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Polyacrylamide/guar gum graft copolymer for preparation of silver nanoparticles

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ABSTRACT

Guar gum/polyacrylamide graft copolymer was prepared in the presence of potassium bromate/thiourea dioxide as initiation system. The so-prepared and separated guar gum/polyacrylamide graft copolymer was used for preparation of silver nanoparticles through reduction of silver nitrate under certain conditions. For comparison, guar gum, polyacrylamide and guar gum/polyacrylamide composite were used individually for the preparation of silver nanoparticles under the same conditions. UV–vis spectra of nanosilver prepared using polyacrylamide showed relatively good plasmon intensity after 45 min but prolonging the reaction time up to 60 min brought about noticeable decrease in the absorption intensity. Using guar gum for nanosilver preparation, the trend in the UV–vis spectra was found to be the same as in case of using polyacrylamide but the peak at 45 min showed higher absorption intensity and the decrease in the absorption intensity after 60 min was not so much. Using the composite or the separated graft copolymer in nanosilver preparation, the UV–vis spectra showed high improvement in the absorption intensity at 45 min and the peaks acquire ideal bell shape, which means that the reduction power got higher. Also no decrease in the peak intensity was noticed after 60 min, which means that the graft copolymer has better stabilization efficiency than each individual component alone.

1. Introduction

Nanoparticles display exclusive spectroscopic, electronic, and chemical properties that arise from their smaller size and large specific surface area, which differ appreciably from those of bulk materials (Watanabe, Menzel, Nilius & Freund, 2006).

A variety of routes have been reported for the preparation of metallic nanoparticles (Pal, Shah & Devi, 2007), notable examples include, reverse micelles process (Song et al., 2007; Xie, Ye & Liu, 2006), salt reduction (Fan et al., 2008; Khanna & Subbarao, 2003; Pillai & Kamat, 2004; Sondi, Goia & Matijevi, 2003), without any reductant in an autoclave (Vigneshwaran, Nachane, Balasubramanya & Varadarajan, 2006), irradiation (Kassaee, Akhavan, Sheikh & Beteshobabrud, 2008) and electrochemical synthesis (Starowicz, Stypuła & Banaś, 2006; Zhu, Liao, Zhao & Chen, 2001).

Increasing the awareness towards green chemistry and other biological processes has led to a desire to develop an eco-friendly approach for the synthesis of nanoparticles which has several advantages such as simplicity, cost effectiveness, compatibility for biomedical and pharmaceutical applications as well as for large-scale commercial production. In very recent years, many interesting methods are being applied currently to the green preparation of nano-sized metal particles (El-Rafie, Mohamed, Shaheen & Hebeish, 2010; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim & Emam, 2010; Liu, Qin, Raveendran & Yukata, 2006; Lu, Gao & Komarneni, 2005, 2006; Raveendran, Fu & Wallen, 2003; Shin, Blackwood, Bae, Arey & Exarhos, 2007; Shin, Bae & Exarhos, 2009). Most of the synthetic methods reported to date for preparation of silver nanoparticles rely heavily on the use of organic solvents and toxic reducing agents like hydrazine (Sakai, Kanda, Shibata, Ohkubo & Abe, 2006), N,N-dimethylformamide (Pastoriza-Santos & Liz-Marzán, 2002) and sodium borohydride (Van Hyning, Klemperer & Zukoski, 2001). All these chemicals are highly reactive and pose potential environmental and biological risks. With the increasing interest in minimization/elimination of waste and adoption of sustainable processes, the development of green chemistry approaches is desirable. Earlier reports have dealt with natural polymers like chitosan (Huang & Yang, 2004), heparin (Yanli1 & Hongtao, 2008) and soluble starch (Vigneshwaran et al., 2006) as reducing and stabilizing agent for preparation of silver nanoparticles.

Plant extracts and gums have been used for stabilizing colloidal metal dispersions and in that category, guar gum or gum acacia is a well-known polysaccharide with a high molecular weight that can be derived from the acacia tree. This natural polymer is extensively used in confectioneries and soft drink processing because it has an inherent ability to emulsify and stabilize flavoring oil

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dispersed in an aqueous medium. Moreover, gum acacia polymer has been employed for solid–liquid dispersion applications. This natural polymer not only is very low cost and abundantly available in nature but also has excellent emulsifying and surface-active properties, which would be beneficial for the design of metal nanoparticles.

