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EXTRACTION OF AGAR FROM *Gelidium* P (RHODOPHYTA) AND GREEN SYNTHESIS OF AGAR /SILVER NANOPARTICLES

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ABSTRACT

Physicochemical and rheological characters of agar sample extracted from(rhodophyta)*Gelidium* sp. collected from the Egyptian coast of the red sea has been investigated. Agar yielded 29% on dry biomass basiswith pretreatment using 0.15 M sodium hydroxide. Agar surface texture was investigated through the usage of the scanning electron microscopy (SEM). Agar is a white flakes and threads, insoluble in cold water, but it swells absorbing much water making hydrogels.The morphology of the agar surface texture was investigated using scanning electron microscopy (SeM).The dynamic rheological measurements of agar solutions (2, 3, 4 mg agar/ml) as a function of shear rate were achieved at 85º C and let to cool gradually (1.5ºC/ min), with the maximum values of viscosity as following 1.26, 3.12 and 5.18cP, respectively at shear rate of 40 sec^{-1}.Agr solutions revieled the presence of non-Newtonian fluid material demonstrating shear thinning (Pseudoplastic) flow behavior in aqueous solution (2 mg agar/ml) giving up to formation of an elastic gel. At higher concentrations (3 & 4 mg agar/ml) induce shear thickening representd as viscosity increases as shear rate increased giving up to Newtonian fluid behavior.The AgNPs were synthesized and characterized on the bases of spectral (FT-IR and UV-visible), morphological (Transmission electron microscopy-TEM), zeta potential and atomic force microscopy (AFM) measurements. The resulted Agar Nanoparticles (AgNPs) are showing gradualproperities as gradual increase in absorbance with increasing the intensity of the yellow-brown color, it showed peak maximum located at 410 nm with absorbance value of 0.579.The average size distributions of AgNPs were found to be .It was illustrated that zeta potential value for AgNPs was -28.0 mV.

Keywords:*Gelidium*sp.,Agar,Elastic Gel, Biopolymer,FT-IR, Thermal Analysis, Dynamic Rheology,SiverNanoparticles (AgNPs), Phycocolloids, TEM, SEM, AFM

INTRODUCTION

For decades, red seaweeds are considered to be an important source of metabolites for the food and non-food industry.Agar and carrageenan, have been used as texturing agents in food industry. Recently, polysaccharides from seaweeds have also been reported as having anticancer and antitumor properities.

Agar is gel-forming polysaccharide, widely used in industry and in scientific applications. Lahaye (2001)reported that agar is extracted from the walls of certain red seaweeds or agarophytes genera(*Gracilaria, Gelidium, Pterocladia,* and*Gelidiella*). Arnott *et al.* (1974)found that agar is a gel-forming polysaccharide with a sugar skeleton as a principal chainconsisting of alternating 1,3-linked β-D-galactopyranoseand 1,4-linked 3,6 anhydro-α-L-galactopyranose units forming a “crosslinked network” model.*Agarobiose* is the basicdisacchariderepresenting the structural unit of all agar polysaccharides.Agar isdivided into: agaroseandagaropectin. Agarose is a neutral polysaccharide withgellingcabability whileagaropectinrepresented the charged polysaccharidecomponent(Lahrech *et al.*, 2005).Agar forms a thermoreversiblegel in aqueous solutions. Mopreover, gels have a gelling/settingtemperature close to 40ºC and a melting temperature near90ºC as found by (Djabourov *et al.*, 1989). In respect to biotechnological potentiality agar gels in supporting bacterial cultures, separation media in column chromatography andelectrophoresis, usage in medicine and pharmacyas well as in food industry where act as thickeningand gelling agents (Djabourov *et al.*, 1989).

Nanotechnology is a rapid growing field with multifaceted applications of a new materials at the nanoscale level. Metalic nanoparticles are one of the most promising type of nanomaterials for antimicrobial food packaging applications as they show strong antimicrobial activity due to their large surface area and hig specificity (Shanker et al., 2014). Synthes of silver nanoparticles (AgNPs) is a significant area of reaserch, because AgNPs have potential applications in various fields such aswound healing, antimicrobial, bone stimulation, biochemistry, environment, medicin, catalysis, electrononicn and optics (Navaladian *et al.*, 2007 and El Hawary*et al*., 2014).

This study aimed to extract the phycocoloid agar from the red macroalga*Gelidium* sp., investigate its chemical and rheological behavior, physical properities as well as the biological preparation of agar based silver nanoparticles (agar/AgNPs) and study its characteristics.

MATERIALS AND METHODS

Red macroalgae

Specimens of *Gelidium*sp.werecollected from the shorelineof theRedSea at Ghordaga city – Egypt.Algalthalliwashed thoroughly withtap water, dried at 60°C.

Agar extraction

Whole dried *Glelidium*thallisample, 5 g, was treated with sodium hydroxide solution (0.15 M) at 85º C for 60 min followed by washingthoroughly with distilled water. *Gelidium*thalliwere soaked in 0.5 % acetic acid for 60 min, then after washing with water, thalli were extracted with 250 ml distilled water at 85º C for 2 h. After filtration agar was obtained using freez-thawing method and dehydrated with ethanol (96%) and finally dried at 60º C. Agar yield is calculated as percent of the thalli dry biomass(Villanueva *et al.*, 2010).

Scann Electron Microscopy

Scanning electron microscopy examination of the dry agar specimen was carried out on JEOL JSM 6510/V, Japan (Center of Electron Microscopy – Mansoura University).

Thermal Analysis

The Thermogravimetric Analysis (TGA)of agar was achieved using ThermoAnalyzer of the type 50-H, obtained inthe range of 25°C-1000°C under nitrogen atmosphere. Differential Scanning Calorimetry (DSC)of agar was investigated using a Differential ScanningCalorimeter (60-A) in the range of 25-1000°C.

Sulphate content

Sulphate content was determined according to the method of Kawai *et al.*(1969).

