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Novel and Cost Effective Method for Nanosilver Preparation as Marine Antifouling Additive via Wet Chemical Reduction Method.

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ABSTRACT

Currently nanosilver received great attention in many industrial applications especially in paint industry. Due to the high antimicrobial and antifungal actions of nanosized silver particles, it could be used as excellent antifouling additive in marine coating polymers. Nanosized of 20nm to 50nm especially 35nm are the optimum particle size of nanosilver which could be used as marine antifouling additives in paint composition. The investigation of optimum operating conditions for the preparation of 35nm nanosized silver particles was the target of the study. Wet chemical reduction method via hydroxyethyl cellulose (HEC) as green reducing and stabilizing agent was used. The results show that these optimum conditions were silver ion concentration 0.76g/l, HEC concentration 1.4g/l with silver ion to HEC concentration ratio of 0.54, at reaction temperature of $80^{O}C$ for interval time 45min. at rate of stirring of 150rpm and pH of 10.6. The maximum percentage obtained of the target size (35nm) at these reaction conditions was 57%.

Keywords: nano silver, marine, antifouling, and chemical reduction

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INTRODUCTION

Currently nanosilver particles received much attention in many industrial applications, due to its excellent electrical, thermal, optical, antimicrobial and/or catalytic properties (Kan-Sen Chou, *et al,* Magdassi, *et al* 2003, Pradhan, *et al* 2002, Nie and S.R. Emory 1997, Haes, and R.P. Van Duyne 2003and Ye, *et al* 1999). The high surface-area-to-volume ratio of nanoparticles can create their unique physical, chemical, mechanical, and quantum size effect properties (Bawendi, *et al* 1990 and Tsung, *et al* 2003). Nano silver could be used as disinfecting agent for water, conductor, catalyst, and chemical sensor, etc. Two major techniques are used to synthesize these nanosized silver particles. Physical technique may contain UV and IR radiation (Tien *et al* 2008 and Abid, *et al* 2002), aerosol technology and lithography, evaporation (Fei, *et al* 1997) or laser ablation (Chen and S. Yeh 2002), from metal substrates to generate nanoparticles. Chemical methods may include wet conventional chemical (one- or two-phase system), photochemical (Huang, *et al* 1996), sonochemical (Li *et al* 2000), electrochemical (Yu, *et al* 1997), and radiolytic reduction (Henglein 2000). Wet chemical reduction method is the most popular one because of its ease of control, low cost and simplest of manipulation of the production process. Many reducing agents had been reported in the literature for the chemical production of nanosized silver particles, these reducing agents may be formaldehyde, hydrazine, glucose, fructose, ascorbic acid, and ferric ion, ethylene glycol (Chou, and Y.S. Lai 2004, Nersisyan, *et al* 2003, Wu, and S.Y. Meng 2005, Sondi and Goia, E. Matijevic 2003, Kim, *et al* 2004, Wei, *et al* 2003, and Silvert, *et al* 1996), etc. Depending upon the reducing power of these reagents, the synthesis reactions were then carried at various temperatures to achieve reasonable rates. In general, the reduction reaction of metallic ions is sensitive to the solution's pH. Moreover, it may also affect the product's morphology via the formation of certain species. (Lee, *et al* 2004) reported that increase of pH led to a decrease of aspect ratio of silver nanorods and an increase of monodispersity. The change in reduction rate of silver with pH was explained as the possible reason. (Fukuyo and Imai 2002) varied the morphology of silver by changing pH while using ascorbic acid as the reducing agent. The antibacterial properties of copper, silver, and zinc have been widely utilized in advanced coating technologies, such as the design of materials for biomedical devices, hospital equipment, food processing and storage equipment, household materials, antifouling paints and marine coatings (Anyaogu, *et al* 2008, Mann *et al* 2002, Avery et al 1996, Antonietta, *et al* 1996, Stoimenov, *et al* 2002, and Yoichi, *et al* 2005). In recent years, nanoparticle/polymer composites have become important owing to their small size and large surface area, and because they exhibit unique properties not seen in bulk materials. As a result, nanoparticles (NPs) have useful applications in photovoltaic cells, optical and biological sensors, conductive materials, and coating formulations (Sambhy, *et al* 2006). Biofouling prevention remains a major challenge, and there is a need for antifouling systems that exhibit minimal/no eco toxicity, active durability, and easy affordability (Ho, *et al* 2005). Silver, Copper and their oxides are common biocides in a large number of commercial antifouling marine paints. Incorporation of Cu-based biocides is mainly achieved by mechanical doping into paint matrixes. There are several reports on the antimicrobial activities of metal NP/polymer composites. (Ho, *et al* 2005, Trapalis, *et al* 2003, Esteban, *et al* 2006, Cioffi, *et al* 2005, and Anderson, *et al* 2004). However, there are still challenges such as the instability of the NPs, control of their size and shape, uniform dispersity in a matrix, and control of the release rate. Recent reports have shown that Cu NP/polymer composites exhibit antifungal and antibacterial properties (Esteban *et al* 2006, Cioffi, *et al* 2005, Gu, *et al*, Anderson, *et al* 2004 and Nyden, 2007). However, these systems are not optimum because of the poor control of the leaching of the active biocide. This is crucial considering the growing concern on the amount of potentially toxic metals, particularly copper, leached to the marine environment from diverse sources that include antifouling paints (Goia, 2004). Nanosilver could be used as excellent antifouling additive in marine coating polymers; this is due to its high antibacterial and antifungal action. Optimum particle size has to be selected to incorporate within the coating polymer matrix to satisfy the antifouling activity and controlling and preventing the leaching of the nanosilver to the marine water in the same time. From literature review the optimum particle size of nanosized silver could be used in marine antifouling paints ranged from 30nm to 50nm (Nyden, 2007).

