

# 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 basis with 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 85°C and let to cool gradually (1.5°C/min), with the maximum values of viscosity as following 1.26, 3.12 and 5.18 cP, respectively at shear rate of 40 sec<sup>-1</sup>. Agar solutions revealed 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 represented 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 gradual properties 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, Silver Nanoparticles (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 properties.

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 chain consisting of alternating 1,3-linked  $\beta$ -D-galactopyranose and 1,4-linked 3,6 anhydro- $\alpha$ -L-galactopyranose units forming a "crosslinked network" model. Agarobiose is

the basic disaccharide representing the structural unit of all agar polysaccharides. Agar is divided into: agarose and agaropectin. Agarose is a neutral polysaccharide with gelling capability while agaropectin represented the charged polysaccharide component (Lahrech *et al.*, 2005). Agar forms a thermoreversible gel in aqueous solutions. Moreover, gels have a gelling/setting temperature close to 40°C and a melting temperature near 90°C as found by (Djabourov *et al.*, 1989). In respect to biotechnological potentiality agar gels in supporting bacterial cultures, separation media in column chromatography and electrophoresis, usage in medicine and pharmacy as well as in food industry where act as thickening and gelling agents (Djabourov *et al.*, 1989).

Nanotechnology is a rapid growing field with multifaceted applications of a new materials at the nanoscale level. Metallic 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 high specificity (Shanker *et al.*, 2014). Synthesis of silver nanoparticles (AgNPs) is a significant area of research, because AgNPs have potential applications in various fields such as wound healing, antimicrobial, bone stimulation, biochemistry, environment, medicine, catalysis, electronics and optics (Navaladian *et al.*, 2007 and El Hawary *et al.*, 2014).

This study aimed to extract the phyco-colloid agar from the red macroalga *Gelidium* sp., investigate its chemical and rheological behavior, physical properties 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. were collected from the shoreline of the Red Sea at Ghordaga city – Egypt. Algal thalli were washed thoroughly with tap water, dried at 60°C.

### **Agar extraction**

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

### **Scanning 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 in the range of 25°C-1000°C

under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) of agar was investigated using a Differential Scanning Calorimeter (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 5000 FT-IR spectrometer in the frequency range of 400-4000  $\text{cm}^{-1}$  (Unit of Microanalysis – Faculty of Science – Mansoura University).

#### **Rheology properties of Agar**

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

#### **Preparation of silver nanoparticles (Ag-NPs)**

30 mg of the extracted agar powder was dissolved in 90 ml of sterile deionized water with continuous stirring at 85°C. 1 ml of 0.1 mM  $\text{AgNO}_3$  solution was added to the prepared agar solution dropwise with continuous stirring, adjusting pH at 10. The prepared solution was centrifuged for 3 min at 3,000 rpm to separate any aggregations. The final volume was adjusted to 100 ml using deionized water and continued stirring at 85°C for 20 min, since the solution color was changed to brown (El-Rafie *et al.*, 2013).

#### **Nanindentation (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-visible Spectrophotometer (Lambda 35) in the wavelength ranged from 200 to 800 nm.

#### **TEM analysis**

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

#### **Atomic Force Microscopy**

Images of the excepted nanoindentation 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 Potential Analyzer (Malven Zeta size Nano-Zs90) in Nanotechnology Center of Mansoura University.

## **RESULTS AND DISCUSSION**

#### **Agar yield and sulphate content**

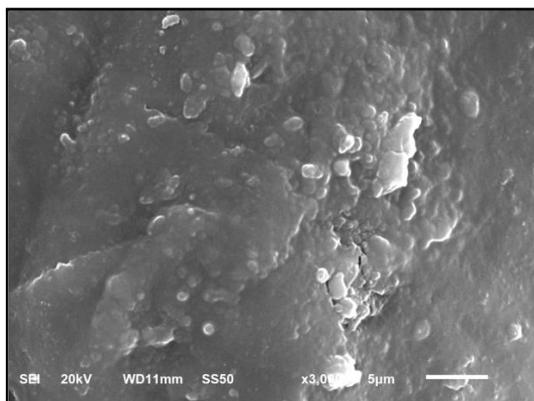
Red algae (Rhodophyta) are famous for being source of unique sulfated galactans, such as agar. The extensive usages of this polysaccharide is based on its ability to form strong gels with water. Results shown that agar yielded about 26.65 % on dry biomass basis, while sulphate represent 1.98% dry biomass. 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 of Martín *et al.* (2013). The yield and physical properties 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 electron micrograph (Fig.1) showed the microstructure of surface of agar when dry. Granular surface morphology was observed. This appearance may be owing to the porous network microstructures the physical composition as previously reported by Zhan *et al.* (2015).