Fourier transform Infrared spectrometry

FT-IR spectrum was recorded on The Mattson 5000FT-IRspectrometer in the frequency range of 400-4000 cm^{-1}(Unit of Microanalysis – Faculty of Science – Mansoura University).

Rheology properties of Agar

The dynamicrheological measurement of extracted agar solutions (2, 3& 4 mg /mL) was carried out on BROOKFIELDDV-3Ultra Programmable Rheometer.

Preparation of silver nanoparticles (Ag-NPs)

30 mg of theextractedagar powder was dissolved in 90mlof sterile deionized water with continuous stirring at 85°C. 1 ml of0.1 mM $AgNO_3$ solution was added to the prepared agar solution dropwise with continuous stirring, adjusting pH at10. The prepared solution was centrifuged for 3min at 3,000 rpm to separate any aggregations. The final volume was adjusted to 100 ml usingdeionized water and continuestirrering at 85° C for 20 min, since the solution color was changed to brown(El-Rafie *et al.*, 2013).

Nanoidentation (Characterization of Silver Nanoparticles Ag-NPs)

The reduction of silver ions to silver nanoparticles was monitored visually by color change of the solution and absorption of light using a UV-vesibleSpectrophotometer (Lambda35) in the wavelength ranged from 200 to 800 nm.

TEM analysis

The structural characterization of Ag-NPswas carried out by Transmission Electron Microscopy (JEOL JEM-2100, Japan).

Atomic Force Microscopy

Images of the exceptnanoindentation of the synthesized nano particles was carried out using Atomic Force Microscope (Nanosurf Flex AFM).

Zeta potential

Zeta potential value for ANPs is determined using Zeta Potenial Analyzer (Malven Zeta size Nano-Zs90) in Nanotechnology Center of Mansoura University.

RESULTS AND DISCUSSION

Agar yield and sulphate content

Red algae (Rhodophyta) are famous for being source of unique sulfated galactans, such as agar. The extensive usages of this polysaccharide is based on its ability to form strong gels withwater. Results shown that agar yielded about 26.65 % on dry biomass basis, while sulphate represent 1.98% dry biomass. On the other hand, Rahelivao *et al.*

(2014)reported that agar from the red alga (*Gelidium*sp) was extracted with hot water and precipitated in presence of ethanol(representing 16 w % on the basis of dried crude algae) forms strong gels in aqueous solutions. The present results are in agreement with that ofMartín *et al.* (2013). The yield and physical properities of agar preparations depend on the source of agarophytes, environmental, physiological factors as well as the extraction and recovery procedures as suggested by Murano (1995).

Agar Characterization

Physicochemical properties

Agar is a white flakes and threads, insoluble in cold water, but it swells absorbing much water. It dissolves in boiling water and sets to a firm gel at concentrations as low as 0.50%. The scanning elctron micrograph (Fig.1) showed the microstructure of surface of agarwhen dry. Grainularsurface morphology was observed. This appearance may be owing to the porousnetwork microstructures the physical composition as previously reported by Zhang*et. al*. (2015).

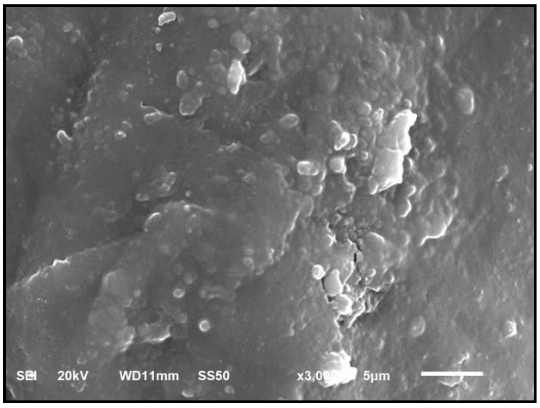

Fig.1: Scanning Electron Microscopymicrograph of dry agar

Thermalstability

TGA thermogram (Fig.2) showed the weight loss pattern on thermal decomposition of agar that following multistep thermal decomposition system as indicating by Rhim *et al.* (2013). The initial decomposition was recorded around 140º C with weight loss of 1.65% which was attributed to desorption of water as reported byRhim *et al.* (2006). By increasing heat,there was a sharp break in the thermogram at around 325º C, characterized by 23.8% weight loss which means the onset of the decomposition process of the biopolymer agar(Elhefian *et al.*, 2012). The last thermal degradation of agar was recorded around 450º C resulted in 8.30% weight loss reached(Du *et al.*, 2006). DSC profile illustrated three endothermic transition of agar. The first stage begane at 50**°** C, giving peak centered at 80º C. The onset of the second stage was at 260º C, exihibiting peak at 273.5º C. The third decomposition stage started at 394.0º C, having peak at 397.0º C.This thermal analysis indicated that decomposition of agar is endothermic as reported previously by Rhim *et al.* (2013)**.**

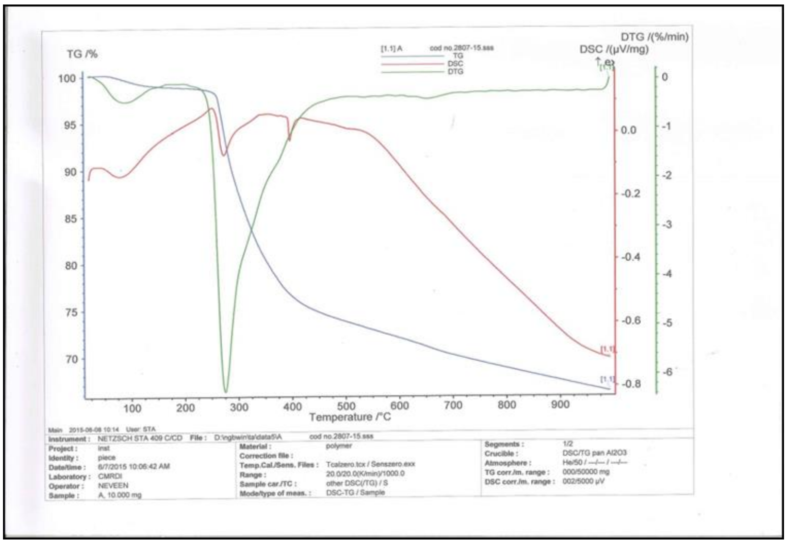

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Fig.2 Thermogravimetric analysis of agar extracted from *Gelidium* sp.

