc silver crystals, respectively (Ahmad *et al.,* 2009). The XRD pattern thus clearly illustrated that the Ag-NPs formed in this study are crystalline in nature. The main crystalline phase was silver and there were no obvious other phases such as impurities found in the XRD patterns. The presence of a narrow distribution of Ag-NPs in TEM images are in accordance with the UV–Vis spectral study. TEM images and their corresponding particle size distributions of Ag/ *C. longa* emulsion with the different volume of *C. longa* extract (5, 10 and 20 mL) are shown in Figure 14. For the TEM study, a drop of the Ag-NPs solutions synthesised by treating $AgNO_3$ solution with different volumes of *C. longa* was deposited onto a TEM copper grid. After drying, the grids were imaged using TEM. The TEM images and their size distributions revealed that the mean diameters and standard deviation of Ag-NPs were about 10.46 ±5.58, 8.18 ±3.53, and 4.90 ±1.42 nm for 5, 10, and 20 mL (Figure 14a–c) of *C. longa* extract, respectively.

The numbers of Ag-NPs counted for TEM images were around 1,006, 1,041, and 1,065 for 5, 10, and 20 mL for *C. longa* extract, respectively. These results proved that the diameters of the Ag-NPs synthesised in this method depended on the volumes used of *C. longa* extract. Also, Figure 14 shows the Ag-NPs surrounded by the *C. longa* extract. The dark points in these figures represent that the large-scale distribution and size homogeneity of Ag-NPs increases with the increase of volume extract.

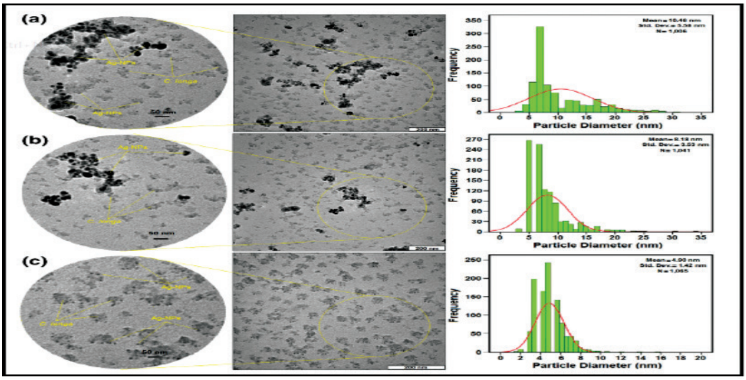


Figure 14 TEM images and corresponding size distributions of Ag/*C. longa* (5, 10, and 20 mL) after 24 h of stirring reaction time (a–c)

Figure 15 shows the SEM images and EDXRF spectrum for the *C. longa* and Ag/*C. longa* emulsion (10 and 20 mL) after 24 h stirring time. The structure of *C. longa* extract without Ag-NPs showed a mass with specific form, that is a typical shape of plant extract. As shown, for the synthesis of Ag-NPs in *C. longa* extract (10 and 20 mL), the size of nanosilver decreases with increasing the volume of extract. Thus, the results confirm that extract of *C. longa* can control the shape and size of the Ag NPs. Also, the exterior surfaces of Ag/ *C. longa* become shiny in the spherical-shaped spots, due to the presence of small sized Ag-NPs. Figure 15d shows the EDXRF spectra for the *C. longa*; the peaks around 1.7, 2.8, 3.8, and 4.5 keV are related to the binding energies of *C. longa*. In Figure 15d, the peaks around 1.3, 3.1, 3.3, and 3.4 keV are related to the silver *C. longa* elements in the extract (Shameli *et al.,* 2011; Ahmad *et al.,* 2012). Additionally, the EDXRF spectra for the Ag/ *C. longa* confirmed the presence of Ag-NPs in the *C. longa* extraction without any impurity peaks. Also, with the increased percentages of Ag-NPs in the *C. longa* extract (10 and 20 mL), the intensity of the Ag-NP peaks in the EDXRF spectra increased. The EDXRF spectra clearly show that with increases in the volume of *C. longa* extract (10 and 20 mL) in Ag/*C. longa* emulsion, the percentage yields increases to 38.58 and 45.53%, respectively. The results indicate that the synthesised nanoparticles are composed of high purity Ag-NPs.

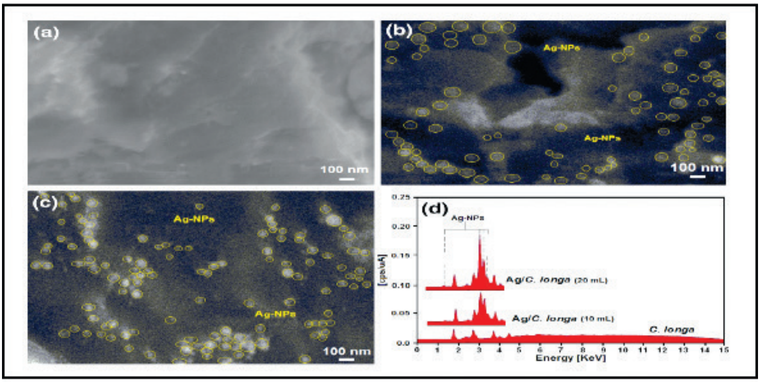


Figure 15 SEM image and EDXRF spectra of *C. longa* **a**nd Ag/*C. longa* (10 and 20 mL) formation after 24 h of biosynthesis reaction time

The Ag-NPs obtained possess a negative zeta potential value. Zeta potential is an essential parameter for characterisation of stability in aqueous Ag/*C. longa* emulsion. A minimum of ±30 mV zeta potential values is required for an indication of stable nano-suspension (Shameli *et al.,* 2011). The narrow and sharp peaks in the zeta potential analysis indicate uniformity and good distribution of Ag-NPs. The zeta potential for the *C. longa* extract and Ag/ *C. longa* emulsion were equal to -18.3±4.6, -9.8±3.8, and -4.2±2.5 mV, respectively. So, these results clearly indicate that the particles are unstable for long time, and the surface charge of the particles increases with the decreases of volume of the *C. longa* extract from 20 to 10 mL.

The FT-IR spectra were recorded to identify the possible biomolecules responsible for the reduction of the Ag ions and capping of the bio reduced Ag-NPs synthesised by the *C. longa* extract. The *C. longa* tuber powder extract after complete bioreduction of Ag was centrifuged at 15,000 rpm for 20 min to isolate the Ag-NPs from proteins and other compounds present in the solution. Figure 16a shows the FT-IR spectrum of *C. longa* tuber powder extract that does not contain $AgNO_3$, whereas Figures 16b and c show the spectra of the Ag-NPs biosynthesised in 10 and 20 mL of *C. longa* extract. Three absorption peaks at about 865, 1,004, and 1,141 and 867, 1,011, and 1,147 cm^{-1} which can be assigned to the absorption of –C–N stretching vibrations of the amine –C–O–C or –C–O groups, respectively (Shameli *et al.,* 2012). The broad and strong bands at 3,321–2,904 cm^{-1} and 3,329–2,920 cm^{-1} are due to bonded hydroxyl (–OH) or amine groups (–NH) and aliphatic C–H of the *C. longa* tuber powder extract, respectively. The broad peaks at 1,943, 510, and 302 cm^{-1} and 1,952, 510, and 299 cm^{-1} are related to the Ag-NP banding with oxygen from the hydroxyl group of *C. longa* extract compounds, respectively.

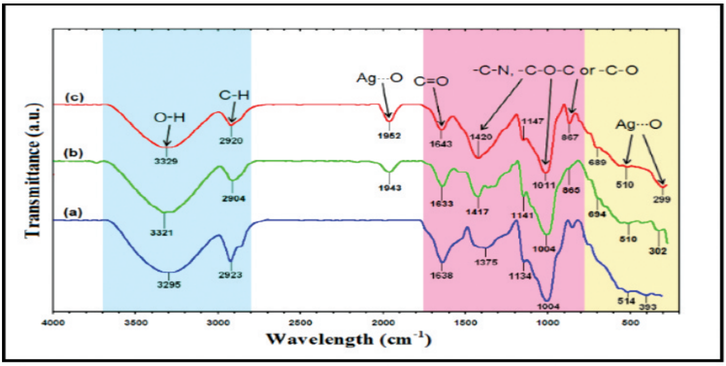


Figure 16 FT-IR spectra for the *C. longa* tuber powder extract (a) and Ag/*C. longa* with different volumes of *C. longa* extracts after 24 h from biosynthesis reaction, respectively (10 and 20 mL,b,c)

Ag-NPs Synthesis in the presence of Kappa Carrageenan

A green sonochemical method was developed by Elsupikhe *et al.* (2015a) for preparing silver nanoparticles (Ag-NPs) in different concentrations of kappa carrageenan (κ-carrageenan). The Ag-NPs were synthesised by reducing $AgNO_3$ using ultrasonic waves in the presence of κ-carrageenan. The κ-carrageenan was used as a natural eco-friendly stabiliser, and ultrasonic irradiation was used as a green reducing agent. Five suspensions were prepared, by adding 10 mL of 0.1 M AgNO3 to 40-mL κ-carrageenan of different concentrations; 0.1, 0.15, 0.20, 0.25, and 0.3 wt.%. The solutions were stirred for 1 h to obtain AgNO3/κ-carrageenan. Then, the samples were exposed to high-intensity ultrasound irradiation under amplitude of 50% for 90 min at room temperature. Formation of Ag/κ-carrageenan was determined by UV-visible spectroscopy where the surface plasmon absorption maximum was observed at 402 to 420 nm. The XRD analysis shows that the Ag-NPs are of a face-centered cubic structure. The Fourier transform infrared spectra indicate the presence of Ag-NPs in κ-carrageenan (Figure 17). Transmission electron microscopy (TEM) image for the highest concentration of κ-carrageenan showed the distribution of Ag-NPs with an average particle size near to 4.21 nm

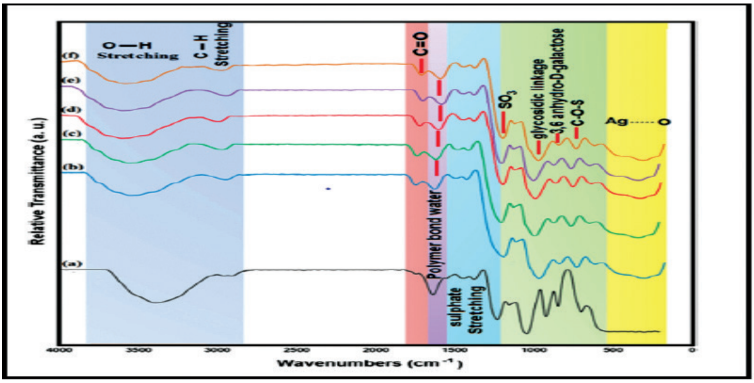


Figure 17 FT-IR spectra for κ-carrageenan (a) and Ag/ κ-carrageenan at different concentrations of κ-carrageenan; 0.10, 0.15, 0.20, 0.25 and 0.30%, respectively.

The TEM images and their corresponding particle size distributions for Ag-NPs at different concentrations of κ-carrageenan are shown in Figures 18a, b and c for 0.10, 0.20, and 0.30%, respectively. TEM images and their size distributions indicated that the mean diameters and standard deviation of Ag-NPs were about 56.36 ± 24.33, 9.08 ± 3.33, and 4.21 ± 3.91 nm for 0.10, 0.20, and 0.30%, respectively.