**Fig.1: Scanning Electron Microscopy micrograph of dry agar**

#### **Thermal stability**

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

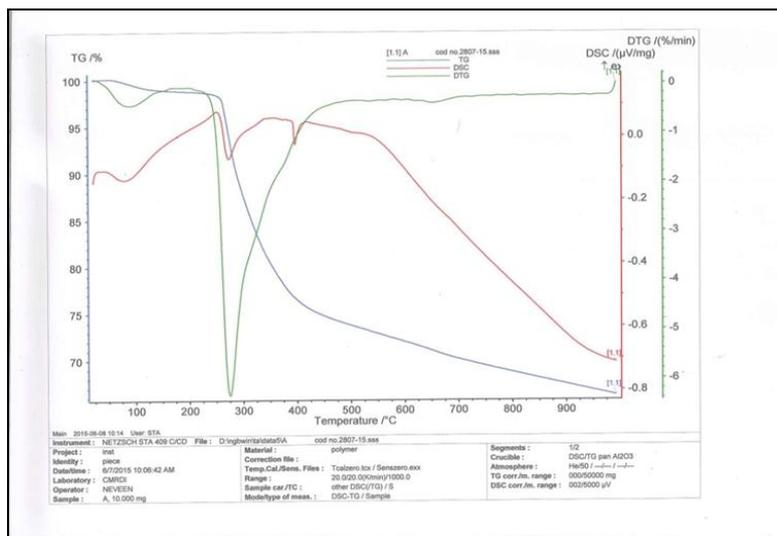


Fig.2 Thermogravimetric analysis of agar extracted from *Gelidium* sp.

### Fourier transform infrared spectrometry

FTIR of agar (Fig.3) showed that the characteristic absorption spectra of agarose were detected. Bands between  $3444\text{ cm}^{-1}$  is assigned to (OH) of hydroxyl group and spectra at  $1091\text{ cm}^{-1}$  designated to presence of glycosidic bonding and (C-OH) a very weak band of absorption at  $1257\text{ cm}^{-1}$  illustrated (C-O-C) (Tako *et al.*, 1999). Strong bands at around  $1156$  and  $1091\text{ cm}^{-1}$  demonstrating the presence of C-O-C vibration of the 3,6 anhydrogalactopyranose bridge and the D-galactose residues, respectively (Whyte *et al.*, 1985; Wuttisela *et al.*, 2008). The bands at  $2988$ ,  $2961$  and  $2925\text{ cm}^{-1}$  can be assigned to the alkane C-H stretching symmetric and asymmetric or assigned to the secondary amine. The absorption bands observed at  $1560$ ,  $1540$  and  $1524\text{ cm}^{-1}$  can be assigned to the amide group of protein or to the carbonyl stretching group of the algal polysaccharides. Band at  $1156\text{ cm}^{-1}$  is allocated to -C-O groups of polyols of polysaccharides. Bands at  $1456$ ,  $1399$  and  $1319\text{ cm}^{-1}$  corresponded to the stretching vibrations of hydroxyl, C-H, carboxyl, and C-H bending of aliphatic  $\text{CH}_2$  (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 Diaz *et al.* (2011) who investigated the polysaccharide fractions of the red algae *Hypnea spinella* (Gigartinales) and *Halopithys incurve* (Ceramiales).

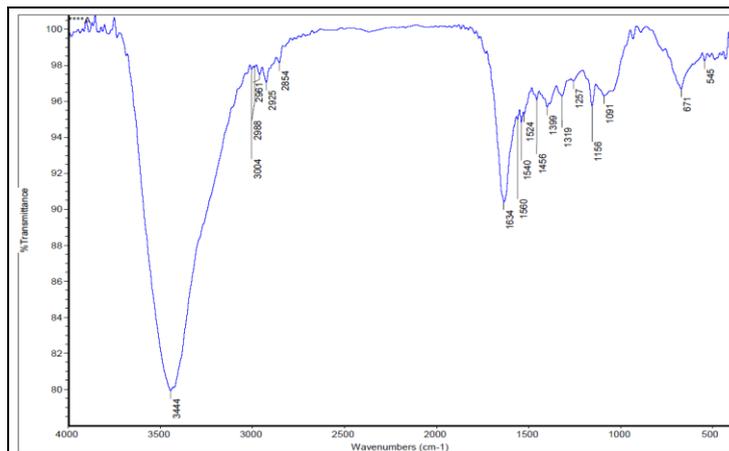


Fig.3: FT-IR analysis of agar extracted from *Gelidium* sp.