Fourier transform infrared spectrometry

FTIR of agar (Fig.3) showed thatthe characteristic absorption spectra of agarose were detected.Bands between 3444 cm^{-1}is assigned to (OH) of hydroxyl group and spectra at 1091Cm^{-1} designated to presence of glycosidic bonding and(C-OH) a very weak band of absorption at 1257 cm^{-1} illustrated (C-O-C) (Tako *et al.*, 1999). Strong bands at around 1156and 1091 cm^{-1} demonstrating the presence of C-O-C vibration of the 3,6 anhydro-galactopyranose bridge and the D-galactose residues, respectively(Whyte *et al.*, 1985; Wuttisela *et al.*, 2008).The bands at 2988, 2961 and 2925 Cm^{-1} can be assigned to the alkane C=H stretching symmetric and asymetric or assigned to the secondary amine. The absorption bands observed at 1560, 1540 and 1524 Cm^{-1} can be assigned to the amide group of protein or to the carbonyl stretching group of the algal polysaccharides. Band at 1156 Cm^{-1} is allocated to -C-O groups of polyols of polysaccharides. Bands at 1456, 1399 and 1319 Cm^{-1} corresponded to the stretching vibrations of hydroxyl, C-H, carboxyl, and C-H bending of aliphatic CH$_2$(El-Rafie *et al.*, 2013; Xia *et al.*, 2014).Agar is a polyanionic molecule as reported by Babak and Ahhoori (2012).The present FTIR profile, in general demonstrate the same spectra as that of Díaz *et al.* (2011) who investigated the polysaccharide fractions of the red algae *Hypneaspinella* (Gigartinales) and *Halopithys incurve* (Ceramiales).

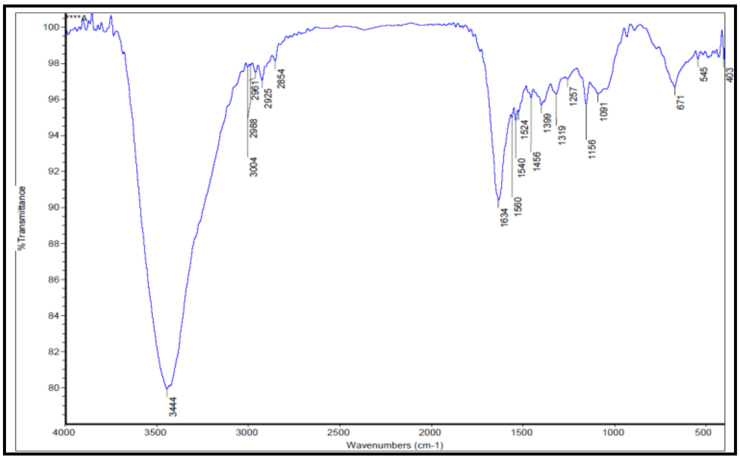

Fig.3: FT-IR analysis of agar extracted from *Gelidium*sp.

Dynamic rheologicalproperities

The viscosity of a material in respect to its shear rate gives significant criteria sindustrialapplications.In the present investigation, the dynamic rheological measurements of agar solutions (2, 3, 4 mg agar/ml) as a function of shear rate were achieved at 85ºC and let to cool gradually (1.5ºC/ min), giving the maximum valuesof viscosity as following 1.26, 3.12 and 5.18cP, respectively at shear rate of 40 sec^{-1} (Fig.4), While increasing shear rate to 500 sec^{-1}viscosityincreasedreaching values of 1.89, 4.05 and 7.63 cP, respectively.Figure 5 illustrats the flow curve of shear stress as a function of shear rate for agar aqueous solutions with different concentrations (2, 3, 4 mg agar/ml). Increasing shear rate stimulates high increases in the corresponding shear stress (dynes/cm^2) values, under the effect of gradual cooling in the higher biopolymer concentrations (3& 4mg agar / ml), while the low concentration (2 mg agar / ml) the shear stress tended to level off andnear stable magnitude as adecline in shear rate towards zero level of shear rate, indicating that this concentration of the polymer system inducedarestricted magnitude of yield stress.Data revealed also, the dependence of shear stress on agar concentration. Rheograms(Fig. 6) represent a map for the rheological prorertiesrevealingthe presence ofNewtonian fluid material demonstrating shear thickening (Dilatant) flow behavior inthehigh concentrations (3 & 4 mg/ml) of aqueous agar solutions , i.e., viscosity is independent of shear rate. The highest viscosities and the prominent shear thickening properties were recorded in concentrations 4&3 mg/ml agar, while the lower concentration (2 mg/ml) illustrated non-Newtonian fluid material behavior exepressing shear thinning as pseudoplastic gel. Data illustrated that torque percent increased with increasing spindle speed (RPM) and consequently viscosity decreased except for agar solution (4 mg/ml) as well as the same patern was recorded for the concentration of agar solution and spindle speed and viscosity.