Grafting of synthetic polymers onto biopolymers results in novel products having wide range of applications. This way of chemical modification yields new molecules with desirable properties of both biopolymer and synthetic polymer. Modern technologies require materials with precisely tuned properties by varying a set of parameters during synthesis, i.e. tailor-made materials. Grafted polymers fit well in this category of materials as their properties can be precisely controlled by controlling the percentage grafting.

Chemical grafting is one of the most effective methods of modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides (Chen et al., 2005; Joshi & Sinha, 2007; Ly et al., 2010; Meshram, Patil, Mhaske & Thorat, 2009; Rui-He et al., 2006; Singh, Sharma, Tripathi & Sanghi, 2009; Szamel, Domjan, Klebert & Pukanszky, 2008; Zhu, Dong, Wang & Wang, 2010). The grafted polymers are usually synthesized by conventional redox grafting method (da Silva, de Paula & Feitosa, 2007; Hebeish, Abd El-Thalouth, El-Kashouti & Abdel-Fattah, 2003; Kaith, Singha & Kalia, 2007; Kang, Cai & Liu, 2006; Singh, Tiwari & Sanghi, 2005), by microwave irradiation (Kaith et al., 2007; Masuhiro, Shafiul, Takayuki, Alessandra & Giuliano, 2005; Singh, Tiwari, Pandey & Singh, 2007), by γ-ray irradiation (Geresh et al., 2004; Wang, Chen, Zhang, & Yu, 2008; Xu, Yang, Jiang, Sun, & Pang, 2008) or by using electron beam (Vahdat, Bahrami, Ansari, & Ziaie, 2007).

The aim of the present work is to prepare strong reducing and stabilizing agent for green synthesis of silver nanoparticles, through grafting of acrylamide onto guar gum.

2. Experimental

2.1. Chemicals

Guar gum was supplied by Fluka and acrylamide was supplied by Aldrich. Potassium bromate, thiourea dioxide, sulfuric acid, silver nitrate and sodium hydroxide were all laboratory grade reagents.

2.2. Preparation of polyacrylamide/guar gum graft copolymer

Twenty grams of guar gum was dissolved in 100 ml water and pH 2–2.5 was adjusted using dilute sulfuric acid. Ten grams of acrylamide, dissolved in 20 ml water was added to the guar gum solution and the temperature of the medium was raised to 60 °C under continuous stirring. At this end potassium bromate (6 mmol/100 g gum) and thiourea dioxide (6 mmol/100 g gum) were added and the polymerization reaction was allowed to proceed for 120 min. Polyacrylamide/guar gum graft copolymer was separated from the homopolymer (polyacrylamide) via precipitation using alcohol (Abdel-Halim, Emam & El-Rafie, 2008). The graft copolymer was washed thoroughly with alcohol, dried, ground and its nitrogen content was determined according to standard Kjeldhal method (Vogel, 1975). The graft yield was calculated from the measured nitrogen content and was found to be 40%.

2.3. Preparation of silver nanoparticles

Four substrates were used individually to prepare silver nanoparticles, namely, polyacrylamide (A), guar gum (B), the so-prepared polyacrylamide/guar gum composite (without separating the graft copolymer from the homopolymer) (C) and the separated polyacrylamide/guar gum graft copolymer (D). This is done to compare the efficiency of each substrate as reducing and/or stabilizing agent in the preparation of silver nanoparticles. 0.3 g of each substrate was dissolved in 100 ml distilled water using heating magnetic stirrer. After complete dissolution, the pH of the solution was adjusted to 12.5 using dilute sodium hydroxide solution, followed by raising the temperature of the reaction medium to 70 °C. One millilitre of 0.1 N silver nitrate solution was then added drop wise. The reaction mixture was kept under continuous stirring for 60 min (Hebeish et al., 2010). Short time after addition of silver nitrate, the reaction medium acquires a clear yellow color indicating the formation of silver nanoparticles. The progression of the reaction was controlled by recording UV–vis absorption; aliquots from the reaction bulk were withdrawn at given time intervals and evaluated.

2.4. Characterization

Ultraviolet–visible (UV–vis) spectra were measured on a 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. Transmission electron microscopy (TEM) images were recorded with a Tecnai (Phillips, Oregon, USA) F 12 Transmission Electron Microscope. TEM samples were prepared by the dispersion of 2–3 drops of the colloidal silver nanoparticles solution on a copper grid and dried at room temperature after the removal of excess solution with filter paper.