### Dynamic rheological properties

The viscosity of a material in respect to its shear rate gives significant criteria in industrial applications. 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 85°C and let to cool gradually (1.5°C/ min), giving the maximum values of viscosity as following 1.26, 3.12 and 5.18 cP, respectively at shear rate of 40 sec<sup>-1</sup> (Fig.4), While increasing shear rate to 500 sec<sup>-1</sup> viscosity increased reaching values of 1.89, 4.05 and 7.63 cP, respectively. Figure 5 illustrates 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<sup>2</sup>) values, under the effect of gradual cooling in the higher biopolymer concentrations (3 & 4 mg agar / ml), while the low concentration (2 mg agar / ml) the shear stress tended to level off and near stable magnitude as a decline in shear rate towards zero level of shear rate, indicating that this concentration of the polymer system induced a restricted magnitude of yield stress. Data revealed also, the dependence of shear stress on agar concentration. Rheograms (Fig. 6) represent a map for the rheological properties revealing the presence of Newtonian fluid material demonstrating shear thickening (Dilatant) flow behavior in the high 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 expressing 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 pattern was recorded for the concentration of agar solution and spindle speed and viscosity.

Agar is composed of two fractions: agarose, the linear neutral fraction accountable for agar's gelling potentiality, and agaropectin, the charged

polymer fraction that characterized by the presence of numerous substituent groups as sulphates, methylethers and pyruvates. In addition, of being a polyanionic biopolymer, is a sulphated polysaccharide and has been considered as a strong polyelectrolyte (Boral and Bohidar, 2010). The present results of rheological characterization of algal agar (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 algae have elastic response dominates as is typical for gels and solid like materials as samples exhibited mechanical rigidity. Duckworth and Yaphe (1971) suggested that gel properties of the biopolymer agar are greatly dependent on the amount and position of sulfate groups as well as the amount of 3,6-anhydrogalactose fraction of the phyco colloid. At fixed total carrageenan concentrations, k-carrageenan mixtures are characterized by lower elastic moduli and a higher fracture strain, resulting in a peak of the fracture stress around 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 proportionally 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 by Lahrech *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 by Arnott *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.

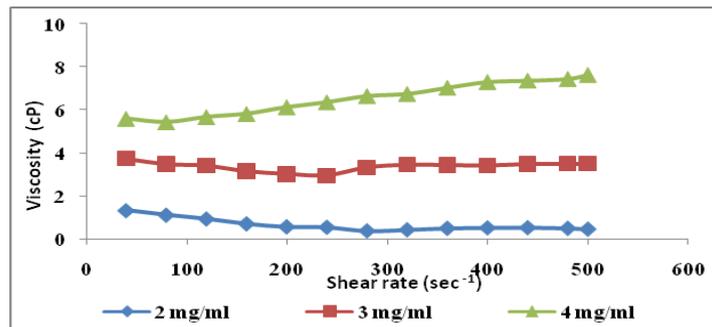


Fig.4: Viscosity (cP) as a function of shear rate (sec<sup>-1</sup>) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

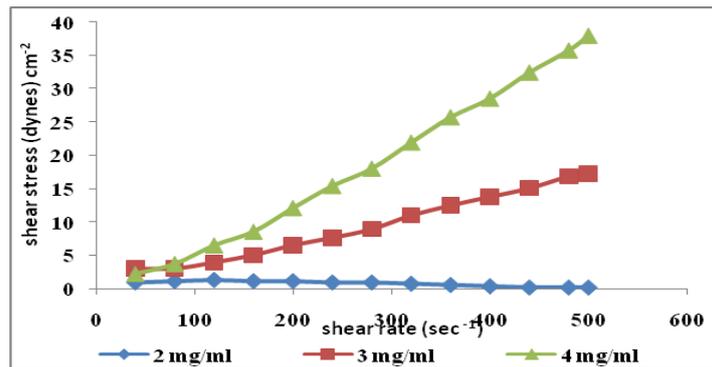


Fig.5: Flow curve of the shear stress (dynes cm<sup>-2</sup>) vs. shear rate (cm<sup>-1</sup>) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