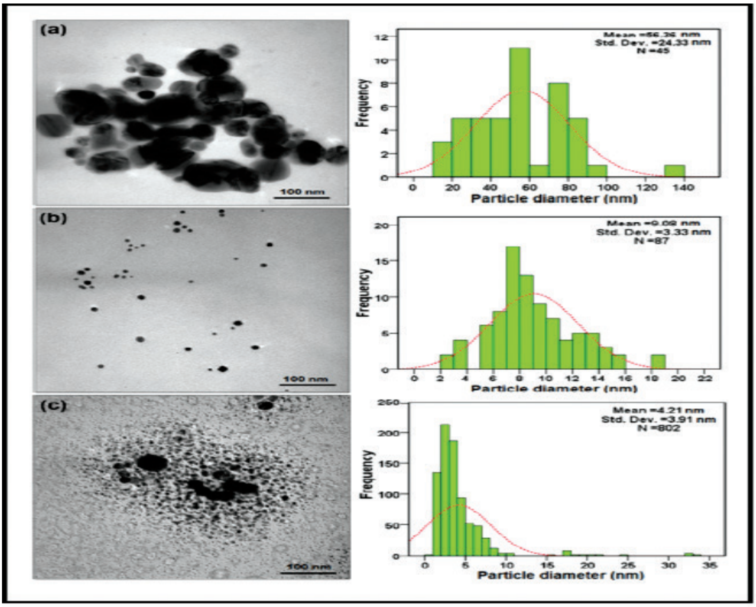


Figure 18 TEM images and corresponding size distributions for Ag/κ-carrageenan at different concentrations of κ-carrageenan. [0.1, 0.2 and 0.3%, respectively (a, b, c)].

UV-visible spectroscopy data determined the formation of Ag-NPs by observing the surface plasmon resonance (SPR) bands. The X-ray diffraction patterns of the prepared Ag/κ-carrageenan at different concentrations of κ- carrageenan indicated the formation of the Ag-NPs. Figure 19 shows all the samples had the same diffraction profiles. The XRD peaks at 2θ of 38.18°, 44.36°, 64.66°, 77.58°, and 82.01° can be attributed to the (111), (200), (220), (311), and (222) crystallographic planes of the face-centered cubic (fcc) silver crystals, respectively.

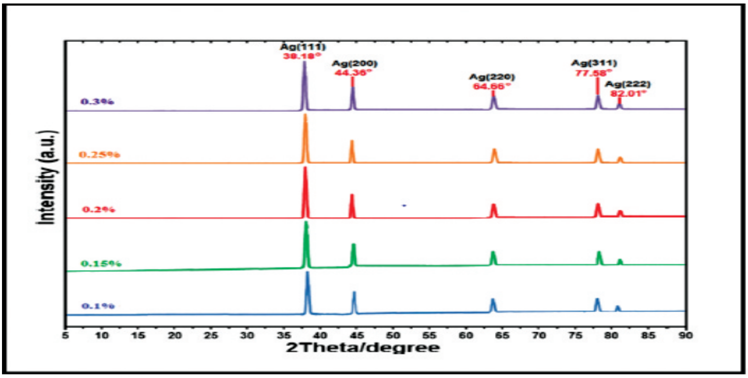


Figure 19 X-ray diffraction patterns for the Ag/κ-carrageenan at different concentrations of κ-carrageenan; 0.10, 0.15, 0.20, 0.25 and 0.30%, respectively.

Synthesis of Ag-NPs in κ-carrageenan at different concentrations of $AgNO_3$ was also carried by Elsupikhe *et al.* (2015b). The Ag-NPs were synthesised by reducing $AgNO_3$ using ultrasonic waves in the presence of k-carrageenan. Five samples were prepared by adding 10 ml of $AgNO_3$ at different concentrations (0.05, 0.1, 0.15, 0.20, and 0.25 M) solution to 40 ml κ-carrageenan (0.25 wt.%). The solutions were stirred to obtain $AgNO_3$/κ-carrageenan. The samples were exposed to high-intensity ultrasound irradiation under ambient conditions for 90 min at an amplitude of 50 Hz at room temperature. The κ-carrageenan was used as an eco-friendly stabiliser and ultrasonic irradiation as a green reducing agent. The number of Ag-NPs increased with increasing concentrations of $AgNO_3$. Formation of Ag/ κ-carrageenan was determined by UV–visible spectroscopy where the surface plasmon absorption maximum was observed at 410–416 nm. TEM images showed the well-dispersed Ag-NPs with an average particle size of 5 nm. SEM images showed the spherical shape of the Ag-NPs. The use of photo irradiation provides a green and economic method features to the synthesis reported in the study.

The TEM images and their corresponding particle size distributions of Ag-NPs at different concentrations of $AgNO_3$ are shown in Figure 20. TEM images and their size distributions revealed that the mean diameters and standard deviation of Ag-NPs were about 7.07 ± 2.54, 4.08 ± 2.09, and 5.01 ± 6.48 nm for 0.05, 0.15, and 0.25 M, respectively. The concentrations of $AgNO_3$ were increased to 0.15 M, the size of Ag-NPs and the distribution decreased, while afterwards, at 0.25 M the size of Ag-NPs became bigger and the distribution decreased. SEM images indicating the changes in the surface of Ag/ κ-carrageenan, when the concentration increased, i.e. when the concentrations of $AgNO_3$ increased, the yield of Ag-NPs was also increased with smaller spherical shape.

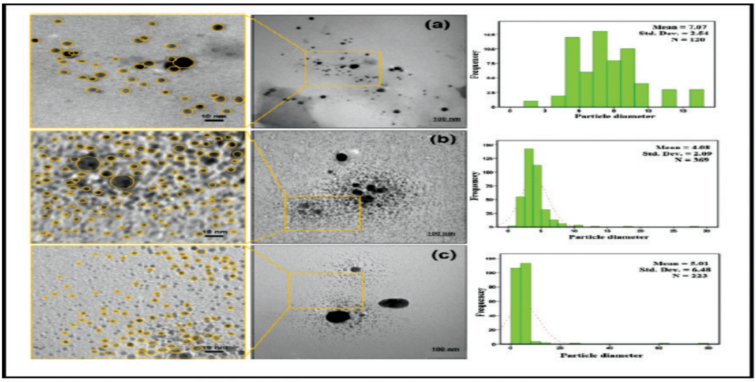


Figure 20 TEM images and corresponding size distributions for Ag/ κ-carrageenan at different concentrations of AgNO3 respectively, [0.05, 0.15, and 0.25 M, (a–c)]

Effect of ultrasonic radiation times to the control size of silver nanoparticles in κ-carrageenan was investigated by Elsupikhe *et al.* (2015c). The samples were exposed to high-intensity ultrasound irradiation for 10, 30, 50, 70, and 90 min, respectively, at amplitude of 50 Hz. Formations of Ag/ κ-carrageenan were determined by electronic spectroscopy where the surface plasmon absorption maxima were observed at 437–412 nm. The FT-IR spectra indicate the presence of κ-carrageenan in capping with Ag-NPs. The XRD analysis proved that the Ag-NPs were of a face-centered cubic structure. TEM images displayed well-dispersed Ag- NPs with an average particle size of less than 10 nm. SEM images indicated the spherical shape of the Ag-NPs. Schematic illustration of the interaction between the negative charge in κ-carrageenan and positive charge in Ag-NPs (Figure 21).

In another study, silver nanoparticles were synthesised using *Artocarpus elasticus* stem bark extract (Abdullah *et al.* 2015). A green synthetic route for the production of stable silver nanoparticles (Ag-NPs) by using aqueous silver nitrate as metal precursor and *A. elasticus* stem bark extract act both as reductant and stabiliser is being reported for the first time.

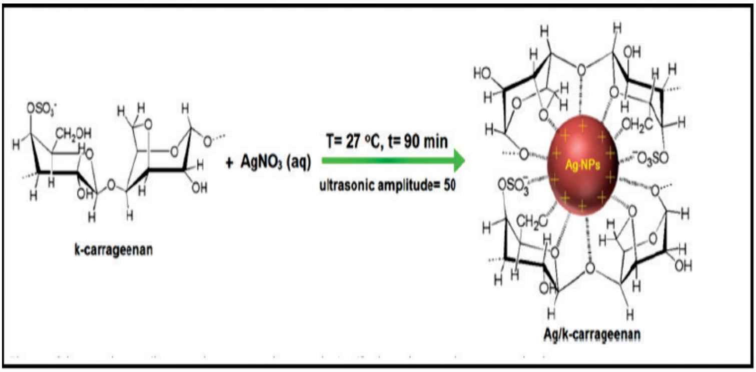


Figure 21 Schematic illustration of the interaction between the negative charge in κ-carrageenan and positive charge in Ag-NPs.

The morphological study using TEM and SEM show resultant Ag-NPs in spherical were formed with an average size of 5.81 ± 3.80, 6.95 ± 5.50, 12.39 ± 9.51, and 19.74 ± 9.70 nm at 3, 6, 24, and 48 h, respectively (Figure 22). Thus, with the increase of reaction time in the room temperature the size of Ag-NPs increases and *A. elasticus* can play an important role in the bioreduction and stabilisation of silver ions to Ag-NPs.

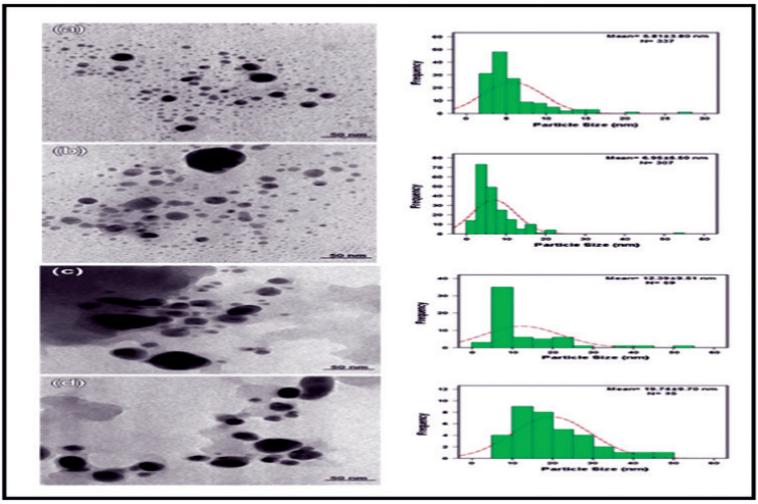


Figure 22 TEM image and histogram of Ag/*A. elasticus* nanoparticles at 3, 6, 24 and 48 h reaction time (a–d).

PREPARATION AND CHARACTERISATION OF BIONANOCOMPOSITES

Bionanocomposite, a new generation of nanocomposite materials, signify an emerging field in the frontier of materials science, life science, nanotechnology (Drader *et al*., 2007). Bionanocomposites are composed of a natural polymer matrix and organic/inorganic filler with at least one dimension on the nanometer scale. They show remarkable advantages of biodegradability and biocompatibility in various medical, agricultural, drug release and packaging applications (Ahmad *et al*., 2010, Mangiacapra, *et al*., 2006).

Recent developments of lignocellulosic bionanocomposite, chemical modifications techniques as well as composite processing methodologies that enhance the biomaterial performance were reviewed by Fernandes *et al*. (2013). Lignocellulosic materials and their chemical constituents were highlighted as promising alternatives for the development of drug-delivery vehicles and for the engineering or regeneration of bone and cartilage. Lin *et al*. (2014) prepared castor oil-based polyurethane bionanocomposites with improved mechanical properties by the introduction of crab chitin nanocrystals from partial surface acetylation. Through controlled acetylation, some of the hydrophilic hydroxyl groups on the nanocrystals were replaced by hydrophobic acetyl groups in order to enhance the compatibility between the chitin nanoparticles and polyurethane; and some of the hydroxyl groups were preserved on the surface of nanocrystals for the purpose of rigid network formation among chitin nanoparticles. Results showed that the presence of acetylated chitin nanocrystals at moderate concentration (6 wt.%) significantly promoted the nano-reinforcing effect in composites, and simultaneously improved the strength, stiffness and toughness of thermoplastic polyurethane-based nanocomposites. Due the restriction of rigid nanocrystals to soft segments, the glass transition temperatures of the nanocomposites surprisingly increased with the higher loading levels of acetylated chitin nanocrystals.