3. Results and discussion

Polymers having large number of hydroxyl groups represent a dynamic supramolecular associations rich in inter- and intramolecular hydrogen bonding resulting in molecular level capsules, which can act as ideal templates for nanoparticle growth and stabilization (Raveendran et al., 2003). UV–vis absorption spectra have been proved to be quite sensitive to the formation of metal nanoparticles, especially silver because silver nanoparticles exhibit an intense absorption peak at 405 nm due to the surface plasmon excitation, which represents the collective excitation of conduction electrons in the metal (Filippo, Serra, & Manno, 2009).

In this study we have evaluated four substrates for their reduction and stabilization efficacy towards silver nanoparticles, namely, polyacrylamide (A), guar gum (B), the so-prepared polyacrylamide/guar gum composite (without separating the graft copolymer from the homopolymer) (C) and the separated polyacrylamide/guar gum graft copolymer (D). The evaluation was done by following up the UV–vis spectra of silver nanoparticles prepared using these different substrates at different time intervals and then taking and analyzing TEM images for the prepared nanoparticles at the end of the reaction duration (60 min).

Significant information drawn from the UV–vis spectra of silver nanoparticles produced using polyacrylamide alone (A) (Fig. 1) illustrates that polyacrylamide has low reduction potential to convert silver ions to silver nanoparticle, that at the early stage reaction duration (after 15 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. Prolonging the reaction duration up to 30 min, then 45 min leads to enhancement in the plasmon intensity indicating that larger amounts of silver ions are reduced and used for cluster formation. Further increase in the reaction duration up to 60 min is accompanied by noticeable decrease in the absorption intensity which could be attributed to some aggregation of the formed silver nanoparticles. This aggregation gives an indication about the low stabilization ability of polyacrylamide alone.

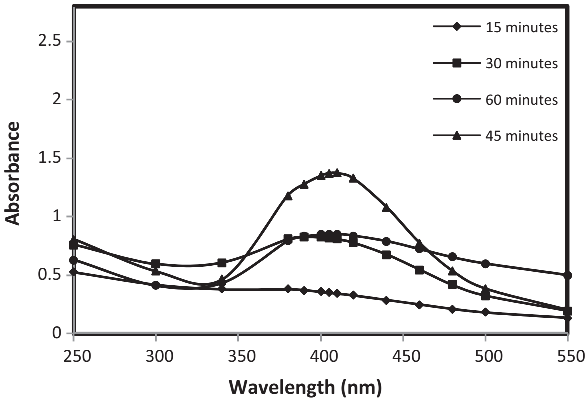

Fig. 1. UV–vis spectroscopy of silver nanoparticles prepared using polyacrylamide. Reaction conditions: polyacrylamide concentration, 0.3% (w/v); 1 ml (0.1 N) $AgNO_3$/100 ml solution; pH 12.5; temperature, 70 °C; duration, 60 min.

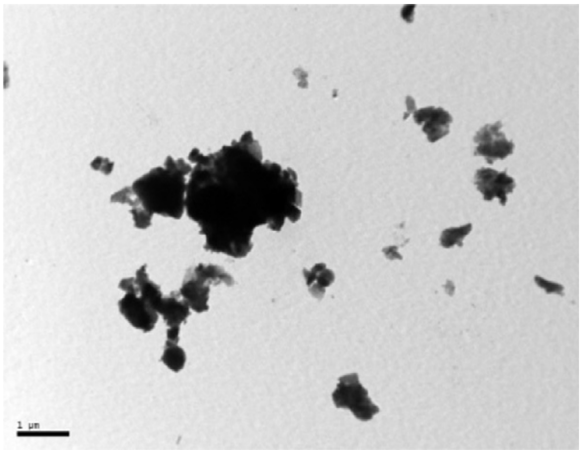

Fig. 2. TEM monograph of silver nanoparticles produced using polyacrylamide.

Fig. 2 shows typical TEM image of silver nanoparticles extracted from polyacrylamide. The nanoparticles should be found as dark spherical objects, but actually instead of spherical objects, the image shows aggregates from silver nanoparticles, that is why it was not possible to get particle size distribution histogram for silver nanoparticles in this case. The aggregates noticed in the TEM image, again indicates the low reduction/stabilization effect of polyacrylamide alone.

