Ecofriendly peanut skin extracts mediated in situ fabrication of rGO@AgNCs for degradation of dyes

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Abstract
The study reports facile green *in situ* method for fabrication of reduced graphene oxide (rGO) based silver nanocomposites (rGO@AgNCs) using peanut skin (*Arachis hypogaea)* extract. The synthesized rGO@AgNCs were characterized by UV-visible spectroscopy, FTIR, SEM, EDX, particle size and zeta potential analysis. Furthermore, methylene blue (MB) and malachite green (MG) dyes degradation ability of rGO@AgNCs was investigated. The MB and MG dyes were found to be eliminated completely within 40 minutes in dark condition in the presence of 5 mg rGO@AgNCs.The investigation describes an ecofriendly and cost effective method for the *in situ* synthesis rGO@AgNCs.

Keywords: Nanocomposites, Carbon materials, Agriculture waste, Nanoparticles, Peanut skin, Dye degradation.

Introduction
Graphene oxide (GO) and GO based nanocomposites has recently drawn much attention as an effective in varieties of applications including adsorption platform owing to its high surface area, distinct electronic and mechanic properties.[1,2] Silver nanoparticles can be synthesized by numerous methods viz. chemical reduction and green approaches.[3] Several methods have been well documented in the literature for synthesis of graphene silver nanocomposites.[4,5] However, this suffers from many disadvantages such as the use of hazardous chemicals, time consuming and costly. Hence the present investigation is an attempt to afford a sustainable method for fabrication of graphene silver nanocomposites using peanut skin extract.

Dyes have potential application in various industries.[6] Removal of color from dye bearing wastewater is a complex problem.[7,8] Several methods have been reported previously including adsorption for the treatment of dye bearing effluents, but are generally inefficient for the complete removal of dyes.[9,10] Peanut is an important food crop grown in more than 100 countries with overall production of 38 million tons.[11] The peanut skin has a pink-red color and is typically removed before peanut consumption or inclusion in confectionery and snack products therefore it is considered as agricultural waste. The chemical constituents present in peanut skin are phenol, carbohydrate, flavanoids and terpenoids etc.[12,13]

Several chemical as well as physical processes have been widely explored for the synthesis of graphene-metal nanomaterials.[14] On the other hand, these methods face challenges such as use toxic chemicals as reducing as well as capping agents. Therefore, there has been a huge demand for development of ecofriendly and cost-effective synthesis of metal nanoparticles.[3,15] Green synthesis of GO-AgNCs were achieved using an environmentally friendly reducing agents viz., amino acid,[16] vitamin C[17] and peanut shell.[18]

Therefore, in the present investigation an innovative attempt of *in situ* fabrication of reduced graphene oxide silver nanocomposites (rGO@AgNCs) was made by exploring agro waste i.e peanut skin extracts as an ecofriendly and a cost-effective method for degradation of dyes.

Experimental methods

Preparation of Arachis hypogaea L.(Peanut Skin) extract (PSE)

The peanut skin extract was prepared by taking 10 gm of fresh peanut skin, washed thoroughly with in 100 mL of beaker then the addition of 50 mL of distilled water and boiled for 15 min. prepared extract was filtered and used for further reaction and tested for presence of several potential phytoconstituents.[19,20]

Preparation of rGO@AgNCs

Graphene oxide (10 mg), $AgNO_3$ (10 mg) and polyethylene glycol-400 (5 mL) were mixed and triturated in a mortar for 30 min. Subsequently, PSE (5 ml) was added and the mixture was triturated for 60 min. In the course of process, light brown colour changes to dark brown to black this indicate formation of rGO@AgNCs.Finally, the solution was centrifuged at 14000 rpm for 10 min and the precipitate was washed with distilled water and ethanol. The final product was dried and used as it is for further studies.

Dye elimination activity

Exactly 50 ml of the 5 ppm dye (MG and MB) solution was added with rGO@AgNCs and stirred in the dark. A known volume of the slurry was drawn at specific intervals and absorbance was recorded for MB and MG (665 and 617nm respectively). The percentage removal of the dye was determined using the relation % of elimination = $(C_i - C_f / C_i) * 100$ Where, C_i and C_f are initial and final dye concentrations, respectively.

Results and Discussion

Phytochemical studies

Majorly, flavonoids, carbohydrate, alkaloids, phenols and terpenoids were found present, whereas steroids and amino acids were absent.