In this work the optimum conditions for preparation of controllable nanosized silver particles mainly 35nm (to be used as antifouling agent in marine coatings) using hydroxyethyl cellulose as green reducing agent were investigated. The main controlling parameters to be studied were pH, reaction temperature, stirring time, concentration of reducing agent and metal ion source concentration.

EXPERIMENTAL

Materials

Hydroxyethyl cellulose (HEC), isopropanoal, silver nitrate, sulfuric acid, and sodium hydroxide (all of high laboratory grade) were used for this study. Reducing agent formula used was also acts as the stabilizer for synthesized nanosized silver colloids.

Experimental Method

Preparation of the reducing agent formula

Hydroxyethyl cellulose polymer was heated with 10% isopropanoal solution in slightly alkaline conditions at 40^{o}C till the formation of transparent gel. The obtained gel was added as reducing and stabilizing agent for the silver ion to prepare nanosized silver particles.

Preparation of Nanosized silver Particles

Fixed weight of HEC gel was dissolved in distilled water using heating magnetic stirrer at 40^{o}C. After complete dissolution, the pH of the solution was adjusted to the desired value, followed by raising the temperature of the reaction medium to the desired temperature. Silver nitrate solution was then added drop wise. The reaction mixture was kept under constant rate of stirring (150rpm) for the desired experiment duration. Once the addition of silver nitrate, the reaction medium acquires a clear yellow color converted to dark brown indicating the formation of silver nanoparticles. The propagation of the reaction was controlled by UV–Vis absorption; aliquots from the reaction bulk were withdrawn at given time intervals and evaluated. The focus of this work is to study the effect of several operating conditions such as pH, temperature rate, time of stirring, and concentration of both reducing agent and silver nitrate. pH was adjusted using electrode (Mettler Toledo Le 409, USA).

Testing and evaluation

Ultra violet–visible spectra have been proved to be quite sensitive to the formation of nano silver particles because they exhibit an intense absorption peak due to the surface Plasmon excitation (it describes the collective excitation of conduction electrons in a metal). The UV–Vis spectra of silver nanoparticles embedded in HEC were recorded by means of a 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. A solution containing silver nitrate dissolved in de-ionized water was used as a blank.

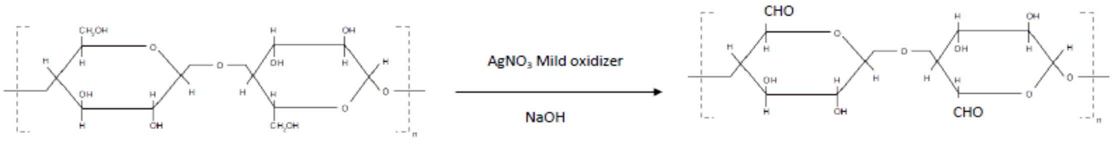
Shape and size of the obtained nanosized silver particles were characterized by means of a JEOL-JEM-1200 Transmission Electron Microscope (ETM). The ETM sample was prepared by adding a drop of the nanosilver solution on a 400 mesh copper grid coated by an amorphous carbon film and lifting the sample for drying in air at room temperature. The average diameter of the silver nanoparticles was determined from the diameter of 100 nanoparticles found in several chosen areas in enlarged microphotographs. Also the same apparatus used for the examination of the morphology and X-ray diffraction test of the obtained particles.

RESULTS AND DISCUSSION

Reaction mechanism for formation of silver nanoparticles

Goia, 2004 have disclosed that the solutions of polymers can be used for the synthesis and stabilization of nanoparticles. Linear and dendritic polymers have been successfully used for nanoparticles synthesis. Polyhydroxylated macromolecules present interesting dynamic supramolecular associations facilitated by inter and intra-molecular hydrogen bonding resulting in molecular level capsules, which can act as templates for nanoparticles growth. HEC macromolecules consist of chemically modified cellulose chains containing reducing groups and carboxyl groups. All these components with their anionic and reducing properties support the utilization of HEC as reducing and stabilizing agent for the synthesis of silver nanoparticles. The negatively charged solubilized HEC facilitates the attraction of the positively charged silver cations to the polymeric chains followed by reduction with the existing reducing groups. For the synthesis of silver nanoparticles, the generally accepted mechanism suggests a two-step process, i.e. atom formation and then polymerization of the atoms. In the first step, a portion of metal ions in a solution is reduced by the available reducing groups of the HEC. The atoms thus produced act as nucleation centers and catalyze the reduction of the remaining metal ions present in the bulk solution. Subsequently, the atoms coalesce leading to the formation of metal clusters. The surface ions are again reduced and in this way the aggregation process does not cease until high values of nuclearity are attained, which results in larger particles. The process is stabilized by the interaction with the polymer so preventing further coalescence

(Goia, 2004). The following equations may be explained the mechanism of formation of nanosized silver using HEC as a green reducing agent.



+ Ag^0

$$Ag_1^0 + Ag_2^0 + Ag_3^0 + \ldots\ldots Ag_n0 \xrightarrow{} \text{Cluster Shape (Nano Silver)}$$