Agar is composed of two fractions: agarose, thelinear neutral fraction accountablefor agar’s gelling potentiality,andagaropectin, the charged polymer fraction that characterized by thepresence of numeroussubstituent groups as sulphates, methylethers and pyruvates. In addition, of being apolyanionicbiopolymer,isasulphated polysaccharide and has been considered as a strongpolyelectrolyte(Boral and Bohidar, 2010). The present results of rheological characterization of algalagar (Fig.5)showed general decrease in viscosity with increasing shear rate as well as increasing viscosity with increasing agar concentration. According to (Barnes, 2000), the previously mentioned rheologic characteristics of low concentration of agar solution (2 mg/ml) demonstrate a typical non-Newtonian pseudoplastic flow behavior and shear thinning. Lyons *et al.* (2009) and Brenner *et al.* (2014) documented that agar extracted from red algaehave elastic response dominates as is typical for gels and solid like materials as samples exhibited mechanical rigidhty. Duckworth and Yaphe (1971)suggested that gel properities of the biopolymer agar are greatly dependent on the amountand position of sulfate groups as well as theamount of 3,6-anhydrogalactose fraction of thephycocolloid. Atfixed total carrageenan concentrations, k-carrageenan mixturesare characterized by lower elastic moduli anda higher fracture strain, resulting in a peak of the fracture stressaround equal mixing ratios(Rochas and Lahaye, 1989). In high temperatures, the conformation of agar chain in solution are only influenced by the molecular size. The intrinsic viscosity increase propotionally with molecular size. In low concentrations, the gelling temperature are affected by agar structure, since the gelation enthalpy of agarose, indicating the presence of sulphate which limits the number of hydrogen bonds among the chain and the double helix formation, in contrast, in high concentration the effect of molecular size is dominated as suggested byLahrech *et al.* (2005). Agar solution system demonstrate the typical behavior of several physical polymeric gels as indicated by Lapasin *et al.* (2001). Agar form thermoreversible gels with melting temperatures (80-90°C) significantly higher than setting temperatures (30 - 40°C) as indicated byArnott *et al.* (1974).They reported that this hysteresis loop is formed consequently to gelling mechanism in which the events during melting are not a straightforward reversal of those during setting. It was suggested that polysaccharides in random coils at high temperature first fold into helices stabilized by intrachain hydrogen bonding during cooling, the helices combine by interchain hydrogen bonding into joint zones which shared to form the gel network. On rising temperature , the junction zones fall down after the helices have unfolded, allowing the gel to continue intact at far above its setting temperature(Lahaye, 2001).The present results are in agreement with that of Prasad *et al*. (2006), who found that under the steady shear flow, a Newtonian flow behavior was observed at the low limiting shear rate region and a strong shear thinning at higher shear rate for agar sols at lower concentrations. Duckworth and Yaphe (1971)suggested that stronger gels are valuable owing to their strength, resilience, elasticity and thermostability.

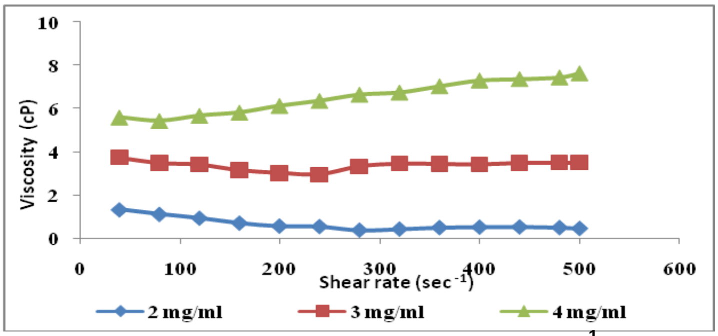

Fig.4: Viscosity (cP) as a function of shear rate (sec^{-1}) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

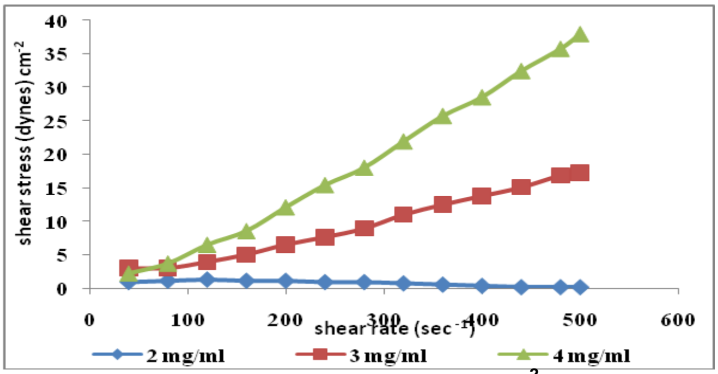

Fig.5: Flow curve of the shear stress (dynes cm^{-2}) vs. shear rate (cm^{-1}) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

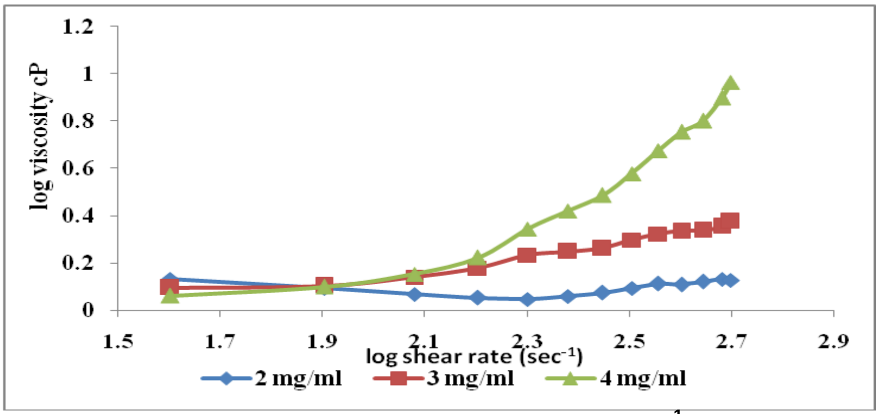

Fig.6: Log plot of the viscosity (cP) vs. shear rate (cm^{-1}) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

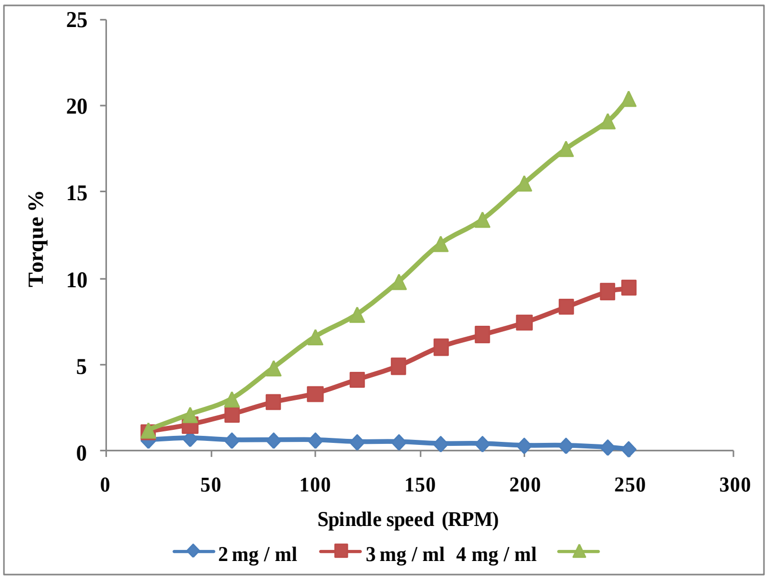

Fig.7: Rheogram of the Torque vs. spindle speed (RPM) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