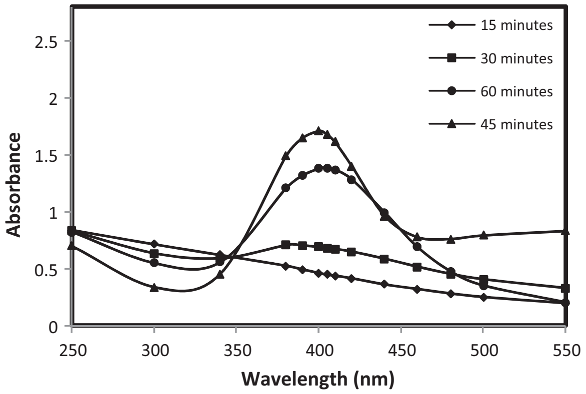

Fig. 3. UV–vis spectroscopy of silver nanoparticles prepared using guar gum. Reaction conditions: guar gum concentration, 0.3% (w/v); 1 ml (0.1 N) $AgNO_3$/100 ml solution; pH 12.5; temperature, 70 °C; duration, 60 min.

Fig. 3 shows the UV–vis spectra of silver nanoparticles produced using guar gum alone (B). The trend is more or less the same as in case of polyacrylamide but the peak at 45 min in case of using guar gum shows higher absorption intensity than the corresponding peak using polyacrylamide, which indicates better reduction. Also the decrease in the absorption intensity after 60 min due to aggregation is not so much compared with the corresponding decrease using polyacrylamide, which indicates better stabilization effect for guar gum.

Fig. 4 shows typical TEM image and particle size distribution histogram of silver nanoparticles extracted from guar gum solution. The nanoparticles are found as dark spherical objects. The size distribution was obtained by measuring the diameter of particles present in the TEM image. The histogram shows wide particle size distribution ranging from 10 nm to 30 nm.

Figs. 5 and 6 show the UV–vis spectra of silver nanoparticles produced when using the composite (C) and the separated graft copolymer (D), respectively, for the production of silver nanoparticles. The two figures show high improvement in the absorption intensity at 45 min and the peaks acquire ideal bell shape, which means that the reduction power got higher when polyacrylamide and guar gum were combined together in graft copolymer. Also no decrease in the peak intensity was noticed on prolonging the reaction duration up to 60 min, which means that the graft copolymer has better stabilization efficiency than each individual component alone. However, comparing UV–vis spectra of silver nanoparticles prepared using substrate (D) to those prepared using substrate (C), it is clear that the peak intensity of silver nanoparticles prepared

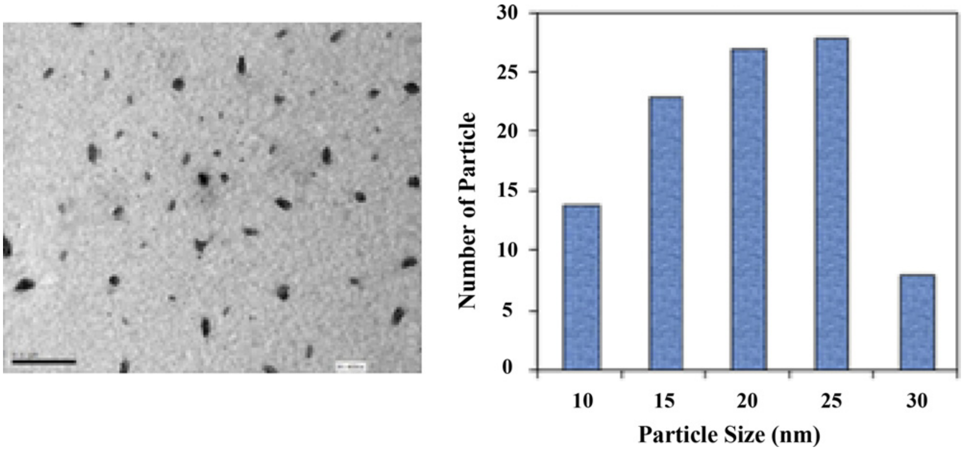

Fig. 4. TEM monograph and particle size distribution histogram of silver nanoparticles produced using guar gum.