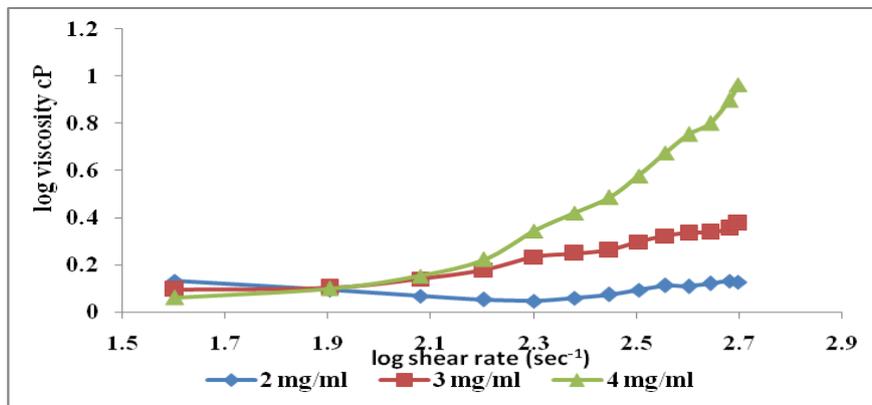


Fig.6: Log plot of the viscosity (cP) vs. shear rate (cm<sup>-1</sup>) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

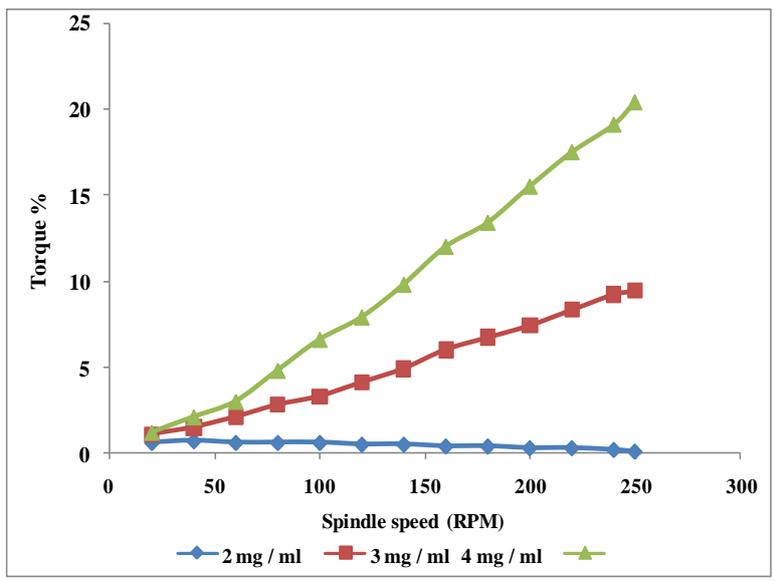


Fig.7:Rheogram of the Torque vs. spindle speed (RPM) of *Gelidium* sp. agar aqueous solutions at concentrations 2, 3 & 4 mg agar/ml

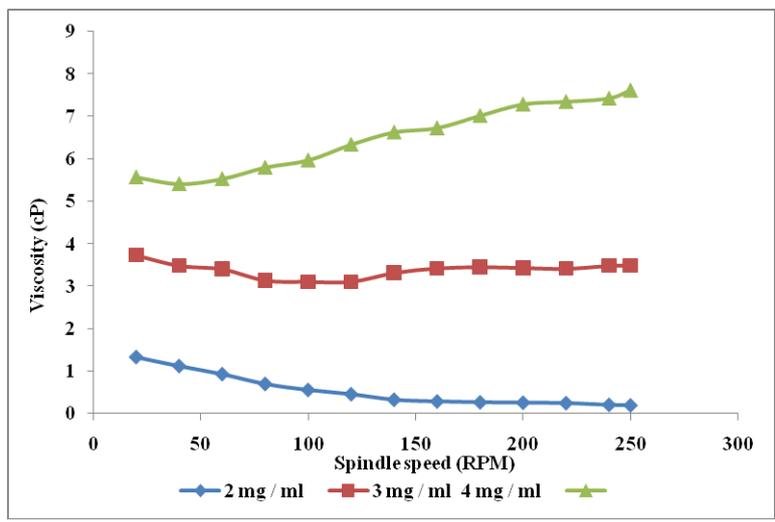
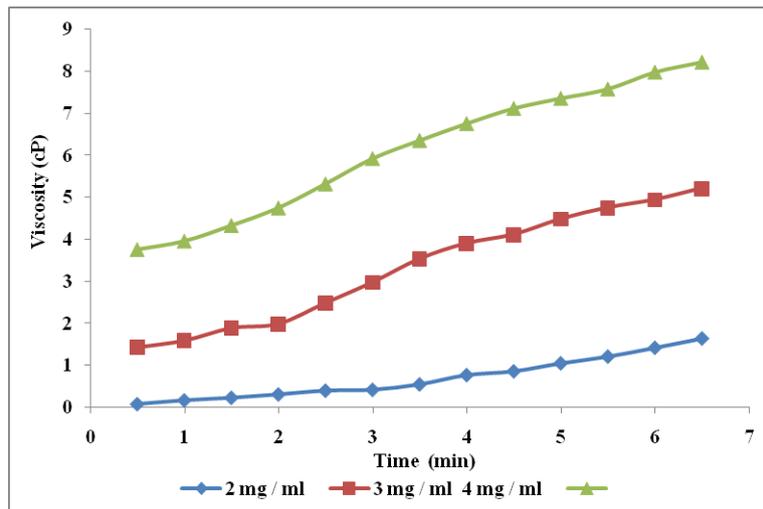