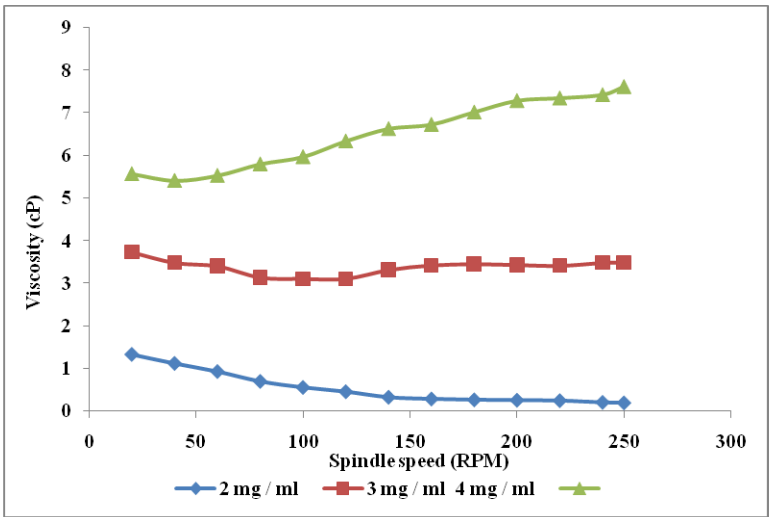

Fig.8: Rheogram of viscosity (cP) dependence of spindle speed (RPM) for aqueous *Gelidium* sp. agar solutions at concentrations 2, 3 & 4 mg agar/ml

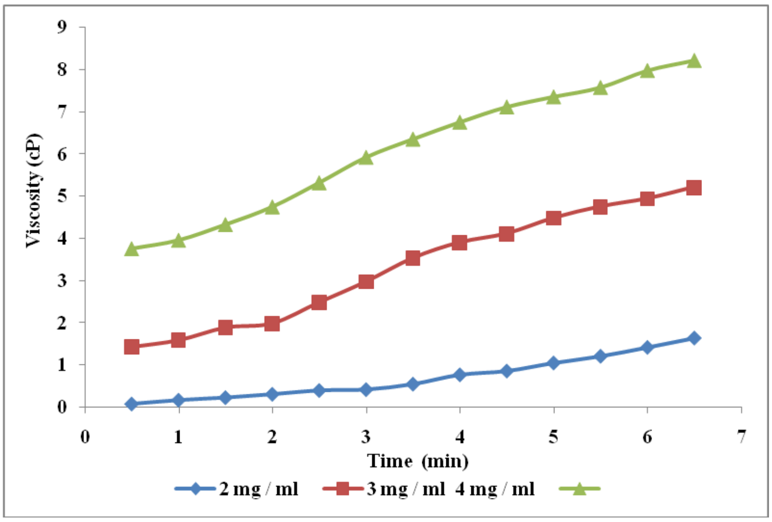

Fig.9:Rheogram of viscosity (cP) dependence of time (min) for aqueous *Gelidium* sp. agar solutions at concentrations 2, 3 & 4 mg agar/ml

Chracterization of Silver/nanoparticles (AgNPs)

UV-vis spectrum of AgNPs is shown in Fig. (10). Complete synthesis of AgNPs is traced by UV-vis measurements every 5 min during incubation time. Asoptical density of the AgNPs preparation showing gradual increase in absorbance with increasing the intensity of the yellow-brown color, it showed peak maximum located at 410 nm with absorbance value of 0.579 (Pandey*et. al*., 2012). This referred to the complete synthesis of AgNPs according to increasing number of nanoparticles formed as a result of reduction of silver ions in experimental solution. With reaching with time to 60 min, color change stopped, which documented that almost all of silver ions altered to Ag nanoparticles. Similar absorption peaks at 403-413 nm and at 401-414 nm for AgNPs prepared by laser ablation of silver for different times in palm oil and coconut oil, respectively as reported previously by Zamiri*et. al*. (2010 and 2011). Yang (2007) suggested that AgNPs are formed through nucleation, transition, and crystal growth of materials that were released from the silver plate upon laser ablation. As indicating from Fig. (10) , the plasmon spectra are relatively broad having an absourbance tail in the longer wavelengths according to the size distribution of the particles. El-Rafie *et al.* (2013)explained the broadening of the peak demonstrated in Fig. (10) as particles being polydispersed. Figure (10) illustrates absence of any peaks at 335 and 560nm, which demonstrates neither nanoparticles aggregation nor nanocluster are formed in the solution and consequently, the high stability and good dispersion of the formed AgNPs in the solution as suggested by Pandey*et.al*. (2012).