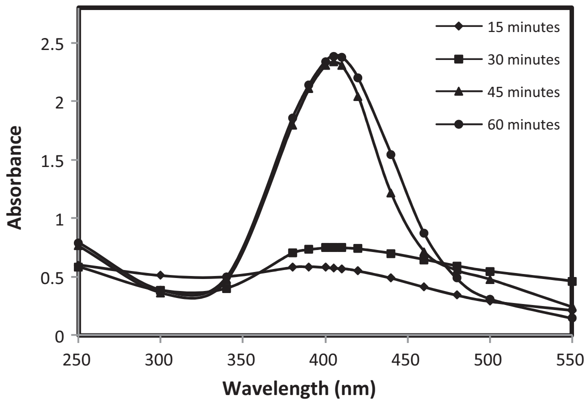

Fig. 5. UV–vis spectroscopy of silver nanoparticles prepared using composite. Reaction conditions: composite concentration, 0.3% (w/v); 1 ml (0.1 N) $AgNO_3$/100 ml solution; pH 12.5; temperature, 70 °C; duration, 60 min.

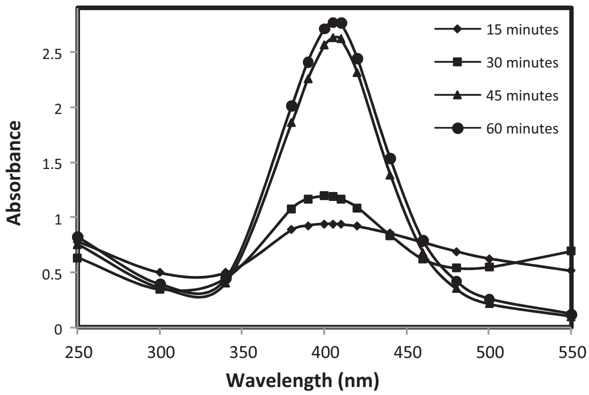

Fig. 6. UV–vis spectroscopy of silver nanoparticles prepared using graft copolymer. Reaction conditions: graft copolymer concentration, 0.3% (w/v); 1 ml (0.1 N) $AgNO_3$/100 ml solution; pH 12.5; temperature, 70 °C; duration, 60 min.

using (D) is higher. Also when comparing the TEM images and particle size distribution histograms of silver nanoparticles extracted from substrate C (Fig. 7) and those extracted from substrate D (Fig. 8), one can notice that in case of using substrate D, 85% of the nanoparticles fall within the narrow range of 15–20 nm, while in case of using substrate C, the histogram shows wide range of particle size distribution.

Understanding the interaction of the polymer matrix with the metal precursor and the resulting metal colloid is very important to get small-sized and homogeneous dispersion of metal nanoparticles. The nanoparticles could have grown through reduction of silver ions inside the polymeric templates, where the hydroxyl and carboxyl groups of guar gum acting as passivation contacts (Gils, Ray & Sahoo, 2010). In case of graft copolymer, the graft network acts as reservoir for metal ions uptake and the silver ions are anchored through carboxylic and hydroxyl groups of the guar gum chain in addition to the ligand effect of the residual amide groups of polyacrylamide, thereby hold larger amounts of metal ions in their network and facilitate the reduction process as well as help in stabilization. For the stabilization of the nanoparticles,

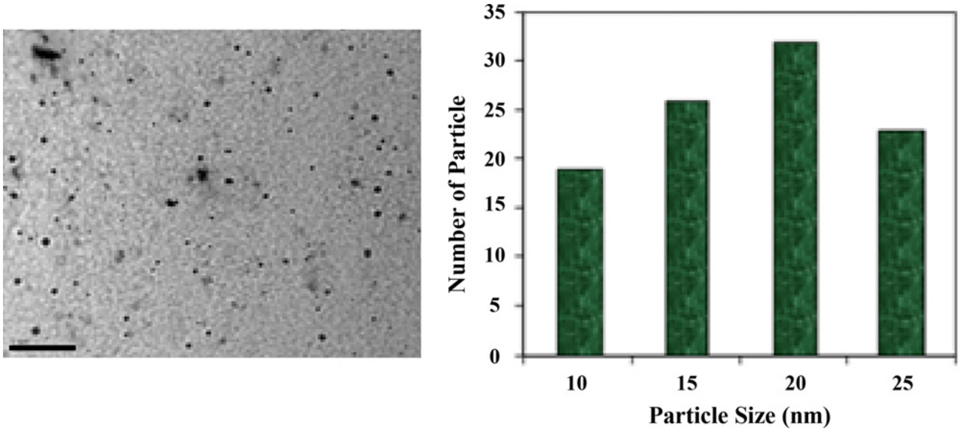

Fig. 7. TEM monograph and particle size distribution histogram of silver nanoparticles produced using polyacrylamide/guar gum composite.