The understanding of clays structure of cationic clay such as montmorillonite and anionic clay such layered double hydroxide (LDH) has widened their application into nanotechnology. Basic building blocks of montmorillonite that consists of octahedral sheet M(O,OH)$_{,}$ (where M=Al^{3+}, Mg^{2+}, Fe^{3+} or Fe^{2+}) is sandwiched between two sheets of tetrahedral Si(O,OH) as illustrated in Figure 23. The combination of these sheets gives rise to the MMT layers with the thickness of ca. 1.0 nm. Naturally occurring substitution of positively metal ions by ions with lesser charges, particularly Si^{4+} by Al^{3+} in tetrahedral positions; and Al^{3+} or Fe^{3+} by Mg^{2+} or Fe^{2+} in octahedral positions, results in negative charges of sheets layers which are then balanced by interlayer cations; commonly Na^{+}, Ca^{2+} and Mg^{2+}. This interlayer cation can be replaced by cationic surfactants via ion exchanged process to make it compatible with polymers.

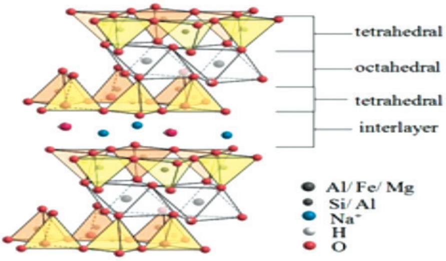


Figure 23 Crystal structural of montmorillonite consist of silicate layers (two tetrahedral sheets fused to one octahedral sheet) and exchangeable interlayer cation

Layered double hydroxides have structures similar to that of brucite Mg $(OH)_2$, and crystallise in a layer-type lattice as a consequence of the presence of relatively small two fold positively charged cations in close proximity to the non-spherosymmetrical and highly polarisable OH^- ions). Each Mg^{2+} randomly occupies the octahedral holes in the close-packed configurations of the OH^- ions and the different octahedra share edges to form infinite sheets. The sheets are stacked one on top of the other with two different symmetries; rhombohedral or hexagonal and are held together by weak interactions through hydrogen bonding. If some Mg^{2+} ions are replaced isomorphously by cations with higher charge, but similar radius, the brucite-type sheets become positively charged and the electrical neutrality is maintained by anions located in disordered interlayer domains containing water molecules. Properties of clays such as low surface activity and large particle size are considered to be poor when they were mixed with polymers even though clays have a long tradition as semi-reinforcing fillers and extenders in the plastic industry.

In the past, surface interactions between polymers and clays were totally depending on the outer surface of clays in the formation of micro-sized filler reinforced polymers without considering the internal layers that consist thousands of clay layers. The clay particles present as bulk in polymer matrix. In order to achieve good compatibility, substantial knowledge in compatibility chemistry is very important. Failure to pre-treat the polymers and/or clays will result in incompatibility between the polymers and clays, thus conventional composites will be obtained rather than nanocomposites. Generally, polymer matrix and clay particles are incompatible due to the reason that polymer matrix is organic in nature whereas clay particles are inorganic in nature. In order to incorporate clay particles into polymer matrixes, either one of the materials or both materials have to be pre-treated to make them become compatible prior to mixing. In our research works, the clay properties were converted from hydrophilic to organophilic via ion exchange method. The intercalation of alkylammonium ion into montmorillonite (Na^+-MMT) galleries was carried out by cation exchange reaction between interlayer sodium and alkyl ammonium cations. While for LDH, dodecylsulphate anion has been intercalated into the gallery region by anion exchange reaction between interlayer anion and dodecylsulphate cations (Abdullah *et al*., 2009: 2010).

Polymer-clay composites were prepared by mixing the molten state of thermoplastic together with the modified micro-size of clay in internal mixer. Depending on the nature of the components used (layered silicates, intercalating agent and polymer matrix) and the method of preparation, three types of composites may be obtained when layered clay is associated with the polymer as shown in Figure 24 (Qutubuddin and Fu, 2001).

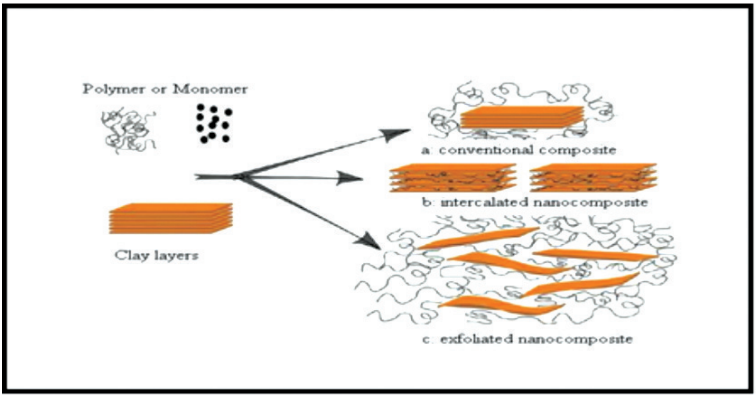


Figure 24 Possible structures of polymer/clay composites (Qutubuddin and Fu, 2001).

The synthesis approach has dramatically increased the surface interaction by breaking up the clays into individual layers which are 1 nm of thickness (Abdullah *et al.*, 2007). The bulk clay layers completely exfoliated and distributed evenly throughout the polymer matrix to formed intercalated or exfoliated structure of nanocomposites. With higher surface interaction between clay layers and polymers that contributes to the stress transfer of reinforcement phases, hence improving the mechanical properties such as tensile strength and modulus.

There is an extra advantage in polymer composites applications when a good dispersion and distribution of the clay layers at nanometer level into the polymer matrix. These nanocomposites possess remarkable property enhancements relative to pristine polymer such tensile strength and modulus. The nanocomposites also give us an advantage to obtain the properties mentioned above without losing the clarity of the polymer. Therefore, polymer/clay nanocomposites are potentially used in various fields such as food packaging as well as the electronics and automotive.

Stearate Mg-Al LDH was successfully modified via ion exchange reaction and PHB/PCL/stearate Mg-Al LDH nanocomposites were prepared via through solution casting method by used of chloroform as organic solvent. Nanocomposites were prepared with the use of PHB/PCL blends with optimum ratio of the blend at 80:20. The nanocomposites of PHB/PCL blend with different amount of stearate Mg-Al LDH (0.25, 0.5, 1, 1.5, 2%) were carried out by solution casting process. PHB, PCL and stearate Mg-Al LDH were dissolved and stirred in 100 mL chloroform for one hour respectively. Different amounts of stearate Mg-Al LDH were added to 80PHB/20PCL blends to formed PHB/PCL/stearate Mg-Al LDH nanocomposites. The 80PHB/20PCL blend was chosen as our optimum blend because of application such as plastics and packaging field were focused on the tensile strength and elongation at break. Meanwhile, this blend weight ratio gives the higher value of mechanical properties. The FT-IR spectra show no major difference between the samples because of similar functional groups in polymers blends and nanocomposites spectra, indicating no strong chemical interaction and bonding between PHB, PCL and stearate Mg-Al LDH. The tensile strength, modulus and elongation at break of PHB/PCL/stearate Mg-Al LDH nanocomposites with effect of different stearate Mg-Al LDH content. The tensile strength of neat PHB is 23.00 MPa and decrease to 17.02 MPa upon the addition of 20PCL. However, addition of 1.0 wt.% of stearate Mg-Al LDH into 80PHB/20PCL blend increasing the tensile strength to 28.23 MPa or an enhancement of 66% compared to the unfilled clay PHB/PCL blends.

Silver/poly(Lactic Acid) Nanocomposites

In this study, antibacterial characteristic of silver/poly (lactic acid) nanocomposite (Ag/PLA-NC) films was investigated, while silver nanoparticles (Ag-NPs) were synthesised into biodegradable PLA via chemical reduction method in diphase solvent (Shameli *et al.,* 2010b). Silver nitrate and sodium borohydride were respectively used as a silver precursor and reducing agent in the PLA, which acted as a polymeric matrix and stabiliser. The silver ions released from the Ag/PLA-NC films and their antibacterial activities were scrutinised. The antibacterial activities of the Ag/PLA-NC films were examined against Gram-negative bacteria (*Escherichia coli and Vibrio parahaemolyticus*) and Gram-positive bacteria (*Staphylococcus aureus*) by diffusion method using Muller–Hinton agar. The results indicated that Ag/PLA-NC films possessed a strong antibacterial activity with the increase in the percentage of Ag-NPs in the PLA.

Figure 25 shows typical results of the tests carried out for the purpose of a first qualitative evaluation for *V. parahaemolyticus*; the antibacterial activity is evidenced by a zone of bacteria-growth inhibition, for the PLA and Ag/PLA-NC (8, 16, and 32 wt.%) films. A similar inhibition zone is not present around the PLA film in Figure 25A, and there is bacteria growth also on the top of the sample. As expected, the most notable antibacterial effect is observed for the Ag/PLA-NCs (32 wt.%) with the highest percentage (Figure 25D); reduced antibacterial effect are noted in Figures 28B and 27C, respectively.

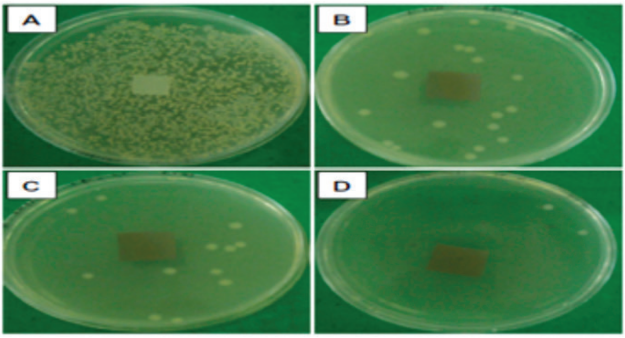


Figure 25 Comparison of inhibition zone test for *Vibrio parahaemolyticus* between PLA (A), Ag/PLA-NC content 8 (B), 16 (C), and 32 (D) wt.% respectively

Poly(vinyl alcohol)/Chitosan Blend Bionanocomposites Reinforced by Cellulose Nanocrystals

Poly(vinyl alcohol)/chitosan (PVA/Cts) blend was prepared as a described work (Costa-Júnior *et al.,* 2009). Briefly, specific quantity of PVA (5.0 *wt./v*%) hydrogel solutions was added into the 1.0 *wt./v*% chitosan solution to obtain PVA/Cs molar ratio of (3:1). The mixture was kept under stirring for 30 min until the PVA and chitosan completely formed a clear solution. Then CNCs were dispersed in a solution of distilled water (100 mL) and ultrasonicated for 30 min. The CNCs filler loading level (0, 0.5, 1, 3 or 5 wt.%) was based on the amount of PVA/Cts blend. The dried composite films were roasted at 45 °C for 6 h. Finally, a series of nanocomposite films with a thickness of ~0.2 mm were prepared (Azizi *et al.,* 2014a).