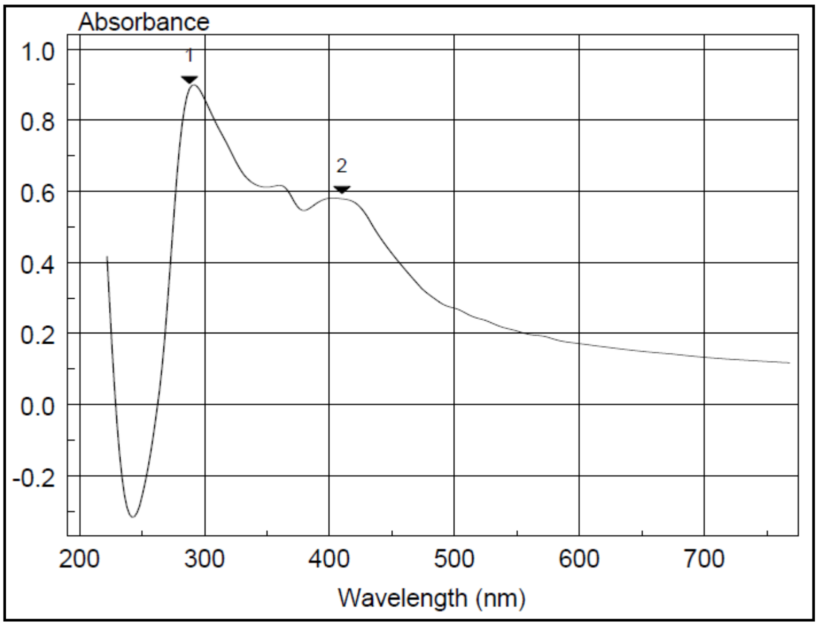

Fig.10: UV- absorbance spectrum of silver nanoparticles

Transmission Electron Micoscopy **(**TEM) picture of AgNPs is shown in Fig.11(A) and the particle size distribution is shown along side in Fig.11 (B). It can be demonstrated that particles are spherical surfaceswith average particle size (radius) of 13.6 nm and distribution in 5.0 – 15.0 nm range as reported by Samiey and Ashoori (2012). These results are in agreement with that of Navaladian *et al.* (2007) found that size range of AgNPs prepared by thermal decomposition of silver oxalate in ethylene glycol as well as polyvinyl alcohol. Results of Fig. (13) confirmed the synthesis of AgNPs.

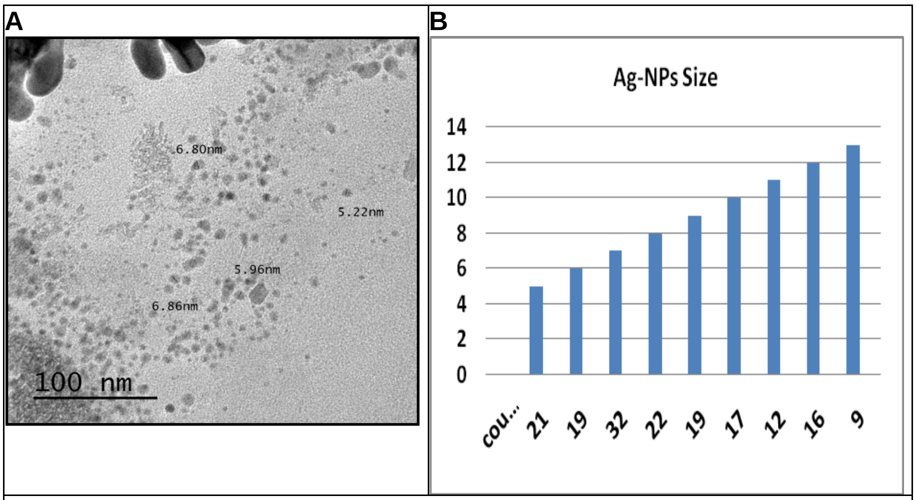

Fig.11: (A) TEM picture of Ag nanoparticles (B) Ag Nanoparticle size

Zeta potential value for ANPs is given in Fig.12. It was illustrated that zeta potential value for AgNPs was -28.0 mV, that was in agreement with results of Yu *et al.* (2012).Zeta potential was an important character to investigate the definite state of nanoparticles and their stability in solutions(Molina *et al.*, 2011). Nanoparticles with a relatively low zeta potential could show a affinity to agglomerate (Feng *et al.*, 2009).This investigation confirmed that the Ag-NPs have an overall negative surface charge (Daima *et al.*, 2014).

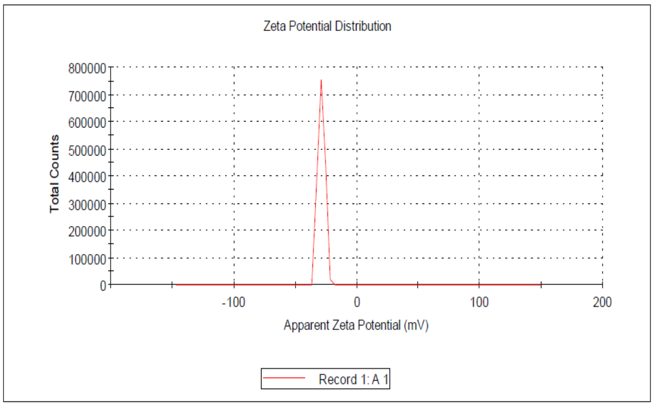

Fig. 12:Zeta potential distribution of AgNPs.

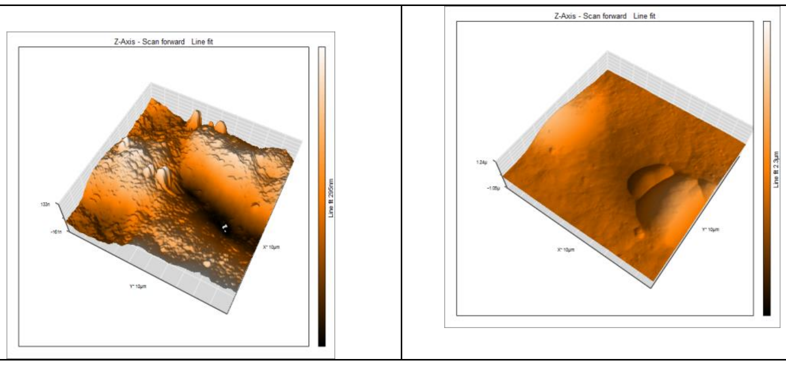

Fig. 13: Atomic Force Microscopy (AFM) analysis of AgNPs

Axis	Diameter
Sy	10.42 nm
Sa	54.70 nm
Sq	61.25 nm
Sz	132.53 nm
Sp	144.66 nm

The present study demonstrated that the simplepreparationmethod of the phycocolloid agar, physicochemical and rheologicalpropertiesas well asthe utilization potential of agar gelshas indicated the biotechnological potentiality of Rhodophyta as good canditae of agar production.In addition the biopreparation of silver nanoparticles using agar as good reducing agent.