Effect of operating Parameters

HEC concentration

Fig.1A shows the UV–Vis absorption spectra of silver nanoparticles prepared using HEC in different concentrations (0.7 to 4.2 g/l), at initial pH of 10.6. Silver ion concentration 0.673g/l and temperature of 60^{O}C for 15min at stirring rate of 50rpm. Regardless of the HEC concentration, similar Plasmon bands are formed at wavelength 400nm with the formation of the ideal bell shape which is characteristic for the formation of Ag^0 nanoparticles. It is clear also that there is a gradual increase in the absorption intensity, by increasing the HEC concentration up to 2.8g/l then no increase in the peak intensity obtained as the HEC concentration increases, this could be attributed to the enhancement in the stabilization efficiency of the formed silver nanoparticles. Fig. 1B shows the variation of the major obtained silver nanosized particle due to the variation of the HEC concentration. As HEC concentration increases the particle size increases till 60 nm at HEC concentration 2.8g/l, then the particle size starts to decrease with more increment of HEC concentration. The desired particle size 35nm is obtained as major particle size at HEC concentration 1.4g/l, so this value is taken as the optimum HEC concentration. Fig. 1C shows the particle size distribution and histogram at the optimum selected sample, it is clear that the desired particle size 35nm percentage reached about 37% at the reaction conditions. Finally fig. 1D TEM image of the obtained nano silver at the optimum selected sample. More control in the reaction conditions have to be carried out to maximize the required particle size percentage. Due to the increment of HEC concentration the librated electrons which are responsible for silver ion reduction increases and at the same time the medium viscosity is still low which give the chance for silver particles to aggregate leading to the increment of nano particle size. At high concentration of HEC although silver ions are completely reduced to silver nano particles, but the high viscosity of the medium prevent silver nano particles to aggregates leads to small nano particle size.

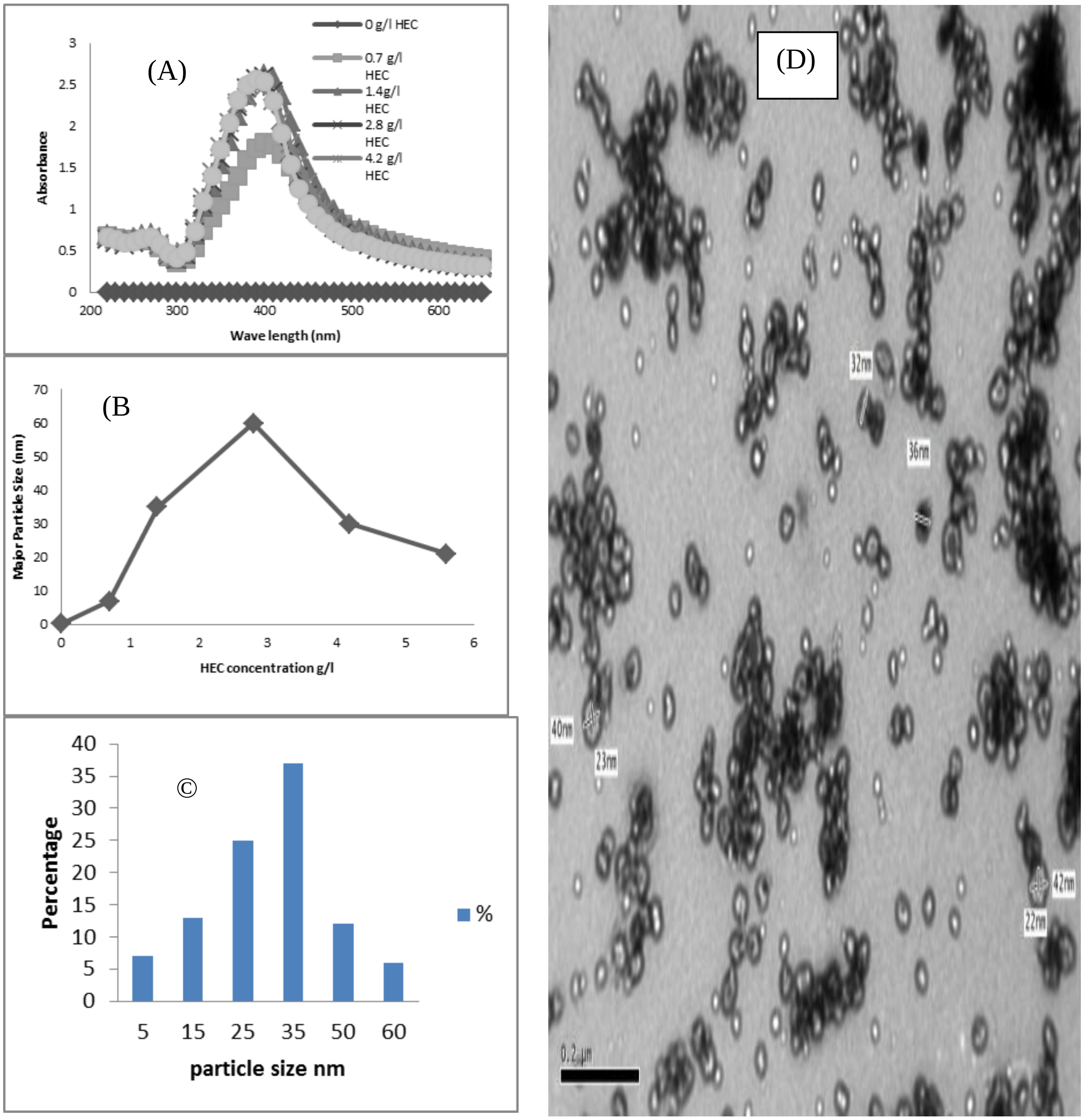


Fig.1 (A) UV–Vis spectroscopy of silver nanoparticles prepared at different HEC concentration. (B) Variation of major obtained particle size of nano silver due to variation of HEC concentration. (C) Histogram for particle size distribution of nano silver at optimum HEC concentration (D) TEM image of silver nanoparticles formed after 15 min.

Effect of pH

After complete dissolution of HEC in distilled water using magnetic stirrer, pH of the sample was adjusted using dilute sulfuric acid or sodium hydroxide while the temperature was raised to 60^0C. Silver nitrate then added drop wise with keeping stirring rate at 150rpm, and the total sample volume of 50ml. The reaction was allowed to proceed under continuous stirring for 15min. whereby silver colloid was formed.