The distribution of CNCs in polymer blend matrices has been observed by TEM analysis. As shown in Figures 26a and b, the rod-like cellulose nanocrystals were dispersed well into polymer matrix, when the low contents of CNCs were used. The nanocrystals at 1.0 wt.% filler loading have an average width of (5.7 ± 1.2) nm and length of (238 ± 16) nm, giving rise to an aspect ratio of about 41.75. This value is generally in the aspect ratio range of cellulose nanocrystals (Dufresne *et al.,* 2008). A study showed that an effective reinforcement effect can be obtained in composites, when nano-sized cellulose with an aspect ratio about 50 are introduced into a polymer matrix in comparison with micro-sized fibres (Eichhorn *et al.,* 2010). On the other hand, it is seen that, with the increase of CNCs contents into polymer matrices, most of the cellulose nanocrystals were agglomerated by hydrogen-bonded free hydroxyl groups (Figures 26c and d).

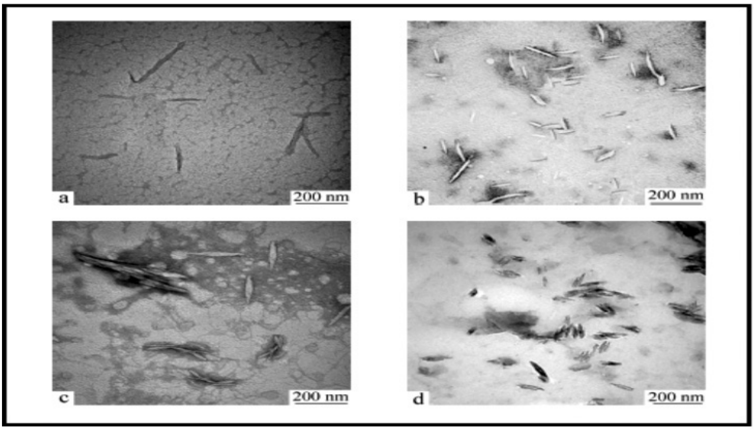
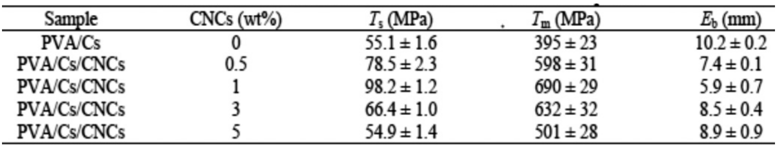


Figure 27 TEM images of PVA/Cts/CNCs bionanocomposites with CNCs contents of 0.5 wt.% (a), 1.0 wt.% (b), 3.0 wt.% (c) and 5.0 wt.% (d)

The effects of CNCs contents on the tensile properties of the PVA/Cts bio-nanocomposite films are given in Table 3. Tensile values show that the addition of CNCs helped to increase the tensile strength (*T*s) and modulus (*T*m) of the films. The highest values were obtained when 1.0 wt.% of cellulose nanocrsytals were incorporated in the PVA/Cts blend matrix. The bionanocomposite showed ~78% and 75% tensile strength and modulus improvements, respectively compared to that of the original polymer blend. The improvement is due to formation of a network structure resulted from filler-matrix interactions in composites, which increases hard portion crystallinity, decreases molecular mobility and promotes rigidity.

Table 3 Tensile data for PVA/Cts and its CNC bionanocomposites



Sample	CNCs (wt%)	T_s (MPa)	T_m (MPa)	E_b (mm)
PVA/Cs	0	55.1 ± 1.6	395 ± 23	10.2 ± 0.2
PVA/Cs/CNCs	0.5	78.5 ± 2.3	598 ± 31	7.4 ± 0.1
PVA/Cs/CNCs	1	98.2 ± 1.2	690 ± 29	5.9 ± 0.7
PVA/Cs/CNCs	3	66.4 ± 1.0	632 ± 32	8.5 ± 0.4
PVA/Cs/CNCs	5	54.9 ± 1.4	501 ± 28	8.9 ± 0.9

The reinforced bio-composites of biopolymer blend matrix with cellulose nanocrystals were prepared and potentiality of cellulose nano-sized filler was evaluated on the structure and properties of resulted hybrids. The observation of TEM-based structures illustrated that the CNCs were homogenously dispersed at lower filler loading. While compared the control PVA/Cts film and the PVA/Cts/CNCs film, the bio-nanocomposite films exhibited higher tensile strength; decreased elongation at break; increased thermal resistance and reduced oxygen transmission rate. This is owing to the parameters such as the nano-scale size effects of the CNC (high *L*/*D*), the high content of cellulose crystalline districts, the well dispersion of CNCs within PVA/Cts matrix, and the strong interaction between CNC and PVA/Cts matrix.

Preparation of PVA/Cts/CNCs/ZnO Biocomposite Films

The PVA/Cts blend was prepared with specific quantity of PVA (5.0 *wt.*/*v*%) was added into the 1.0 *w*/*v*% chitosan solution to obtain PVA/Cts molar ratio of (3:1). The reinforced composites of poly(vinyl alcohol)/chitosan matrix with cellulose nanocrystals/ZnO were prepared and the potentiality of bifunctional nano-sized fillers was measured on the structure and properties of resulting hybrids (Azizi *et al.,* 2014b). The CNCs/ZnO were dispersed in a solution of distilled water (100 mL) and ultrasonicated for 30 min.

The CNCs/ZnO nano-sized filler loading level (0, 1, 3, 5 or 7 wt.%) was based on the amount of PVA/Cts blend. The above suspensions were added into 100 mL of the PVA/Cts under strong string for 2 h at 70°C. The samples were evaluated for antibacterial activity against Gram-negative *Salmonella choleraesuis* and Gram-positive *Staphylococcus aureus*. The biocomposites were effective against *S.choleraesuis* and *S. aureus*, with dependence on the amount of the CNCs/ZnO added. These biocomposites have potential applications in medical, packaging, and UV-shielding materials.

Cellulose nanocrystals,ZnO/silver nanoparticles (CNC/ZnO-AgNPs) were synthesised using our previously reported method (Azizi et al., 2013). Briefly, a sample of $Zn(AcO)_2 \cdot 2H_2O$ alcoholic solution (50 mL, 1 mM) was dispersed in a CNC suspension by magnetic stirring. After complete mixing, a sodium hydroxide solution was added dropwise to the mixed solution under continuous stirring at 80°C until a pH .10 was reached. When a milky colored suspension was observed, a sample of aqueous $AgNO_3$ solution with a concentration of 10 wt% (relative to $Zn(AcO)_2 \cdot 2H_2O$) was added to the above suspension with vigorous stirring, and the reaction was continued for 2 hours. The product was collected by centrifugation and careful washing three times with distilled water. The final product was obtained by drying at 100°C for one hour, with complete transformation of the remaining zinc hydroxide to zinc oxide.

Preparation of PVA/Cs/CNCs/ZnO-Ag Biocomposites

The PVA/Cs blend was prepared as described elsewhere (Costa-Júnior *et al.,* 2009). The CNC/ZnO-AgNPs were then dispersed in a solution of distilled water (100 mL) and ultrasonicated for 30 minutes. The loading level of the CNC/ZnO-AgNP filler (0, 1, 3, 5, or 7 wt.%) was based on the amount of PVA/Cts blend. A similar protocol was used to prepare a PVA/Cts/CNC bionanocomposite, but the loading level for the CNC filler was 0.5, 0, 1, 3, or 5 wt.% based on the amount of PVA/Cs blend.

The X-ray diffraction patterns for CNC/ZnO-AgNPs powder, PVA/Cts, and PVA/Cts/CNC/ZnO-Ag films are shown in Figure 27. The CNC/ZnO-Ag shows three sets of diffraction peaks corresponding to CNC, ZnO, and AgNPs in the 2θ range of 10°–80°. The X-ray diffraction pattern shows the peak of PVA/Cs and several sharp and increased diffraction peaks for PVA/Cts/CNC/ZnO-Ag bionanocomposite films with a relatively high CNC/ZnO-AgNP content. These peaks in the 2θ range of 10°–80° were almost the same as those of the CNC, ZnO, and Ag, although the sharp diffraction peaks increased with increasing CNC/ZnO-Ag content. When a high level of CNC/ZnO-Ag was introduced, the presence of greater numbers of self-agglomerated nanoparticles caused the crystalline character attributed to the CNC, ZnO, and Ag in the bionanocomposite to become clearer. The Bragg equation was used to calculate the mean intermolecular distance, which decreased from 4.87 Å to 4.69 Å as the CNC/ZnO-AgNPs content increased. These results indicated that incorporation of CNC/ZnO-AgNPs did not change the structural uniformity of the matrix polymer blend, but rather improved the molecular ordering in the amorphous polymer blend matrix.

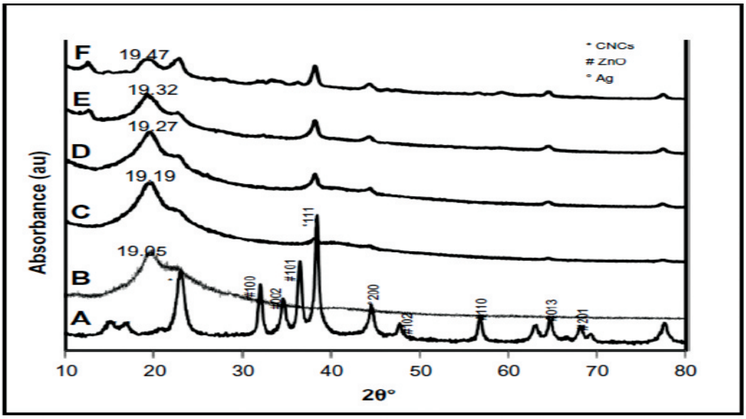


Figure 27 X-ray diffraction patterns for CNC/ZnO-AgNPs (A), PVA/Cs blend (B), and bionanocomposites from 1.0 to 7.0 wt.% (C–F) nanosized filler loading

PVA/Cts blend films reinforced with different CNC/ZnO-AgNPs contents were prepared using a solution casting method. The strong interaction between the CNC/ZnO-Ag nanosized filler and the PVA/Cts matrix contributed to improvement in the properties of the bionanocomposite. At a low filler loading level (below 5.0 wt.%), the CNC/ZnO-Ag bionanocomposites markedly increased the tensile yield strength and Young's moduli of the PVA/Cs/CNC/ZnO-Ag bionanocomposites when compared with the CNC nanosized filler (Azizi *et al.,* 2014c).

Preparation and Characterisation of Silver/Montmorillonite/chitosan Bionanocomposites

Layered silicates, e.g. montmorillonite (MMT), have been used in polymer nanocomposites with a significant improvement in mechanical properties. MMT possesses a 2-to-1 layered structure with a single octahedral aluminum layer located between two layers of tetrahedral silicon (Giannelis *et al.,* 1999). Each layer is about 1 nm thick with a lateral dimension of 100–1000 nm. Furthermore, being lamellar clay, MMT has intercalation, swelling, and ion exchange properties (Shameli *et al*., 2011). MMT can be delaminated into elemental sheets without difficulty. Therefore, it is tempting to utilise these sheets as the substrate for preparation of nanoscale metals by means of electrodeless plating. The MMT interlayer space has been used for the synthesis of material and biomaterial nanoparticles as the support for anchoring transition metal complexes and as adsorbents for cationic ions. Among the natural polymers, chitosan (Cts) has been extensively investigated as a natural cationic biopolymer because of its excellent biocompatibility, biodegradability, nontoxicity, bioactivity, and multifunctional groups, as well as its solubility in aqueous medium for food packaging film, bone substitutes, and artificial skin (Ahmad *et al*., 2009, Darder *et al.,* 2003). Cts can be intercalated in MMT by cationic exchange and hydrogen bonding processes, whereby the resulting bionanocomposites (BNCs) show interesting structural and functional properties. Conversely, BNCs are made of a natural polymeric matrix and inorganic/organic filler with at least one dimension on the nanometer scale. Metal/clay/polymer compounds like BNCs with excellent properties have become promising new areas of research (Ahmad *et al.,* 2009).