REFERENCES

Arnott, S., A. Fulmer; W. Scott; I. Dea; R. Moorhouse and D. Rees (1974). The agarose double helix and its function in agarose gel structure. Journal of molecular biology 90(2): 269-284.

Babak S. and F. Ashoori (2012) Adsorptive removal of methylene blue by agar: effects of NaCl and ethanol. Chem. Cent. J. 6: 14-27.

Barnes, H. A. (2000). A handbook of elementary rheology.Published by The University of Wales Institute of Non-Newtonian Fluid Mechanics, Department of Mathematics, University of Wales Aberystwyth, Penglais, Aberystwyth, Dyfed, Wales, SY23 3BZ.

Boral S. and H. B. Bohidar (2010) Effect of ionic strength on surface-selective patch binding-induced phase separation and coacervation in similarity charged gelatin-agar molecular systems. J. PhysChem B. 114(23): 12027-12035.

Brenner, T.;F. Hayakawa; S. Ishihara; Y. Tanaka; M. Nakauma, K. Kohyama, P. Achayuthakan, T. Funami and K. Nishinari (2014). Linear and nonlinear rheology of mixed polysaccharide gels. Pt. II. Extrusion, compression, puncture and extension tests and correlation with sensory evaluation. J. Texture Studies 45(1): 30-46.

Daima, H. K.; P. Selvakannan; A. E. Kandjani; R. Shukla; S. K. Bhargava and V. Bansal (2014). Synergistic influence of polyoxometalate surface corona towards enhancing the antibacterial performance of tyrosine-capped Ag nanoparticles. Nanoscale 6(2): 758-765.

Díaz, R. T. A.; M. Chabrillón; A. Cabello-Pasini; J. L. Gómez-Pinchetti and F. L. Figueroa (2011). Characterization of polysaccharides from Hypnea spinella (Gigartinales) and Halopithys incurva (Ceramiales) and their effect on RAW 264.7 macrophage activity. J. Appl. Phycology 23(3): 523-528.

Djabourov, M.; A. Clark; D. Rowlands and S. Ross-Murphy (1989). Small-angle x-ray scattering characterization of agarose sols and gels. Macromolecules 22(1): 180-188.

Du, Y., P. Yang; Z. Mou; N. Hua and L. Jiang (2006). Thermal decomposition behaviors of PVP coated on platinum nanoparticles. J.Appl. polymer sci.99(1): 23-26.

Duckworth, M. and W. Yaphe (1971). The structure of agar: Part II. The use of a bacterial agarase to elucidate structural features of the charged polysaccharides in agar. Carbohydrate research 16(2): 435-445.

El-Rafie, H., M. El-Rafie and M. Zahran (2013). Green synthesis of silver nanoparticles using polysaccharides extracted from marine macro algae. Carbohydrate polymers 96(2): 403-410.

El-Hawary Y. M.; F. M. Ibrahim; I. S. Butler; S. J. Mostafa (2014) Bone repaire stimulation in rat mandible by new chitosan silver (I) complexes. Int. J. Polym. Mat., 63: 846-858.

Elhefian, E. A.; M. M. Nasef and A. H. Yahaya (2012). Preparation and characterization of chitosan/agar blended films: part 2. Thermal, mechanical, and surface properties. Journal of Chemistry 9(2): 510-516.

Feng, C.; Z. Shen; Y. Li; L. Gu; Y. Zhang, G. Lu and X. Huang (2009). PNIPAM-b-(PEA-g-PDMAEA) double-hydrophilic graft copolymer: Synthesis and its application for preparation of gold nanoparticles in aqueous media. J. Polymer Sci. Part A: Polymer Chem.47(7): 1811-1824.

Kawai, Y., N. Seno and K. Anno, 1969. A modified method for chondrosulfatase assay. Analytical biochemistry, 32(2): 314-321.

Lahaye, M. (2001). Developments on gelling algal galactans, their structure and physico-chemistry. J.Applied Phycology 13(2): 173-184.

Lahrech, K., A. Safouane and J. Peyrellasse (2005). Sol state formation and melting of agar gels rheological study. Physica A: Statistical Mechanics and its Applications 358(1): 205-211.

Lapasin, R., M. Grassi and N. Coceani (2001). Effects of polymer addition on the rheology of o/w microemulsions. Rheologica acta 40(2): 185-192.

Lyons, J. G.; L. M. Geever; M. J. Nugent; J. E. Kennedy and C. L. Higginbotham (2009). Development and characterisation of an agar–polyvinyl alcohol blend hydrogel. J.The mechanical behavior of biomedical materials 2(5): 485-493.

Martín, L. A.; M. C. Rodríguez; M. C. Matulewicz; E. N. Fissore; L. N. Gerschenson and P. I. Leonardi (2013). Seasonal variation in agar composition and properties from Gracilaria gracilis (Gracilariales, Rhodophyta) of the Patagonian coast of Argentina. Phycological Research 61(3): 163-171.

Molina, R., Y. Al-Salama, K. Jurkschat, P. J. Dobson and I. P. Thompson (2011). Potential environmental influence of amino acids on the behavior of ZnO nanoparticles. Chemosphere 83(4): 545-551.

Murano, E. (1995). Chemical structure and quality of agars from Gracilaria. J. Appl. Phycology 7(3): 245-254.

Navaladian, S., B. Viswanathan, R. Viswanath and T. Varadarajan (2007). Thermal decomposition as route for silver nanoparticles. Nanoscale research letters 2(1): 44-48.

Pandey; S; G. K. Goswami; K. K. Nanda (2012). Green synthesis of biopolymer-silver nanoparticle nanocopmposite: An optical sensor for ammonis detection. Int.J. Biological Macromolecules. 51: 583-589.