Fig. 2A shows the UV–Vis spectra of the silver colloid obtained using HEC as reducing and stabilizing agent at different pHs. The operating conditions were silver ion concentration of 0.673 g/l, HEC concentration of 1.4g/l, reaction temperature 60^{o}C, stirring rate 50rpm, and reaction duration of 15min. The results show that, increasing the pH of the solution is accompanied by increasing of the intensity of the obtained peak at 400nm; this peak reaches its maximum intensity at pH 12.5 with a pronounced bell shape. This band could be assigned to the Plasmon resonance of silver nanoparticles. Fig. 2B shows the variation of the obtained major particle size of the nanosized silver due to variation of the pH value. The results show that as the pH value increases the particle size also increases and the shape of the particles changed from core shell shape at pH10.6 as clear from fig.1D to flakes like shape at pH 12.5 as shown in fig.2C. The reductive properties of HEC are substantially enhanced owing to the oxidative degradation with the formation of low molecular weight reducing chains. The maximum intensity of the Plasmon peak obtained at 400nm at pH 12.5 indicates full reduction of Ag ions and, therefore, reflecting the dual role of HEC as stabilizing and efficient reducing agent in alkaline medium. From the above pH of 10.6 was taken as the optimum pH for the target of the present study. The increment of pH leads to the decrement of the medium viscosity which give the chance for reduced silver nano particles to aggregate. This fact leads to the increment of the obtained particles size and also changes the shape from circular to flakes like one.

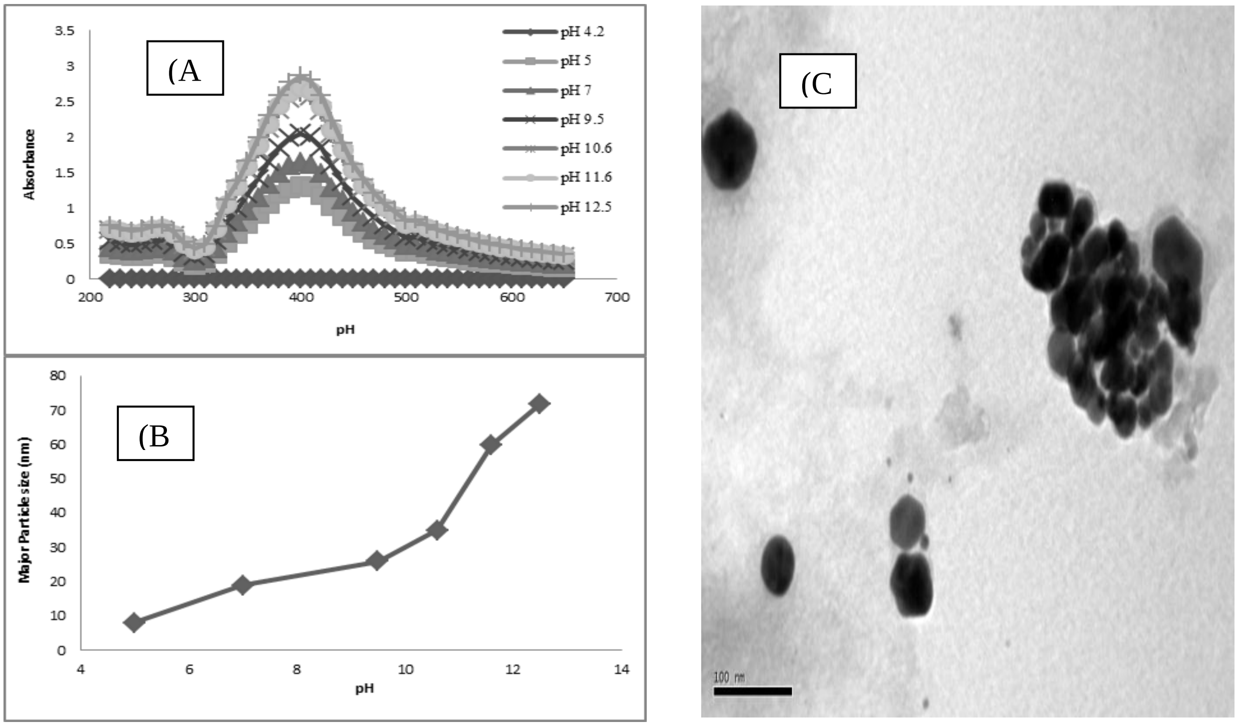


Fig.2 (A) UV–Vis spectroscopy of silver nanoparticles prepared at different pHS. Reaction conditions: 1.4g/l HEC, (0.673g/l) Ag^{+}; temperature 60^{0}C; duration 15 min., and stirring rate 50rpm (B) variation of major obtained particle size of nano silver due to variation of pH value. (C) TEM image of the sample obtained at pH 12.5.