Silver nanoparticles were successfully synthesised into the interlayer space of Montmorillonite by chemical reduction method. $AgNO_3$ and $NaBH_4$ were used as a silver precursor and reducing agent, respectively (Shameli *et al*., 2011). The properties of Ag/MMT nanocomposites were studied as a function of the $AgNO_3$ concentration. The UV-Vis spectra of synthesised Ag-NPs showed that the intensity of the maximum wavelength of the plasmon peaks increased with increasing $AgNO_3$ concentration.

The crystalline structure of the Ag-NPs and basal spacing of MMT and Ag/MMT were also studied by PXRD. The antibacterial activity of Ag-NPs was investigated against gram-negative bacteria (*Escherichia coli*, *Escherichia coli* O157:H7 and *K. pneumonia*) and gram-positive bacterium (*Staphylococcus aureus*) by disk diffusion method using Muller-Hinton Agar at different sizes of Ag-NPs.

The schematic illustration of the synthesis of Ag/MMT/ Cts BNCs from $AgNO_3$/MMT/Cts produced using $NaBH_4$ as the chemical reduction agent is shown in Figure 28. Meanwhile, as shown in Figure 29, the MMT and $AgNO_3$/ MMT/Cts suspensions (A0) were colorless, but after the addition of the reducing agent to the suspensions, they turned light brown (A1), brown (A2), reddish-brown (A3), and dark brown (A4 and A5), indicating the formation of AgNPs in the MMT/Cts suspensions.

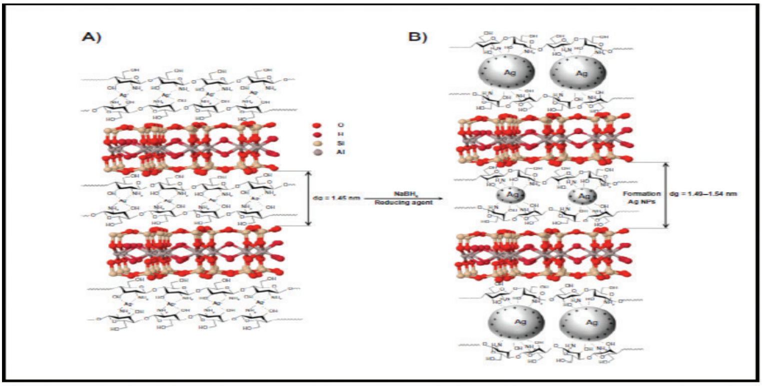


Figure 28 Schematic illustration of the synthesised silver/ montmorillonite/chitosan bionanocomposites from silver nitrate/ montmorillonite/chitosan (A0) by a chemical reduction method.

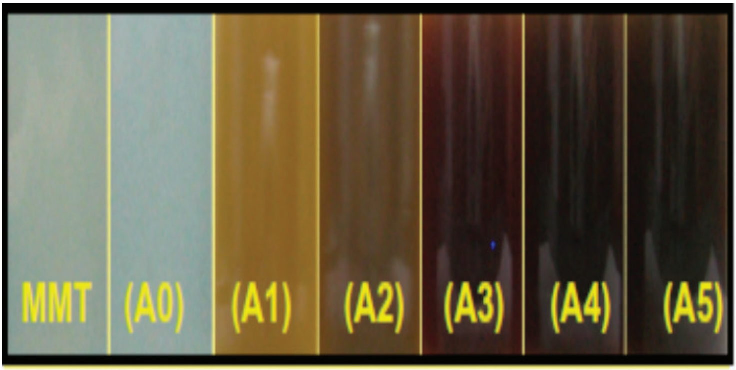


Figure 29 Photograph of montmorillonite/chitosan bionanocomposite suspension (A0) and silver/montmorillonite/chitosan bionanocomposite suspension at different $AgNO_3$ concentrations; (A1) 0.5%, (A2) 1.0%, (A3) 1.5%, (A4) 2.0%, and (A5) 5.0%.

The TEM analysis of the AgNPs showed that the mean diameter of the nanoparticles ranged from about 6.28 nm to 9.84 nm. SEM images indicated that there were no structural changes between the initial MMT, MMT/Cts, and Ag/MMT/ Cts BNCs (A2, A4, and A5) at different AgNO3 concentrations. In addition, the EDXRF spectra for the MMT, MMT/ Cts and Ag/MMT/Cts BNCs (A2, A4, and A5) confirmed the presence of elemental compounds in MMT, Cts, and AgNPs without any other impurity peaks. The chemical structures of MMT, MMT/Cts, and Ag/MMT/Cts BNCs (A2, A4, and A5) were analysed by FT-IR (Figure 30). The antibacterial studies showed comparatively similar effects for all samples, as indicated by the inhibition zone test between Cts, MMT/Cts, MMT, $AgNO_3$/ MMT/Cts (A0), and Ag/MMT/Cts BNCs (A2, A4, and A5) against different bacteria. The antibacterial activities of Ag/MMT/Cts BNCs at the different AgNP particle sizes showed strong antibacterial activity against Gram-positive and Gram-negative bacteria.

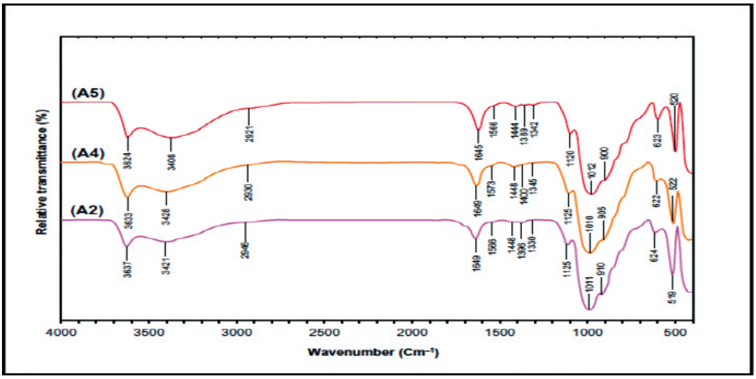


Figure 30 Fourier transforms infrared spectra for the silver/ montmorillonite/chitosan bionanocomposites at different AgNO3 concentrations: (A2) 1.0% (A), (A4) 2.0% (B), and (A5) 5.0% (C).

These results show that the antibacterial resistance of AgNPs in MMT/Cts can be modified according to the size of AgNPs, and decreases with increased particle size. Further studies are required to investigate the bactericidal effects of Ag/MMT/Cts BNCs against different types of bacteria for potential widening of their applications, such as in surgical devices and in drug-delivery vehicles.

Synthesis and Characterisation of Rice Straw/Fe_3O_4 Nanocomposites

In many countries, straw is an abundant cellulosic by-product from the production of crops such as wheat, corn, soybean and rice. The natural fibre comes from stalks, leaves, and seeds, such as kenaf, sisal, flax, wheat straw and rice straw (Garsia *et al.,* 2008) Compared to synthetic fibre, natural fibre has many advantages such as biodegradability, flammability and non-toxicity. In Malaysia, rice straw (RS) is a potential source of energy and also is a value-added by-product. It represents around 45% of the volume in rice production, producing the largest quantity of crop residue. Rice straw has the most amount of cellulose from agricultural crop residues and has traditionally been used as animal feed for cattle, feedstock for the paper industry or organic fertiliser by burning it on the open field or burying it on to the soil. The rice straw has traditionally been removed from the field by the practice of open-field burning. Since the availability of natural biofibres from renewable resources, the use of biocomposites is expanding in recent years. Rice straw as a natural fibre, is being used as a filler to improve the properties of polymer matrix and in biosorption of heavy metals. However, the yield of heavy metal removal by a natural fibre is low and separation of adsorbent from solution is difficult. UPM polymer group was the first to use of rice straw in to prepare nanocomposites with Fe_3O_4 (Khandanlou *et al.*, 2013). Rice straw/Fe_3O_4 nanocomposites were evaluated in the removal of heavy metals and as a filler to improve the polymer properties (Khandanlou *et al.*, 2013; 2014). Spherical Fe_3O_4 nanoparticles (Fe_3O_4-NPs) were synthesized on the surface of rice straw. The optimum condition for the synthesis of Fe_3O_4-NPs on the rice straw surface is described in terms of the initial concentrations of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ and volume of NaOH. The TEM images showed the mean diameters of Fe_3O_4- NPs in solid support decreased gradually from 18.47 to 9.93 nm with the increase of NaOH volumes. The VSM showed that the RS/Fe_3O_4-NCs has magnetic properties. The antibacterial activity of NCs indicated strong antibacterial activity against Gram-negative and Gram-positive bacteria, which was increased with the decreasing particle size.

In addition, the suitability of the rice straw/Fe_3O_4 nanocomposites (RS/Fe_3O_4-NCs) for adsorption of Cu(II) and Pb(II) from aqueous solution was investigated (Khandanlou *et al.,* 2015a). The ability of RS/Fe_3O_4-NCs for Cu(II) and Pb(II) adsorption was measured by atomic absorption spectroscopy (AAS). Various factors affecting the metal uptake behavior such as contact time, amount of adsorbent and initial concentration of metal ions were investigated using response surface methodology (RSM). The characteristic parameters for each isotherm including Langmuir and Freundlich isotherm were determined. The optimum conditions for the sorption of Cu(II) and Pb(II) were obtained 100 and 60 mg/L of initial ion concentration, 41.96 and 59.35 s of removal time and 0.13 g of adsorbent for both ions, respectively. The adsorption data and kinetics fitted well with Langmuir isotherm and second-order kinetic model. The regeneration results confirmed that the prepared nanocomposites can offer excellent reusability from the adsorption medium. Therefore, RS/Fe_3O_4-NCs had highly removal efficiency for elimination of Cu(II) and Pb(II).

Furthermore, unmodified rice straw (RS), modified rice straw (ORS) and ORS/Fe_3O_4-NCs were incorporated with polycaprolactone (PCL) in different percentages loading of the filler by solution casting method (Khandanlou *et al*., 2015b). ORS/PCL composites and ORS/Fe_3O_4/PCL-NCs showed superior mechanical properties due to greater compatibility of ORS and ORS/Fe_3O_4-NCs with PCL, but RS/PCL composites displayed poor adhesion between RS and PCL matrix. The tensile strength was improved with the addition of 5.0 wt.% of ORS and ORS/Fe_3O_4-NCs. The TGA showed the thermal stability of ORS/Fe_3O_4/PCL-NCs was higher than RS/PCL-Cs and ORS/PCL-Cs. The antibacterial activities of ORS/Fe_3O_4-NCs in PCL matrix was investigated against Gram-negative and Gram-positive bacteria by the disc diffusion method. The results showed the strong antibacterial activity against Gram-negative and Gram-positive bacteria, and it was increased with the increasing amount of Fe_3O_4-NPs. Research in our laboratory has shown that nanocomposites of natural fibres have good potential in nanotechnology for development of reliable and ecofriendly processes.