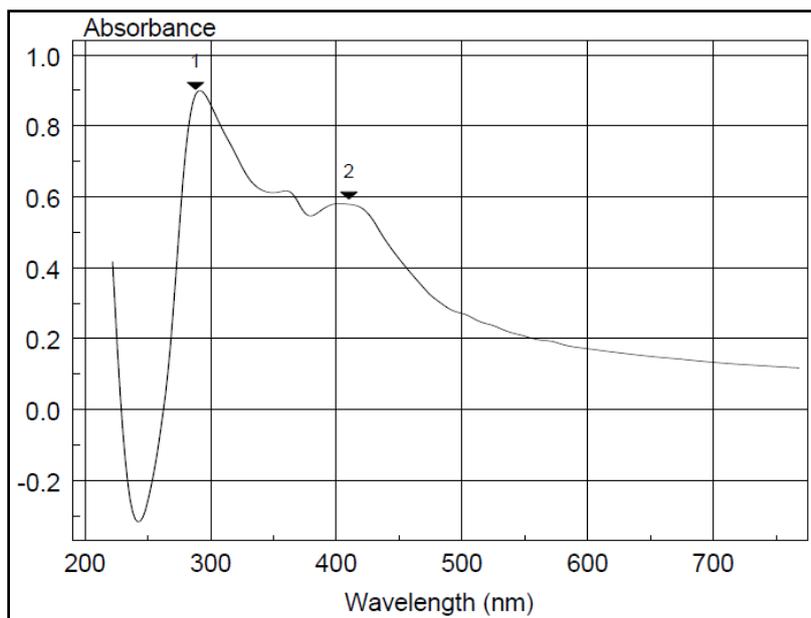
Fig.8:Rheogram of viscosity (cP) dependence of spindle speed (RPM) for aqueous *Gelidium* sp. agar solutions at concentrations 2, 3 & 4 mg agar/ml



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

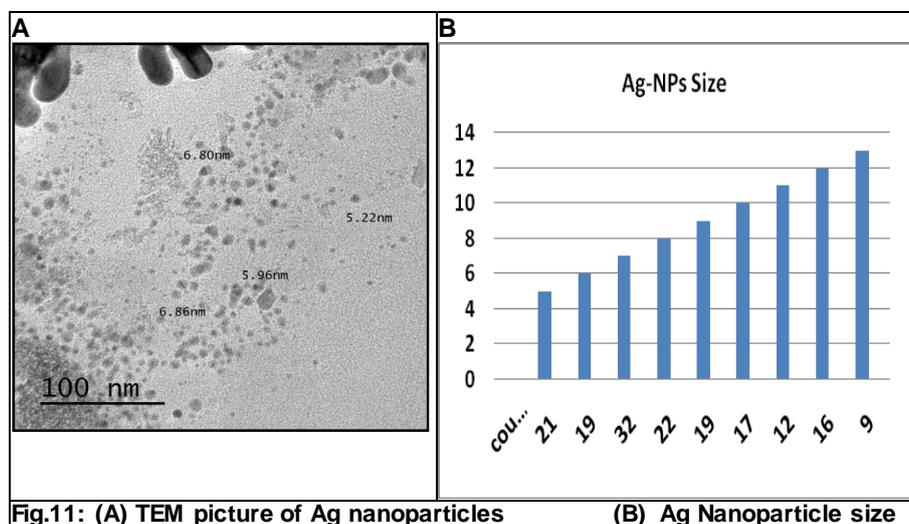
#### **Characterization of Silver/nanoparticles (AgNPs)**

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. As optical 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 absorbance 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 560 nm, 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 Microscopy (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 surfaces with 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 surfade charge (Daima *et al.*, 2014).