Effect of Silver Ion concentration

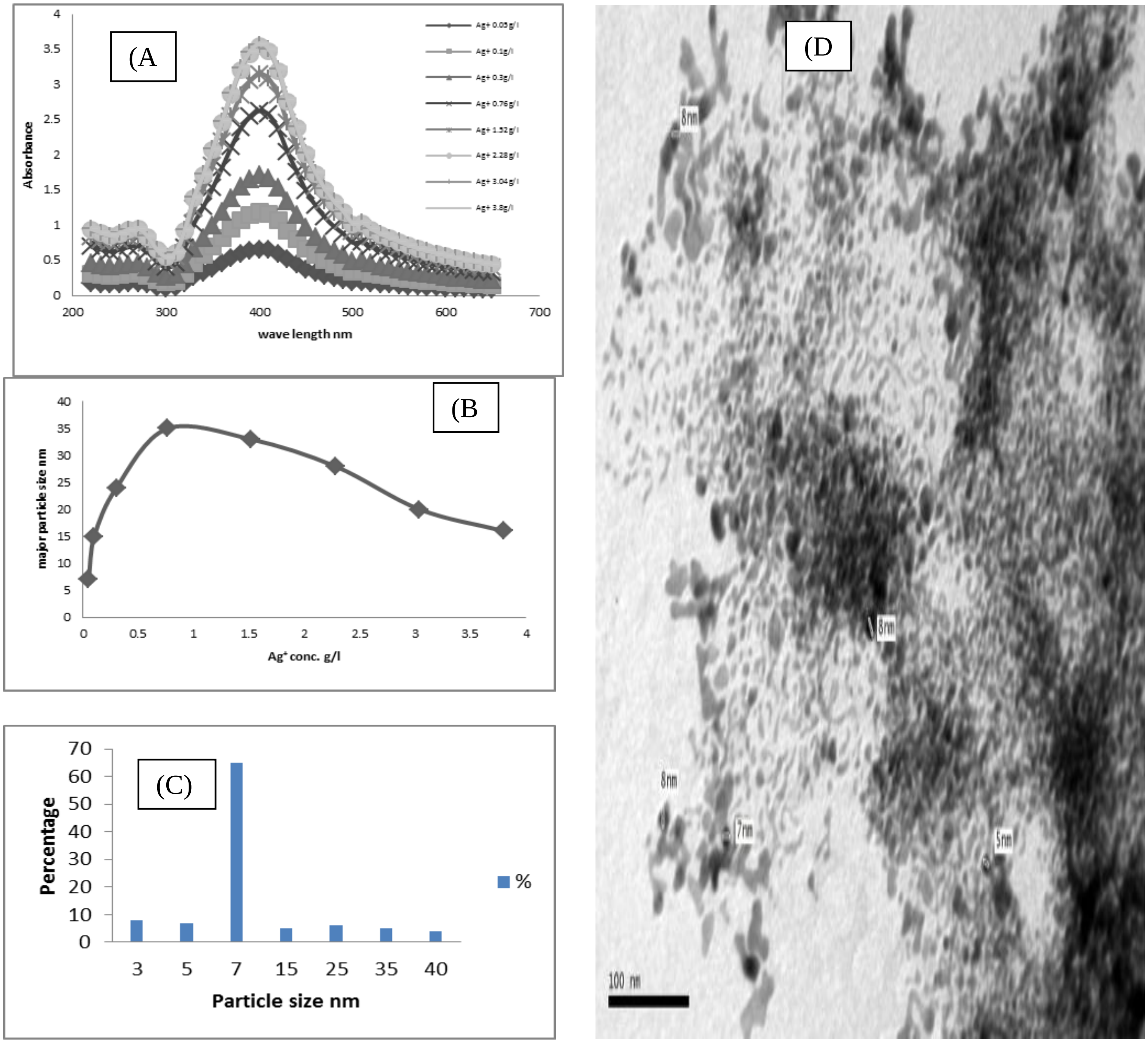


Fig.3 (A) UV–Vis spectroscopy of silver nanoparticles prepared at different silver ion concentrations. Reaction conditions: 1.4g/l HEC, pH 10.6; temperature 60^{0}C; duration 15 min., and stirring rate 50rpm (B) variation of major obtained particle size of nano silver due to variation of silver ion concentration. (C) Particle size distribution histogram (D) TEM image of the sample obtained at silver ion concentration 0.003g/l.

Applications of nanosized silver particles in paint industry acquire large production, so study was undertaken where silver ion was incorporated at different concentrations in the reaction medium. Fig. 3A shows the UV–Vis spectra of Ag^0 resulting from incorporating different amounts of silver ion (0.005–4g/l) and fixing HEC concentration at 1.4g/l for all $AgNO_3$ concentrations. The operating conditions were HEC concentration of 1.4g/l, pH of 10.6, reaction temperature was 60^{O}C, and stirring rate of 50rpm for 15min. Fig. 3A reveals that similar absorption spectra are obtained at wavelength 400nm and that the intensity of the absorption peak increases by increasing $AgNO_3$ concentration in the reaction medium. Fig. 3B shows that as the concentration of silver ion source increases the major obtained particle size increases too reaching to 35nm at Ag^+ of 0.76g/l, then any increases of the silver ion concentration leads to decrement of the obtained major particle size. The above mentioned results show that the ratio of silver ion concentration to HEC concentration have to be in the order of 0.54 to be assure complete conversion of the ionic silver to nanosized colloidal silver with major particle size of 35nm. In order to achieve better stability and efficient reduction for conversion of silver ions to silver nanoparticles with extremely small sizes, certain ratio of silver nitrate to HEC in the reaction medium must be established. Hence, preparation of silver nanoparticles was carried out using higher concentrations of both $AgNO_3$ and HEC. Fig. 3C shows particle size distribution histogram when silver nanoparticles were prepared using silver ion source concentration to HEC concentration at 0.54 per 50ml reaction medium. While fig. 3D shows the TEM micrograph and the particle size distribution histogram when silver nanoparticles were prepared using silver ion source concentration to HEC concentration ratio at 0.03 per 50 ml reaction medium. The image shows that at this concentration ratio all the silver ions were converted to 6nm nanosized silver particles. From all the above mentioned silver ion source concentration to HEC concentration ratio of 0.54 is taken as the optimum for preparation of major particle size 35nm nanosized silver particles as our target in paint application. The increment of silver nitrate concentration leads to the decrement of the pH of the medium and this leads to the increment of the medium viscosity which prevents the aggregation of the reduced silver nano particles, thus small nano particles could be obtained with the increasing of silver ion concentration.