A WAY FORWARD

Research efforts in polymer laboratory at the Department of Chemistry UPM are geared to the development and application of environmentally friendly and sustainable bio-reinforced composites for use in automotive, packaging and medical fields. That addition of nanoparticles to base polymers confers improved properties that make them usable in automotive, packing and medical areas. Properties which have been shown to improve substantially are mechanical properties (e.g., tensile strength, elastic modulus and dimensional stability), thermomechanical properties and permeability (e.g., gases, water and hydrocarbons). Nanocomposite materials consisting of polymeric matrix and nano-scale particles have offered a great opportunity in thermoplastic and rubber industry to make new products/applications with enhanced/unique properties. Although applications of polymeric nanocomposites grow significantly due to the potential capability of addressing current challenges faced in the polymer industry, the potential impact of polymeric nanocomposites on environment should be considered. Because of this nanometres size characteristic, nanocomposites possess superior properties than the conventional composites due to maximising the interfacial adhesion. In the past, major interest has been in the use of synthetic materials such as aliphatic polyesters, polyester amides, polystyrene, nanoclays, glass and carbon fibres and carbon nanotubes etc. for the production of nanocomposites. The use of these materials, however, presents great challenges. The use of polymer composites from renewable sources has advantages over synthetic sources, particularly as a solution to the environmental problems generated by plastic waste. They offer alternatives to maintaining sustainable development of economic and ecologically attractive technology. Green composites is today widely researched because of the need for innovations in the development of materials from biodegradable polymers, preservation of fossil based raw materials, complete biological degradability and reduction in the volume of carbon dioxide release into the atmosphere. Application of agricultural resources (wastes and products) for the production of green materials is some of the reasons why green composites have attracted tremendous research interests. In polymer laboratory at the Department of Chemistry, we have used fibres from oil palm empty fruit bunch, rubberwood, kenaf and rice straw. The use of these bionanocomposites is expected to increase efficiency, improve manufacturing speed and recycling with enhanced environmental compatibility.

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines especially in polymer science and technology. Other areas include polymer-based biomaterials, nanoparticle drug delivery, miniemulsion particles, fuel cell electrode polymer bound catalysts, layer-by-layer self-assembled polymer films, electrospun nanofibres, imprint lithography, polymer blends and nanocomposites. Even with nanocomposites, carbon black reinforcement of elastomers, colloidal silica modification and even naturally occurring fibre (nanoscale fibre diameter) reinforcement are interesting subjects to be investigated in the future. In essence, the nanoscale of dimensions is the transition zone between the macro-level and the molecular level. Recent interest in polymer matrix based nanocomposites has emerged initially with interesting observations involving exfoliated clay and more recent studies with carbon nanotubes, carbon nanofibres, exfoliated graphite (graphene), nanocrystalline metals and a host of additional nanoscale inorganic filler or fibre modifications.

The worldwide demand for environmentally friendly and sustainable methods to prepare nanomaterials requires the application of green chemistry principles. Thus green nanoscience aims at using environmentally benign and economically viable reagents or solvents, designing inherently safe nanomaterials for reduced biological and ecological detriment, and enhancing the material and energy efficiency of safe chemical processes. Metal nanoparticles are of importance due to their remarkable properties and potential applications in a variety of areas, such as catalysis, sensors, electronics, optics and magnetics. To achieve the above-mentioned aims of green nanoscience, the solvent, reductant and stabilising agent should be considered from green perspectives in the preparation of metal nanoparticles. Therefore, the way forward in polymer research should be going green with bionanocomposites.

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BIOGRAPHY

Dr. Mansor Ahmad is a professor of Polymer Chemistry at Universiti Putra Malaysia. He was born in Gurun Kedah into a family of 3 boys and 4 girls. After completing primary school in his hometown, he was selected to study at Sekolah Dato' Abdul Razak (SDAR). He received his B.S. (Chemistry) degree from Indiana University, Bloomington USA in 1979 and his M.S. (Analytical Chemistry) from the University of Kentucky, Lexington USA in 1982. Later, he pursued his doctoral program at the University of Salford, Manchester UK and obtained his PhD (Polymer Chemistry) in 1993. He began his academic career as a lecturer at Universiti Pertanian Malaysia, Serdang Campus in 1983 and served UPM Sarawak Campus in Semenggok for four years. Although his main teaching duties are in the areas of his expertise (i.e. Polymer Chemistry, Industrial Chemistry and Analytical Chemistry), Dr. Mansor has also been assigned to teach other courses such as Introductory Chemistry, Laboratory Safety and Spectroscopy both at the undergraduate and graduate levels.

Dr. Mansor's research interest is in the area of Polymer Chemistry. The polymer research group at UPM, that he is currently heading, has been actively engaging collaborators from different research institutions and universities in projects and activities, namely Malaysian Nuclear Agency, MRB, MPOB, FRIM, Monash University Malaysia, UPNM and UKM. Dr. Mansor has to date, authored or co-authored more than 200 journal articles in refereed and indexed journals. With commendable H-Index (Google Scholar Citations 35; Scopus 30), Dr. Mansor is among the top five percentile highly-cited authors in UPM. By the end of 2015, Dr. Mansor has successfully supervised and graduated 29 postgraduate scholars (10 PhD, 19 MSc). As a co-supervisor, he has helped in graduating another 25 scholars (6 PhD, 19 MSc). Currently, he is supervising and co-supervising 14 postgraduate students.

As an administrator, he has held numerous positions such as Head of Laboratory at ITMA, Deputy Director of Centre of Academic Development (*CADe)*, Head of Department of Chemistry and Deputy Director of Corporate Strategy and Communication (CoSComm). Besides, he is also currently a member of UPM Senate. Realizing the need to keep abreast with the latest development of chemistry, Dr. Mansor affiliates himself with the professional fraternity. He is a Fellow of the Malaysian Scientific Association (MSA); Council member, Malaysian Institute of Chemistry (IKM); Executive Committee member, Malaysian Nanotechnology Association (MNA); Life Member, Malaysian Analytical Sciences Association (ANALIS); Life Member, Malaysian Senior Scientists Association (MSSA); Life Member, Malaysian Solid State Association (MASS) and Deputy President, Confederation of Scientific and Technological Associations of Malaysia (COSTAM).

Dr. Mansor is a member of Occupational Health and Safety Committee UPM since 2002, and serves as a member of the Technical Committee (TC) on Safe System of Work and Practices in Occupational Setting under the Department of Occupational Safety and Health which produced three OSHMS standards MS 1722. Dr. Mansor also served as the Chairman of the Working Group (WG) on Malaysian Standard on Safety Signage used in the Workplace which produced MS 2558:2014. He was appointed as a Member, Board of Examiners (BOE), National Institute of Occupational Safety and Health (NIOSH), serving 2013-2015. Dr. Mansor has served as the President of the Academic Staff Association of UPM (PPAUPM) for 6 years. Currently, Dr. Mansor is the treasurer of UPM Cooperative Berhad and the secretary of

Selangor's ANGKASA, an apex cooperative in the country. He reveives UPM excellent awards numerous occassions. One of the proudest moments when he was selected as the recipient of 2013 UPM Examplary staff award (Tokoh Pekerja UPM) for academics.

In a nutshell, Dr. Mansor Ahmad is a well-rounded academic – teacher, researcher, scholar, mentor, administrator, social activist and a good friend. Despite his numerous involvements at various levels, he remains committed towards his family. Nothing beats having a family picnic on weekends or going for a holiday with his family. When apportunity arises, he also like to spend his time gardening. His family members are his biggest fan. He is married to Normah Omar and they have four children; Nurulhuda, Munirah, Nur Shuhadah and Muhammad Arif. The "MN" family now also welcomes Akzal, Zhafri, Bazli, Ezra Elyas and Soraya Nuhaa. *ALHAMDULILLAH.*

ACKNOWLEDGEMENTS

Alhamdulillah, all praise is due to Allah.

First and foremost, I thank Allah for His blessings and mercy. Time really flies. It felt like it was just yesterday that I started my academic career at UPM. Unlike many of my other colleagues who started together with me in 1983, I was not an alumni of the then Universiti Pertanian Malaysia. I was a fresh graduate from two US universities and I had this deep anxiety within me: can I cope with this new environment? Interestingly, thirty three years later, I am still with UPM and within the next two months, will be retiring from this great university that I now call "home". Throughout my journey with this university, I have personally and professionally met a lot of people and have made friends with most of them. Thank you UPM for creating a memorable path for me. The experiences with the university have impacted my life tremendously.

It is almost impossible to list all the names of individuals who have contributed greatly to my academic career at UPM. Nevertheless my early career with the university was shaped and influenced by a few mentors. The late Prof. Badri, who was the dean when I joined the university, has helped me to chart my career path, gave vision of the need to be versatile and the importance to become an all-rounder academic. Prof. Dato' Dr Wan Md. Zin Wan Yunus and Prof. Dato' Dr Abu Bakar Salleh were my role models and mentors as they were the ones responsible in providing me research direction, especially during and after my PhD. I remember being invited by them to be in their research group. From both of them, I learned a lot about research strategies, research collaboration, research outcome, time management and teamwork. My colleague, Prof. Dr Mahiran Basri, who was also in the same research group, provided a lot of encouragements and advice on the need to stay focused. Today, I lead a research group of my own with colleagues and former students and I try to emulate lessons I learned from my great mentors. There were so many heads of departments who were not just friends, but more importantly provided me with invaluable advices on work-life balances. I am also indebted to the current Head of Department Assoc. Prof. Dr. Irmawati, colleagues and all staffs in the Faculty of Science, CoSComm, CADe and ITMA who were always there when I needed them. The current Faculty of Science's Dean, Prof. Dr. Zainal Abidin Talib has always been instrumental in encouraging me to work with professional bodies and to forge national and international collaborations with industry players.

I am blessed to be able to work with seven out of eight UPM vice chancellors. The three vice chancellors that have influenced me significantly at different stages of my academic career are namely; Prof. Emeritus Dato' Dr. Ir. Muhamad Zohadie Bardaie, Prof. Dato' Dr. Mohd Fauzi Hj. Ramlan and Prof. Datin Paduka Dr Aini Ideris. To all of you, thank you.

In preparing this inaugural lecture, friends and polymer research group members contributed with constructive suggestions. My students, former and present postgraduate, are of great help and have been of giving me tremendous reinforcement. Thank you all.

Last but not least, I express gratitude to my late parents (*Al-Fatihah for them*), my brothers and sisters for their inspiration and prayers. Special thanks goes to my beloved family for all their support, understanding and love.