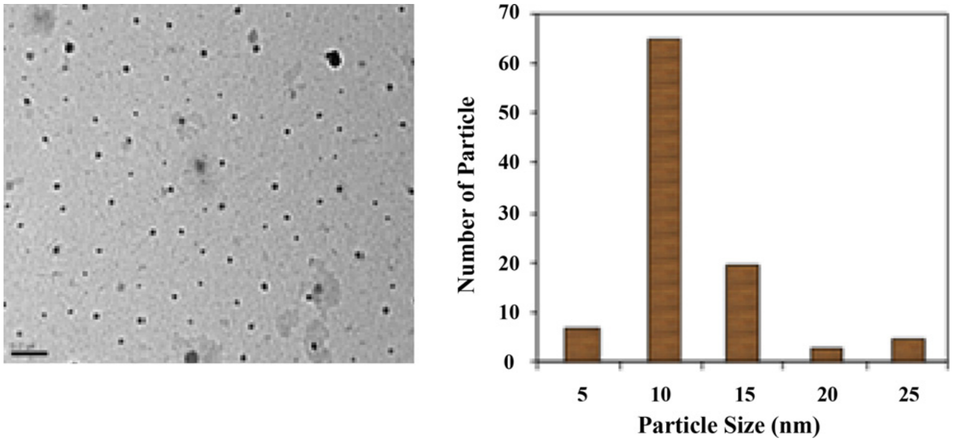

Fig. 8. TEM monograph and particle size distribution histogram of silver nanoparticles produced using the separated polyacrylamide/guar gum graft copolymer.

the uniformly distributed functional groups inside the polymeric template provide electron-rich oxygen atoms as binding sites for Ag+ ions that were later reduced to give uniformly distributed Ag nanoparticles (Mohan, Raju, Sambasivudu, Singh & Sreedhar, 2007). Guar gum component in the copolymer arrests the agglomeration of silver nanoparticles, that the intramolecular and intermolecular association of guar gum lead to the formation of hydrogen bonds, which are ultimately responsible for network formation within the polymeric chains, and these networks provide nanoscopic domains in which the nanoparticles can grow. Because of the complexation ability of the guar gum with silver metal nanoparticles through the carboxyl-functional groups of the polymeric chains and networks, they surround and protect the particles over longer periods. On the other hand, a strong physical adsorption of the guar gum onto the surface of the silver nanoparticles is also an indication of better stabilization. Polyacrylamide side chains in the copolymer not only modifies the guar gum properties, but also allows achieving extra stabilization of the nanoparticles, because vinyl polymers having high density of polar groups in side chain can stabilize metal nanoparticles grown in the matrix at nanometric dimension because they wrap the particles avoiding the agglomeration.

4. Conclusion

Potassium bromate/thiourea dioxide was used to initiate graft copolymerization of acrylamide onto guar gum. Aqueous solution of the so-prepared and separated guar gum/polyacrylamide graft copolymer was used for preparation of silver nanoparticles through reduction of silver nitrate under certain conditions. For comparison, guar gum, polyacrylamide and guar gum/polyacrylamide composite (without separating the graft copolymer from the homopolymer) were used individually for the preparation of silver nanoparticles under the same conditions. UV–vis spectra of nanosilver prepared using polyacrylamide showed relatively good plasmon intensity after 45 min but prolonging the reaction time up to 60 min brought about noticeable decrease in the absorption intensity which could be attributed to some aggregation of the formed silver nanoparticles, an assumption which was confirmed by TEM imaging. Using guar gum in preparation of nanosilver, the trend in UV–vis spectra was found to be the same as in case of using polyacrylamide but the peak at 45 min showed higher absorption intensity, indicating better reduction efficiency and also the decrease in the absorption intensity after 60 min due to aggregation was not so much, which indicates better stabilization effect for guar gum. Using either the composite or the separated graft copolymer in preparing nanosilver, the UV–vis spectra showed high improvement in the absorption intensity at 45 min and the peaks acquired ideal bell shape, which means that the reduction power got higher when polyacrylamide and guar gum were combined together in graft copolymer. Also no decrease in the peak intensity was noticed after 60 min, which means that the graft copolymer has better stabilization efficiency than each individual component alone. However, TEM images showed that 85% of silver nanoparticles prepared using the separated graft copolymer fall within the narrow range of 15–20 nm, while in case of using the composite for silver nanoparticles preparation, the histogram showed wide range of particle size distribution.

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