Prasad, P. S. R. K.; A. V. Reddy; P. K. Rajesh; P. Ponnambalam and K. Prakasan (2006). Studies on rheology of ceramic inks and spresd of ink droplets for direct ink jet printing. J. Materials Processing Tech.176 (1-3): 222-229.

Rahelivao, M. P.; H. Andriamanantoanina;A. Heyraud and M. Rinaudo (2014). Structure and rheological behaviour of agar extracted from Madagascar sea coast algae. Open Macromol J 7: 1-6.

Rhim, J., L. Wang and S. Hong (2013). Preparation and characterization of agar/silver nanoparticles composite films with antimicrobial activity. Food Hydrocolloids 33(2): 327-335.

Rhim, J. W.; A. K. Mohanty;S. P. Singh and P. K. Ng (2006). Effect of the processing methods on the performance of polylactide films: thermocompression versus solvent casting. J. Appl. Polymer Sci.101(6): 3736-3742.

Rochas, C. and M. Lahaye (1989). Average molecular weight and molecular weight distribution of agarose and agarose-type polysaccharides. Carbohydrate polymers 10(4): 289-298.

Samiey, B. and F. Ashoori (2012). Adsorptive removal of methylene blue by agar: effects of NaCl and ethanol. Chem. Central J.6(1): 14.

Shanker, S. J. Chorachoo; L. Jaiswal and S. P. Vorauthikunchai (2014) The effect of reducing agent concentrations and temperature on characteristics and antimicrobial activity of silver nanoparticles. Materials Letters. 137: 160-163.

Tako, M., M. Higa; K. Medoruma and Y. Nakasone (1999). A highly methylated agar from red seaweed, Gracilaria arcuata. Botanica Marina 42(6): 513-517.

Villanueva, R.; A. Sousa; M. Gonçalves; M. Nilsson and L. Hilliou (2010). Production and properties of agar from the invasive marine alga, Gracilaria vermiculophylla (Gracilariales, Rhodophyta). J. Appl. Phycology 22(2): 211-220.

Whyte, J. N.; S. P. Hosford and J. R. Englar (1985). Assignment of agar or carrageenan structures to red algal polysaccharides. Carbohydrate research 140(2): 336-341.

Wuttisela, K.; B. Panijpan; W. Triampo and D. Triampo (2008). Optimization of the water absorption by crosslinked agar-g-polyacrylic acid. Polymer (Korea) 32(6): 537-543.

Xia, K.; X. Liu; J. Zhao and X. Zhang (2014). The physicochemical property characterization of agar acetate. Carbohydrate polymers 110: 32-37.

Yang, G. W. (2007). Laser ablation in liquids: Applications in the synthesis of nanocrystals. Progress in Materials Sci. 52: 648-698.

Yu, B.; Y. Zhang; W. Zheng; C. Fan and T. Chen (2012). Positive surface charge enhances selective cellular uptake and anticancer efficacy of selenium nanoparticles. Inorganic chem.51(16): 8956-8963.

Zamiri, R.; A. Zakaria; H. A. Ahangar; A. R. Sadrolhosseini and M. A. Mahdi (2010). Fabrication of silver nanoparticles dispersed in palm oil using laser ablation. Int. J. Molecular Sci. 11: 4764-4770.

Zamiri, R.;A. Zakaria; H. A. Ahangar; A. R. Sadrolhosseini and M. A. Mahdi (2011). Preparation of silver nanoparticles in virgin coconut oil using laser ablation. Int. J. Nanomedicine. 6: 71-75.

Zhang X.; X. Liu; M. Cao; K. Xia and Y. Zhang (2015). Preparation of hydroxypropyl agars and their properties. Carbohydrate polymers 129: 87-91.

التوصيف و التخليق الأخضر لدقائق أجار الفضة النانومترية لآجار مستخلص من الطحلب الأحمر *Gelidium* sp.

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أجريت هذه الدراسة بهدف إستخلاص و توصيف الآجار من الطحلب الأحمر *Gelidium* sp. و قد تم تجميع العينات من شواطئ البحر الأحمر المصرية عند منطقة الغردقة و الذى يمثل جزء مهم من غطاء الأعشاب البحرية بالمنطقة وقد تم توصيف هذا البوليمر فيزيائيا و كيميائيا من أجل التطبيقات التكنولوجية . أظهرت نتائج إستخلاص الآجار أنه يمثل 26,65 % من الوزن الجاف لطحلب *Gelidium* sp. فى صورة رقائق و خيوط غير ذائبة فى الماء البارد و تذوب و تكون مادة هلامية فى الماء بدرجة حرارة 100 مئوية مكونة مادة هلامية فى تركيزات منخفضةو قد أوضحت الدراسة أن التحليل بالاشعة تحت الحمراء اطيافا متشابهة مع ظهور قمم مميزة تؤكد وجود الآجار بصورة نقية. و لقد وجد أن آجار طحلب Gelidium sp. ثابتا حراريا حتى درجة حرارة 325 مئوية . كما إتضح من دراسة خواص اللزوجة الديناميكية أن محاليل الآجار تكون محاليل غروية لها hydro gel with shear thinning and pseudoplastic behavior فى المحاليل منخفضة التركيز (أقل من 2 mg/ml) و يكون محاليل غروية shear thickening فى التركيزات المرتفعة من الآجار. كذلك أظهرت الدراسة زيادة لزوجة المحلول مع زيادة التركيز. تم دراسة التخليق الأخضر صديق البيئة الحيوى لدقائق الفضة النانومترية بإستخدام الآجار كعامل مختزل. و لقد أوضحت النتائج الخواص الجيدة لدقائق الفضة النانومترية المتكونة بإستخدام الآجار من حيث التوزيع و الإنتشار بالمحلول و أيضا حجم الدقائق التى قدرت بنصف قطر متوسط 13,6 نانومتر. و عليه أوضحت الدراسة أ طحلب Gelidium sp. مصدر جيد لإنتاج الآجار ذو الخواص الجيدة التى تتيح تطبيقات تكنولوجية للآجار المستخلص و أيضا سهولة تحضير دقائق الفضة النانومترية.