Effect of Reaction Temperature

Fig. 4.A shows the UV–Vis spectra of nanosized silver particles prepared at different temperatures. The operating conditions were pH10.6, HEC concentration was 1.4g/l, silver ion concentration of 0.76g/l, silver ion to HEC ratio was 0.54, stirring rate 50rpm and reaction duration 15min. The data indicate that at 60^{O}C the reduction efficiency is not enough for complete transformation of Ag+ into silver nanoparticles. Increasing the reaction temperature above this limit, 80^{0}C leads to the increase of the 35nm major particle size present percentage to about 43% while it was about 37% at 60^{0}C as indicated in fig.4.B and fig. 4.C. Also there is significant enhancement in the absorption band by rising the temperature up to 80^{0}C. It is also clear from the data that preparation of silver nanoparticles at 80^{O}C represents the optimum condition, taking in mind the TEM images as shown in fig.4.D and particle size distribution histograms in fig. 4C of silver nanoparticles prepared.

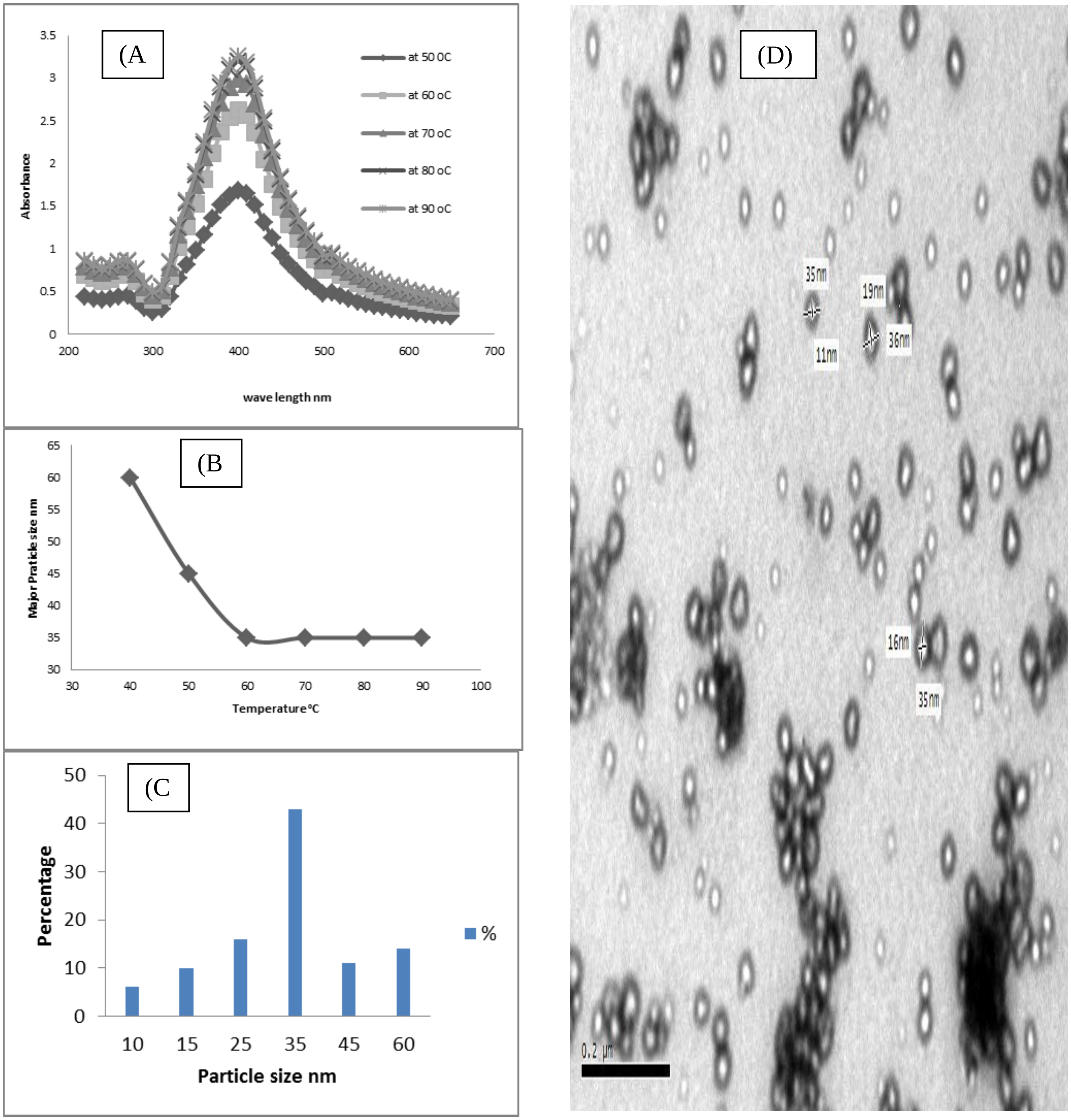


Fig.4 (A) UV–Vis spectroscopy of silver nanoparticles prepared at different reaction temperatures. Reaction conditions: silver ion concentration 0.76g/l, 1.4g/l HEC, pH 10.6; duration 15 min., and stirring rate 50rpm (B) variation of major obtained particle size of nano silver due to variation of reaction temperature. (C) Particle size distribution histogram and (D) TEM image of the sample obtained at 80^{O}C