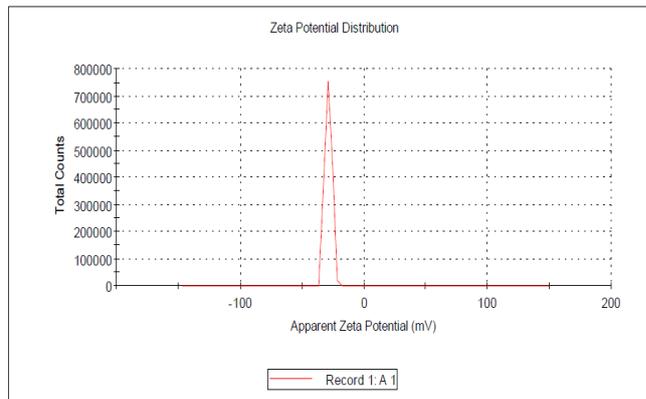


Fig. 12: Zeta potential distribution of AgNPs.

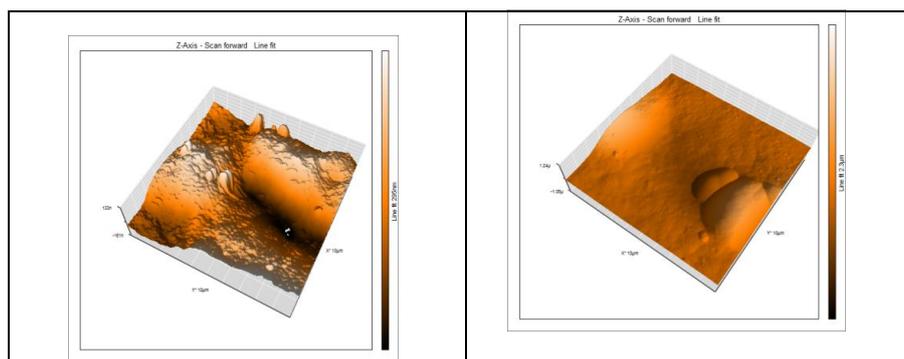


Fig. 13: Atomic Force Microscopy (AFM) analysis of AgNPs

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 simple preparation method of the phycocolloid agar, physicochemical and rheological properties as well as the utilization potential of agar gels has indicated the biotechnological potentiality of Rhodophyta as good candidates of agar production. In addition, the biopreparation of silver nanoparticles using agar as a good reducing agent.

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التوصيف و التخليق الأخضر لدقائق أجار الفضة النانومترية لأجار مستخلص من  
الطحلب الأحمر *Gelidium sp.*  
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أجريت هذه الدراسة بهدف إستخلاص و توصيف الأجار 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 و قد تم توصيف هذا البوليمر فيزيائيا و كيميائيا من أجل التطبيقات التكنولوجية . أظهرت نتائج إستخلاص الأجار أنه يمثل ٢٦,٦٥ % 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 ١٠٠ مئوية مكونة مادة هلامية فى تركيزات منخفضة و قد أوضحت الدراسة أن التحليل بالأشعة تحت الحمراء اطيافا متشابهة مع ظهور قمم مميزة تؤكد وجود الأجار بصورة نقية. و لقد وجد أن أجار طحلب *Gelidium sp.* ثابتا حراريا حتى درجة حرارة ٣٢٥ مئوية . كما إتضح من دراسة خواص اللزوجة الديناميكية أن محاليل الأجار 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 الأجار. كذلك أظهرت الدراسة زيادة لزوجة المحلول مع زيادة التركيز. تم دراسة التخليق الأخضر صديق البيئة الحيوى لدقائق الفضة النانومترية بإستخدام الأجار كعامل مختزل. و لقد أوضحت النتائج الخواص الجيدة لدقائق الفضة النانومترية المتكونة بإستخدام الأجار من حيث التوزيع و الإنتشار بالمحلول و أيضا حجم الدقائق التى قدرت بنصف قطر متوسط ٦,٦ نانومتر. و عليه أوضحت الدراسة أ طحلب *Gelidium sp.* مصدر جيد لإنتاج الأجار ذو الخواص الجيدة التى تتيح تطبيقات تكنولوجية للأجار المستخلص و أيضا سهولة تحضير دقائق الفضة النانومترية.