LIST OF INAUGURAL LECTURES

1. Prof. Dr. Sulaiman M. Yassin
   The Challenge to Communication Research in Extension
   22 July 1989

2. Prof. Ir. Abang Abdullah Abang Ali
   Indigenous Materials and Technology for Low Cost Housing
   30 August 1990

3. Prof. Dr. Abdul Rahman Abdul Razak
   Plant Parasitic Nematodes, Lesser Known Pests of Agricultural Crops
   30 January 1993

4. Prof. Dr. Mohamed Suleiman
   Numerical Solution of Ordinary Differential Equations: A Historical Perspective
   11 December 1993

5. Prof. Dr. Mohd. Ariff Hussein
   Changing Roles of Agricultural Economics
   5 March 1994

6. Prof. Dr. Mohd. Ismail Ahmad
   Marketing Management: Prospects and Challenges for Agriculture
   6 April 1994

7. Prof. Dr. Mohamed Mahyuddin Mohd. Dahan
   The Changing Demand for Livestock Products
   20 April 1994

8. Prof. Dr. Ruth Kiew
   Plant Taxonomy, Biodiversity and Conservation
   11 May 1994

9. Prof. Ir. Dr. Mohd. Zohadie Bardaie
   Engineering Technological Developments Propelling Agriculture into the 21st Century
   28 May 1994

10. Prof. Dr. Shamsuddin Jusop
    Rock, Mineral and Soil
    18 June 1994

11. Prof. Dr. Abdul Salam Abdullah
    Natural Toxicants Affecting Animal Health and Production
    29 June 1994

12. Prof. Dr. Mohd. Yusof Hussein
    Pest Control: A Challenge in Applied Ecology
    9 July 1994

13. Prof. Dr. Kapt. Mohd. Ibrahim Haji Mohamed
    Managing Challenges in Fisheries Development through Science and Technology
    23 July 1994

14. Prof. Dr. Hj. Amat Juhari Moain
    Sejarah Keagungan Bahasa Melayu
    6 August 1994

15. Prof. Dr. Law Ah Theem
    Oil Pollution in the Malaysian Seas
    24 September 1994

16. Prof. Dr. Md. Nordin Hj. Lajis
    Fine Chemicals from Biological Resources: The Wealth from Nature
    21 January 1995

17. Prof. Dr. Sheikh Omar Abdul Rahman
    Health, Disease and Death in Creatures Great and Small
    25 February 1995

18. Prof. Dr. Mohamed Shariff Mohamed Din
    Fish Health: An Odyssey through the Asia - Pacific Region
    25 March 1995

19. Prof. Dr. Tengku Azmi Tengku Ibrahim
    Chromosome Distribution and Production Performance of Water Buffaloes
    6 May 1995

20. Prof. Dr. Abdul Hamid Mahmood
    Bahasa Melayu sebagai Bahasa Ilmu-Cabaran dan Harapan
    10 June 1995

21. Prof. Dr. Rahim Md. Sail
    Extension Education for Industrialising Malaysia: Trends, Priorities and Emerging Issues
    22 July 1995

22. Prof. Dr. Nik Muhammad Nik Abd. Majid
    The Diminishing Tropical Rain Forest: Causes, Symptoms and Cure
    19 August 1995

23. Prof. Dr. Ang Kok Jee
    The Evolution of an Environmentally Friendly Hatchery Technology for Udang Galah, the King of Freshwater Prawns and a Glimpse into the Future of Aquaculture in the 21st Century
    14 October 1995

24. Prof. Dr. Sharifuddin Haji Abdul Hamid
    Management of Highly Weathered Acid Soils for Sustainable Crop Production
    28 October 1995

25. Prof. Dr. Yu Swee Yean
    Fish Processing and Preservation: Recent Advances and Future Directions
    9 December 1995

26. Prof. Dr. Rosli Mohamad
    Pesticide Usage: Concern and Options
    10 February 1996

27. Prof. Dr. Mohamed Ismail Abdul Karim
    Microbial Fermentation and Utilization of Agricultural Bioresources and Wastes in Malaysia
    2 March 1996

28. Prof. Dr. Wan Sulaiman Wan Harun
    Soil Physics: From Glass Beads to Precision Agriculture
    16 March 1996

29. Prof. Dr. Abdul Aziz Abdul Rahman
    Sustained Growth and Sustainable Development: Is there a Trade-Off 1 or Malaysia
    13 April 1996

30. Prof. Dr. Chew Tek Ann
    Sharecropping in Perfectly Competitive Markets: A Contradiction in Terms
    27 April 1996

31. Prof. Dr. Mohd. Yusuf Sulaiman
    Back to the Future with the Sun
    18 May 1996

32. Prof. Dr. Abu Bakar Salleh
    Enzyme Technology: The Basis for Biotechnological Development
    8 June 1996

33. Prof. Dr. Kamel Ariffin Mohd. Atan
    The Fascinating Numbers
    29 June 1996

34. Prof. Dr. Ho Yin Wan
    Fungi: Friends or Foes
    27 July 1996

35. Prof. Dr. Tan Soon Guan
    Genetic Diversity of Some Southeast Asian Animals: Of Buffaloes and Goats and Fishes Too
    10 August 1996

36. Prof. Dr. Nazaruddin Mohd. Jali
    Will Rural Sociology Remain Relevant in the 21st Century?
    21 September 1996

37. Prof. Dr. Abdul Rani Bahaman
    Leptospirosis-A Model for Epidemiology, Diagnosis and Control of Infectious Diseases
    16 November 1996

38. Prof. Dr. Marziah Mahmood
    Plant Biotechnology - Strategies for Commercialization
    21 December 1996

39. Prof. Dr. Ishak Hj. Omar
    Market Relationships in the Malaysian Fish Trade: Theory and Application
    22 March 1997

40. Prof. Dr. Suhaila Mohamad
    Food and Its Healing Power
    12 April 1997

41. Prof. Dr. Malay Raj Mukerjee
    A Distributed Collaborative Environment for Distance Learning Applications
    17 June 1998

42. Prof. Dr. Wong Kai Choo
    Advancing the Fruit Industry in Malaysia: A Need to Shift Research Emphasis
    15 May 1999

43. Prof. Dr. Aini Ideris
    Avian Respiratory and Immunosuppressive Diseases- A Fatal Attraction
    10 July 1999

44. Prof. Dr. Sariah Meon
    Biological Control of Plant Pathogens: Harnessing the Richness of Microbial Diversity
    14 August 1999

45. Prof. Dr. Azizah Hashim
    The Endomycorrhiza: A Futile Investment?
    23 October 1999

46. Prof. Dr. Noraini Abdul Samad
    Molecular Plant Virology: The Way Forward
    2 February 2000

47. Prof. Dr. Muhamad Awang
    Do We Have Enough Clean Air to Breathe?
    7 April 2000

48. Prof. Dr. Lee Chnoong Kheng
    Green Environment, Clean Power
    24 June 2000

49. Prof. Dr. Mohd. Ghazali Mohayidin
    Managing Change in the Agriculture Sector: The Need for Innovative Educational Initiatives
    12 January 2002

50. Prof. Dr. Fatimah Mohd. Arshad
    Analisis Pemasaran Pertanian di Malaysia: Keperluan Agenda Pembaharuan
    26 January 2002

51. Prof. Dr. Nik Mustapha R. Abdullah
    Fisheries Co-Management: An Institutional Innovation Towards Sustainable Fisheries Industry
    28 February 2002

52. Prof. Dr. Gulam Rusul Rahmat Ali
    Food Safety: Perspectives and Challenges
    23 March 2002

53. Prof. Dr. Zaharah A. Rahman
    Nutrient Management Strategies for Sustainable Crop Production in Acid Soils: The Role of Research Using Isotopes
    13 April 2002

54. Prof. Dr. Maisom Abdullah
    Productivity Driven Growth: Problems & Possibilities
    27 April 2002

55. Prof. Dr. Wan Omar Abdullah
    Immunodiagnosis and Vaccination for Brugian Filariasis: Direct Rewards from Research Investments
    6 June 2002

56. Prof. Dr. Syed Tajuddin Syed Hassan
    Agro-ento Bioinformation: Towards the Edge of Reality
    22 June 2002

57. Prof. Dr. Dahlan Ismail
    Sustainability of Tropical Animal-Agricultural Production Systems: Integration of Dynamic Complex Systems
    27 June 2002

58. Prof. Dr. Ahmad Zubaidi Baharumshah
    The Economics of Exchange Rates in the East Asian Countries
    26 October 2002

59. Prof. Dr. Shaik Md. Noor Alam S.M. Hussain
    Contractual Justice in Asean: A Comparative View of Coercion
    31 October 2002

60. Prof. Dr. Wan Md. Zin Wan Yunus
    Chemical Modification of Polymers: Current and Future Routes for Synthesizing New Polymeric Compounds
    9 November 2002

61. Prof. Dr. Annuar Md. Nassir
    Is the KLSE Efficient? Efficient Market Hypothesis vs Behavioural Finance
    23 November 2002

62. Prof. Ir. Dr. Radin Umar Radin Sohadi
    Road Safety Interventions in Malaysia: How Effective Are They?
    21 February 2003

63. Prof. Dr. Shamsher Mohamad
    The New Shares Market: Regulatory Intervention, Forecast Errors and Challenges
    26 April 2003

64. Prof. Dr. Han Chun Kwong
    Blueprint for Transformation or Business as Usual? A Structurational Perspective of the Knowledge-Based Economy in Malaysia
    31 May 2003

65. Prof. Dr. Mawardi Rahmani
    Chemical Diversity of Malaysian Flora: Potential Source of Rich Therapeutic Chemicals
    26 July 2003

66. Prof. Dr. Fatimah Md. Yusoff
    An Ecological Approach: A Viable Option for Aquaculture Industry in Malaysia
    9 August 2003

67. Prof. Dr. Mohamed Ali Rajion
    The Essential Fatty Acids-Revisited
    23 August 2003

68. Prof. Dr. Azhar Md. Zain
    Psychotheraphy for Rural Malays - Does it Work?
    13 September 2003

69. Prof. Dr. Mohd. Zamri Saad
    Respiratory Tract Infection: Establishment and Control
    27 September 2003

70. Prof. Dr. Jinap Selamat
    Cocoa-Wonders for Chocolate Lovers
    14 February 2004

71. Prof. Dr. Abdul Halim Shaari
    High Temperature Superconductivity: Puzzle & Promises
    13 March 2004

72. Prof. Dr. Yaakob Che Man
    Oils and Fats Analysis - Recent Advances and Future Prospects
    27 March 2004

73. Prof. Dr. Kaida Khalid
    Microwave Aquametry: A Growing Technology
    24 April 2004

74. Prof. Dr. Hasanah Mohd. Ghazali
    Tapping the Power of Enzymes-Greening the Food Industry
    11 May 2004

75. Prof. Dr. Yusof Ibrahim
    The Spider Mite Saga: Quest for Biorational Management Strategies
    22 May 2004

76. Prof. Datin Dr. Sharifah Md. Nor
    The Education of At-Risk Children: The Challenges Ahead
    26 June 2004

77. Prof. Dr. Ir. Wan Ishak Wan Ismail
    Agricultural Robot: A New Technology Development for Agro-Based Industry
    14 August 2004

78. Prof. Dr. Ahmad Said Sajap
    Insect Diseases: Resources for Biopesticide Development
    28 August 2004

79. Prof. Dr. Aminah Ahmad
    The Interface of Work and Family Roles: A Quest for Balanced Lives
    11 March 2005

80. Prof. Dr. Abdul Razak Alimon
    Challenges in Feeding Livestock: From Wastes to Feed
    23 April 2005

81. Prof. Dr. Haji Azimi Hj. Hamzah
    Helping Malaysian Youth Move Forward: Unleashing the Prime Enablers
    29 April 2005

82. Prof. Dr. Rasedee Abdullah
    In Search of An Early Indicator of Kidney Disease
    27 May 2005

83. Prof. Dr. Zulkifli Hj. Shamsuddin
    Smart Partnership: Plant-Rhizobacteria Associations
    17 June 2005

84. Prof. Dr. Mohd Khanif Yusop
    From the Soil to the Table
    1 July 2005

85. Prof. Dr. Annuar Kassim
    Materials Science and Technology: Past, Present and the Future
    8 July 2005

86. Prof. Dr. Othman Mohamed
    Enhancing Career Development Counselling and the Beauty of Career Games
    12 August 2005

87. Prof. Ir. Dr. Mohd Amin Mohd Soom
    Engineering Agricultural Water Management Towards Precision Framing
    26 August 2005

88. Prof. Dr. Mohd Arif Syed
    Bioremediation-A Hope Yet for the Environment?
    9 September 2005

89. Prof. Dr. Abdul Hamid Abdul Rashid
    The Wonder of Our Neuromotor System and the Technological Challenges They Pose
    23 December 2005