Effect of reaction duration

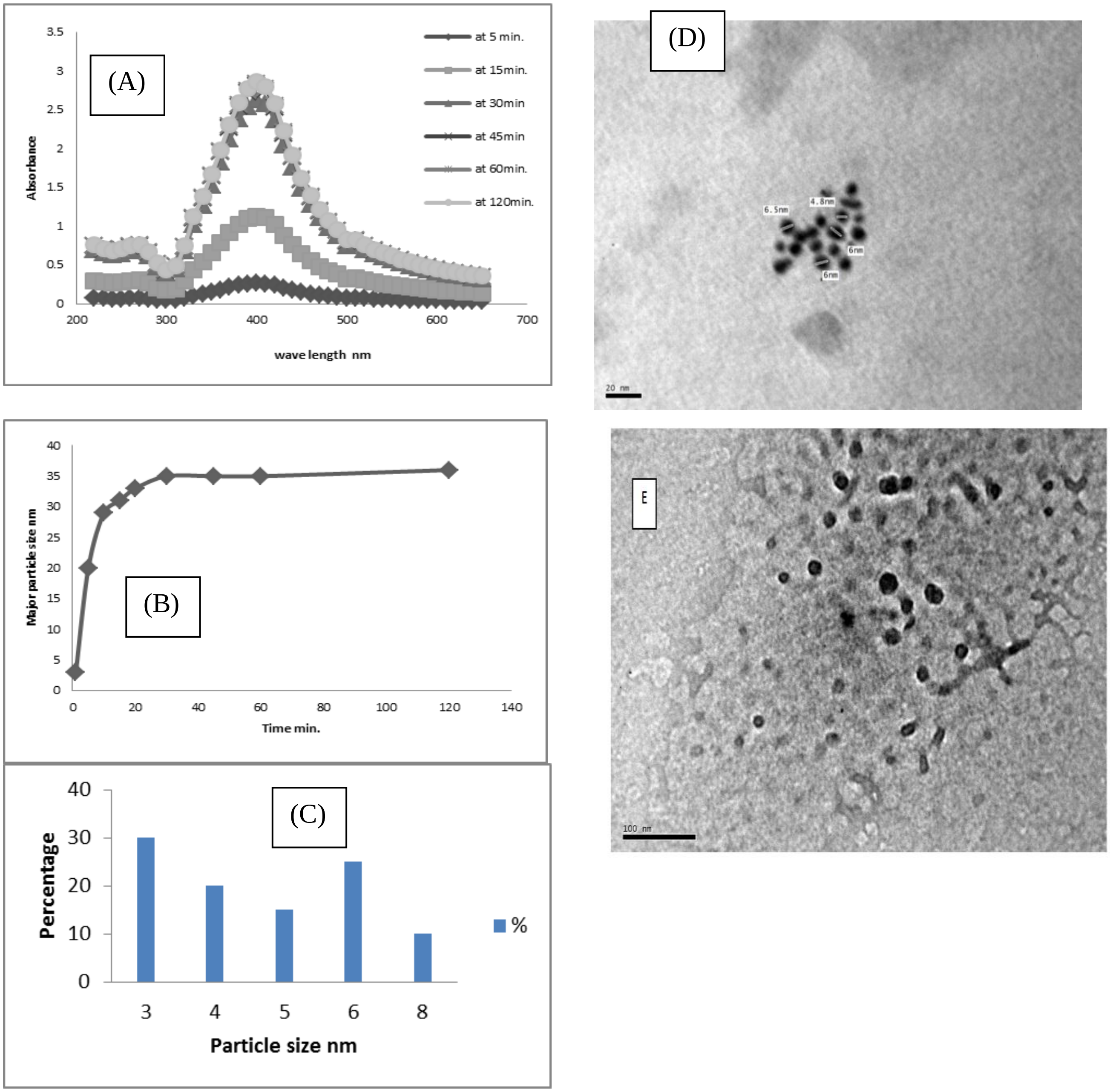


Fig. 5 (A) UV–Vis spectroscopy of silver nanoparticles prepared at different reaction time. Reaction conditions: silver ion concentration 0.76g/l, HEC 1.4g/l , pH 10.6; 80^{0}C., and stirring rate 50rpm (B) variation of major obtained particle size of nano silver due to variation of reaction duration. (C) Particle size distribution histogram and (D) TEM image of the sample obtained after 5min. and (E) TEM image of the sample after 45min.

Fig. 5.A shows the UV–Vis absorption spectra of silver nanoparticles colloidal solutions prepared at different durations. The operating conditions were pH of 10.6, HEC concentration of 1.4g/l, silver ion concentration of 0.76g/l, silver ion to HEC concentration ratio was 0.54,

reaction temperature of 80^{O}C, and stirring rate of 50rpm. The data reveal several important findings which can be presented as follows: (i) at the early stage reaction duration (after 5 min) the Plasmon band is broaden and simple test for silver ion using NaCl solution indicates low conversion of silver ions to metallic silver nanoparticles at this duration, (ii) prolonging the reaction duration up to 45 min leads to outstanding enhancement in the Plasmon intensity indicating that large amounts of silver ions are reduced and used for cluster formation, (iii) further increase in the reaction duration up to 90 min is accompanied by marginal decrement in the absorption intensity which could be attributed to some aggregation of the formed silver nanoparticles, (iv) increasing the reaction duration up to 120 min leads to significant decrease in the absorption intensity. Fig. 5B shows the obtained major particle size present due to the variation of the reaction duration. The results show that as the reaction duration increases the obtained major particle size present increases to reach its maximum 35nm at duration time 45min. then any increment in reaction duration does not affect the obtained particle size. Fig. 5C the particle size distribution histograms of silver nanoparticles formed after 5min while Fig. 5D shows the TEM images of the obtained nano silver after 5mins. The TEM images silver nanoparticles formed after 45min was presented at Fig. 5E. TEM image shows small size spherical particles 5nm after 5min. while it reaches 35nm after 45min. also the corresponding size distribution histogram clearly illustrates that the target size 35nm reaches its maximum percentage at reaction duration 45min. From the above 45min. reaction duration was taken as the optimum.

Effect of Stirring Rate

Fig. 6A shows the UV–Vis spectra of nanosized silver particles prepared at different rate of stirring. The operating conditions were pH of 10.6, HEC concentration of 1.4g/l, silver ion concentration of 0.76g/l, silver ion to HEC concentration ratio was 0.54, reaction temperature 80^{O}C, and reaction duration 45min.The data indicate that at 50rpm the reduction efficiency is not enough for complete transformation of Ag^{+} into silver nanoparticles. Increasing the rate of stirring to 150 rpm leads to the increasing of the 35nm major particle size present percentage to about 57% while it was about 43% at 50rpm as indicated in Fig.6B and Fig. 6C. Also there is significant enhancement in the absorption band by raising the rate of stirring up to 150rpm. It is also clear from the data that preparation of silver nanoparticles at 150rpm represents the optimum condition, taking in mind the TEM images and particle size distribution histograms of silver nanoparticles prepared. Applying selected area electronic diffraction (SAED) test indicating that the obtained material is nano silver as shown in figure 6E.

From the above it is clear that the optimum conditions to get the highest percentage of the desired particle size of nanosized silver (35nm) which is suitable for marine antifouling paint are: pH 10.6, silver ion source concentration 0.76g/l, HEC concentration 1.4g/l, silver to HEC concentration ratio 0.54, reaction temperature 80^{O}C, at reaction duration of 45min. with rate of stirring of 150rpm.

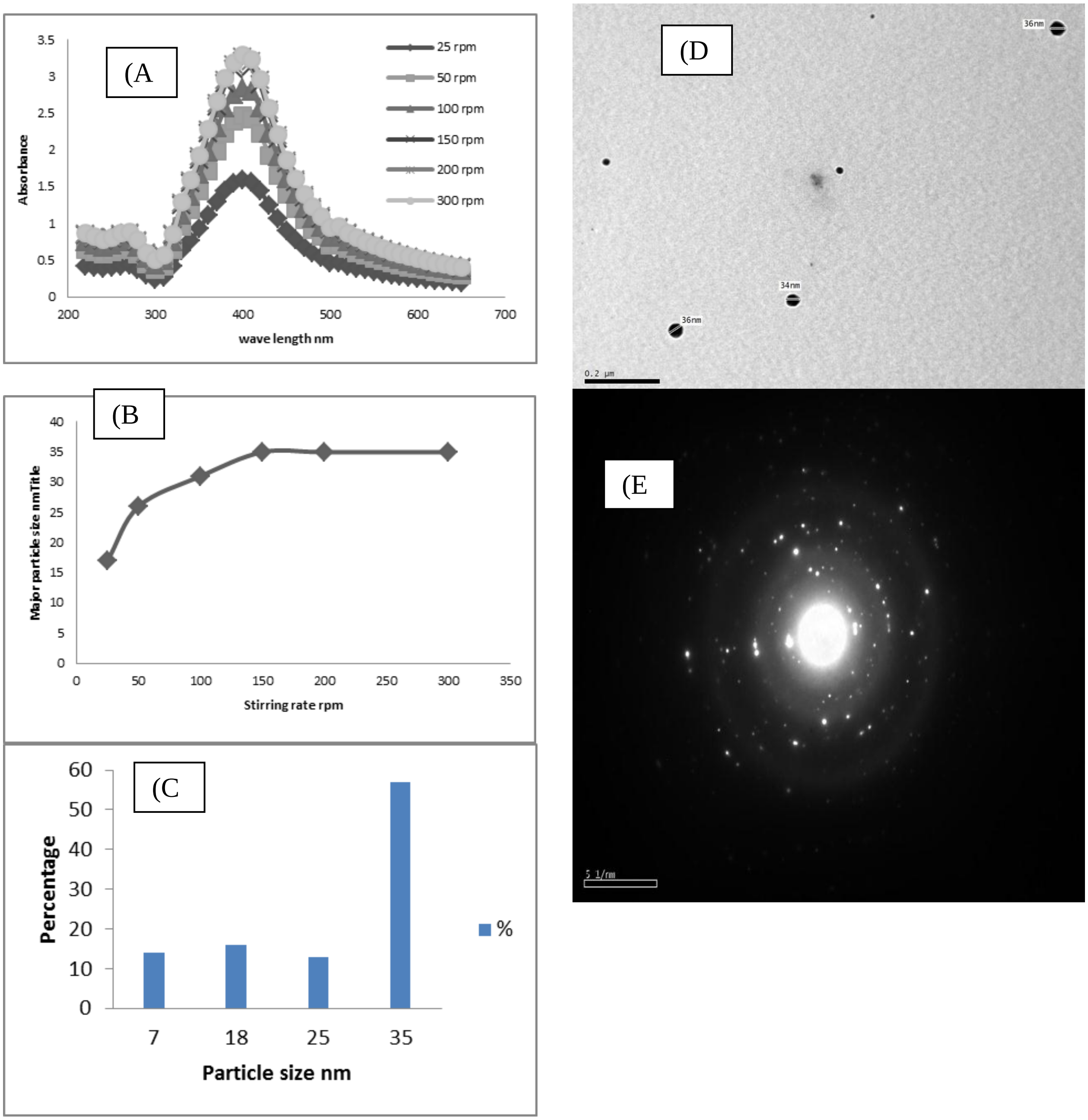


Fig.4.12 (A) UV–Vis spectroscopy of silver nanoparticles prepared at different stirring rates. Reaction conditions: silver ion concentration 0.76g/l, 1.4g/l HEC, pH 10.6; 80^{0}C., and duration time 45min. (B) variation of major obtained particle size of nano silver due to variation of stirring rate. (C) Particle size distribution histogram and (D) TEM image of the sample obtained. (E)

CONCLUSION

Nanosized silver particles of 35nm was prepared in this study as the optimum particle size to used as marine antifouling additive in marine paint composition due to its high antimicrobial and antifungal actions. Wet chemical reduction method was used for the preparation and green hydroxyl ethyl cellulose (HEC) was used as reducing and stabilizing agent. 57% of the desired particle size 35nm was obtained at the optimum operating conditions which are: silver ion concentration of 0.76g/l, HEC concentration of 1.4 g/l with silver ion to HEC concentration ratio of 0.54 and reaction temperature of 80^{O}C for duration of 45min. with rate of stirring of 150rpm at pH of 10.6.

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