90. Prof. Dr. Norhani Abdullah
Rumen Microbes and Some of Their Biotechnological Applications
27 January 2006

91. Prof. Dr. Abdul Aziz Saharee
Haemorrhagic Septicaemia in Cattle and Buffaloes: Are We Ready for Freedom?
24 February 2006

92. Prof. Dr. Kamariah Abu Bakar
Activating Teachers' Knowledge and Lifelong Journey in Their Professional Development
3 March 2006

93. Prof. Dr. Borhanuddin Mohd. Ali
Internet Unwired
24 March 2006

94. Prof. Dr. Sundararajan Thilagar
Development and Innovation in the Fracture Management of Animals
31 March 2006

95. Prof. Dr. Zainal Aznam Md. Jelan
Strategic Feeding for a Sustainable Ruminant Farming
19 May 2006

96. Prof. Dr. Mahiran Basri
Green Organic Chemistry: Enzyme at Work
14 July 2006

97. Prof. Dr. Malik Hj. Abu Hassan
Towards Large Scale Unconstrained Optimization
20 April 2007

98. Prof. Dr. Khalid Abdul Rahim
Trade and Sustainable Development: Lessons from Malaysia's Experience
22 June 2007

99. Prof. Dr. Mad Nasir Shamsudin
Econometric Modelling for Agricultural Policy Analysis and Forecasting: Between Theory and Reality
13 July 2007

100. Prof. Dr. Zainal Abidin Mohamed
Managing Change - The Fads and The Realities: A Look at Process Reengineering, Knowledge Management and Blue Ocean Strategy
9 November 2007

101. Prof. Ir. Dr. Mohamed Daud
Expert Systems for Environmental Impacts and Ecotourism Assessments
23 November 2007

102. Prof. Dr. Saleha Abdul Aziz
Pathogens and Residues; How Safe is Our Meat?
30 November 2007

103. Prof. Dr. Jayum A. Jawan
Hubungan Sesama Manusia
7 December 2007

104. Prof. Dr. Zakariah Abdul Rashid
Planning for Equal Income Distribution in Malaysia: A General Equilibrium Approach
28 December 2007

105. Prof. Datin Paduka Dr. Khatijah Yusoff
Newcastle Disease virus: A Journey from Poultry to Cancer
11 January 2008

106. Prof. Dr. Dzulkefly Kuang Abdullah
Palm Oil: Still the Best Choice
1 February 2008

107. Prof. Dr. Elias Saion
Probing the Microscopic Worlds by Lonizing Radiation
22 February 2008

108. Prof. Dr. Mohd Ali Hassan
Waste-to-Wealth Through Biotechnology: For Profit, People and Planet
28 March 2008

109. Prof. Dr. Mohd Maarof H. A. Moksin
Metrology at Nanoscale: Thermal Wave Probe Made It Simple
11 April 2008

110. Prof. Dr. Dzolkhifli Omar
The Future of Pesticides Technology in Agriculture: Maximum Target Kill with Minimum Collateral Damage
25 April 2008

111. Prof. Dr. Mohd. Yazid Abd. Manap
Probiotics: Your Friendly Gut Bacteria
9 May 2008

112. Prof. Dr. Hamami Sahri
Sustainable Supply of Wood and Fibre: Does Malaysia have Enough?
23 May 2008

113. Prof. Dato' Dr. Makhdzir Mardan
Connecting the Bee Dots
20 June 2008

114. Prof. Dr. Maimunah Ismail
Gender & Career: Realities and Challenges
25 July 2008

115. Prof. Dr. Nor Aripin Shamaan
Biochemistry of Xenobiotics: Towards a Healthy Lifestyle and Safe Environment
1 August 2008

116. Prof. Dr. Mohd Yunus Abdullah
Penjagaan Kesihatan Primer di Malaysia: Cabaran Prospek dan Implikasi dalam Latihan dan Penyelidikan Perubatan serta Sains Kesihatan di Universiti Putra Malaysia
8 August 2008

117. Prof. Dr. Musa Abu Hassan
Memanfaatkan Teknologi Maklumat & Komunikasi ICT untuk Semua
15 August 2008

118. Prof. Dr. Md. Salleh Hj. Hassan
Role of Media in Development: Strategies, Issues & Challenges
22 August 2008

119. Prof. Dr. Jariah Masud
Gender in Everyday Life
10 October 2008

120 Prof. Dr. Mohd Shahwahid Haji Othman
Mainstreaming Environment: Incorporating Economic Valuation and Market-Based Instruments in Decision Making
24 October 2008

121. Prof. Dr. Son Radu
Big Questions Small Worlds: Following Diverse Vistas
31 October 2008

122. Prof. Dr. Russly Abdul Rahman
Responding to Changing Lifestyles: Engineering the Convenience Foods
28 November 2008

123. Prof. Dr. Mustafa Kamal Mohd Shariff
Aesthetics in the Environment an Exploration of Environmental: Perception Through Landscape Preference
9 January 2009

124. Prof. Dr. Abu Daud Silong
Leadership Theories, Research & Practices: Farming Future Leadership Thinking
16 January 2009

125. Prof. Dr. Azni Idris
Waste Management, What is the Choice: Land Disposal or Biofuel?
23 January 2009

126. Prof. Dr. Jamilah Bakar
Freshwater Fish: The Overlooked Alternative
30 January 2009

127. Prof. Dr. Mohd. Zobir Hussein
The Chemistry of Nanomaterial and Nanobiomaterial
6 February 2009

128. Prof. Ir. Dr. Lee Teang Shui
Engineering Agricultural: Water Resources
20 February 2009

129. Prof. Dr. Ghizan Saleh
Crop Breeding: Exploiting Genes for Food and Feed
6 March 2009

130. Prof. Dr. Muzafar Shah Habibullah
Money Demand
27 March 2009

131. Prof. Dr. Karen Anne Crouse
In Search of Small Active Molecules
3 April 2009

132. Prof. Dr. Turiman Suandi
Volunteerism: Expanding the Frontiers of Youth Development
17 April 2009

133. Prof. Dr. Arbakariya Ariff
Industrializing Biotechnology: Roles of Fermentation and Bioprocess Technology
8 May 2009

134. Prof. Ir. Dr. Desa Ahmad
Mechanics of Tillage Implements
12 June 2009

135. Prof. Dr. W. Mahmood Mat Yunus
Photothermal and Photoacoustic: From Basic Research to Industrial Applications
10 July 2009

136. Prof. Dr. Taufiq Yap Yun Hin
Catalysis for a Sustainable World
7 August 2009

137 Prof. Dr. Raja Noor Zaliha Raja Abd. Rahman
Microbial Enzymes: From Earth to Space
9 October 2009

138 Prof. Ir. Dr. Barkawi Sahari
Materials, Energy and CNGDI Vehicle Engineering
6 November 2009

139. Prof. Dr. Zulkifli Idrus
Poultry Welfare in Modern Agriculture: Opportunity or Threat?
13 November 2009

140. Prof. Dr. Mohamed Hanafi Musa
Managing Phosphorus: Under Acid Soils Environment
8 January 2010

141. Prof. Dr. Abdul Manan Mat Jais
Haruan Channa striatus a Drug Discovery in an Agro-Industry Setting
12 March 2010

142. Prof. Dr. Bujang bin Kim Huat
Problematic Soils: In Search for Solution
19 March 2010

143. Prof. Dr. Samsinar Md Sidin
Family Purchase Decision Making: Current Issues & Future Challenges
16 April 2010

144. Prof. Dr. Mohd Adzir Mahdi
Lightspeed: Catch Me If You Can
4 June 2010

145. Prof. Dr. Raha Hj. Abdul Rahim
Designer Genes: Fashioning Mission Purposed Microbes
18 June 2010

146. Prof. Dr. Hj. Hamidon Hj. Basri
A Stroke of Hope, A New Beginning
2 July 2010

147. Prof. Dr. Hj. Kamaruzaman Jusoff
Going Hyperspectral: The "Unseen" Captured?
16 July 2010

148. Prof. Dr. Mohd Sapuan Salit
Concurrent Engineering for Composites
30 July 2010

149. Prof. Dr. Shattri Mansor
Google the Earth: What's Next?
15 October 2010

150. Prof. Dr. Mohd Basyaruddin Abdul Rahman
Haute Couture: Molecules & Biocatalysts
29 October 2010

151. Prof. Dr. Mohd. Hair Bejo
Poultry Vaccines: An Innovation for Food Safety and Security
12 November 2010

152. Prof. Dr. Umi Kalsom Yusuf
Fern of Malaysian Rain Forest
3 December 2010

153. Prof. Dr. Ab. Rahim Bakar
Preparing Malaysian Youths for The World of Work: Roles of Technical and Vocational Education and Training (TVET)
14 January 2011

154. Prof. Dr. Seow Heng Fong
Are there "Magic Bullets" for Cancer Therapy?
11 February 2011

155. Prof. Dr. Mohd Azmi Mohd Lila
Biopharmaceuticals: Protection, Cure and the Real Winner
18 February 2011

156. Prof. Dr. Siti Shapor Siraj
Genetic Manipulation in Farmed Fish: Enhancing Aquaculture Production
25 March 2011

157. Prof. Dr. Ahmad Ismail
Coastal Biodiversity and Pollution: A Continuous Conflict
22 April 2011

158. Prof. Ir. Dr. Norman Mariun
Energy Crisis 2050? Global Scenario and Way Forward for Malaysia
10 June 2011

159. Prof. Dr. Mohd Razi Ismail
Managing Plant Under Stress: A Challenge for Food Security
15 July 2011

160. Prof. Dr. Patimah Ismail
Does Genetic Polymorphisms Affect Health?
23 September 2011

161. Prof. Dr. Sidek Ab. Aziz
Wonders of Glass: Synthesis, Elasticity and Application
7 October 2011

162. Prof. Dr. Azizah Osman
Fruits: Nutritious, Colourful, Yet Fragile Gifts of Nature
14 October 2011

163. Prof. Dr. Mohd. Fauzi Ramlan
Climate Change: Crop Performance and Potential
11 November 2011

164. Prof. Dr. Adem Kiliçman
Mathematical Modeling with Generalized Function
25 November 2011

165. Prof. Dr. Fauziah Othman
My Small World: In Biomedical Research
23 December 2011

166. Prof. Dr. Japar Sidik Bujang
The Marine Angiosperms, Seagrass
23 March 2012

167. Prof. Dr. Zailina Hashim
Air Quality and Children's Environmental Health: Is Our Future Generation at Risk?
30 March 2012

168. Prof. Dr. Zainal Abidin Mohamed
Where is the Beef? Vantage Point form the Livestock Supply Chain
27 April 2012

169. Prof. Dr. Jothi Malar Panandam
Genetic Characterisation of Animal Genetic Resources for Sustaninable Utilisation and Development
30 November 2012

170. Prof. Dr. Fatimah Abu Bakar
The Good The Bad & Ugly of Food Safety: From Molecules to Microbes
7 December 2012

171. Prof. Dr. Abdul Jalil Nordin
My Colourful Sketches from Scratch: Molecular Imaging
5 April 2013

172. Prof. Dr. Norlijah Othman
Lower Respiratory Infections in Children: New Pathogens, Old Pathogens and The Way Forward
19 April 2013

173. Prof. Dr. Jayakaran Mukundan
Steroid-like Prescriptions English Language Teaching Can Ill-afford
26 April 2013

174. Prof. Dr. Azmi Zakaria
Photothermals Affect Our Lives
7 June 2013

175. Prof. Dr. Rahinah Ibrahim
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