UV Spectroscopy Analysis

The UV–vis absorbance spectrum (UV 1700/1800 spectrophotometer, Shimadzu) of rGO@AgNCs demonstrated the peak around 418 nm which confirmed the successful Ag nanoparticle deposition onto the graphene surface. In addition, the peak was observed at 269 nm indicated the concurrent partial reduction of GO.

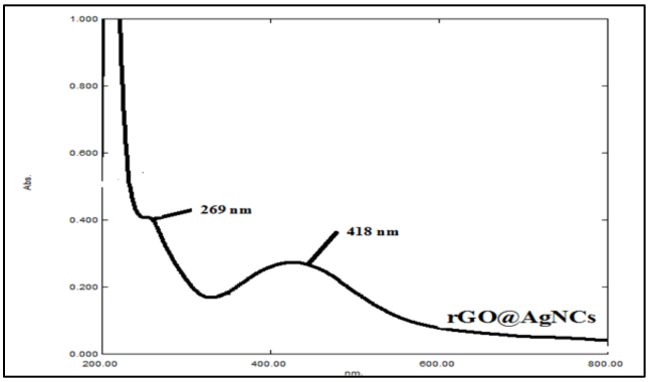

Fig. 1: UV spectrum of rGO@AgNCS

Scanning electron microscopy (SEM) analysis

The Fig 2 shows typical SEM images (Bruker, 1530-2 FESEM/ EDX) of the rGO@AgNCs, which reveals existence of AgNC attached randomly in discrete manner on the fold like surface of the rGO. The folded structure appearing on the surface of the particles could be attributed the existence of rGO. Overall, the morphological finding indicates the Ag ions were introduced via strong cooperation with terminal oxygen containing functional groups on the rGO nanosheets. These SEM results confirmed successful exfoliation of GO and decoration of Ag particles.

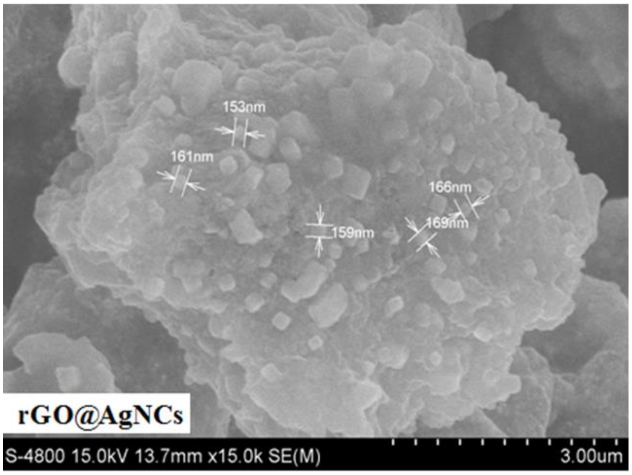

Fig. 2: SEM image of rGO@AgNCs

Elemental analysis using EDX

The spectrum of rGO@AgNCs (Fig. 3) exhibited the presence of 24.53 % silver, 34.25 % oxygen and 41.22 % carbon respectively. It was clearly evident that the percentage of oxygen was decreased in rGO@AgNCs compared to GO due to *in situ* reduction of GO and simultaneous deposition of silver nanoparticles on the surface of GO.

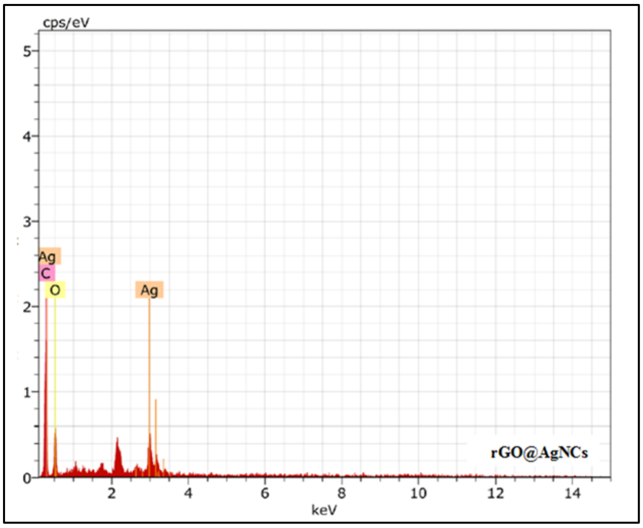

Fig. 3 EDX spectra of rGO@AgNCs

Particle size and zeta potential analysis

The average particle size (Nanoplus 3, Micromeritics, USA.) of the prepared rGO@AgNCs was found to be 137.2 nm (Fig. 4) and the zeta potential was found to be 31.58 mV.

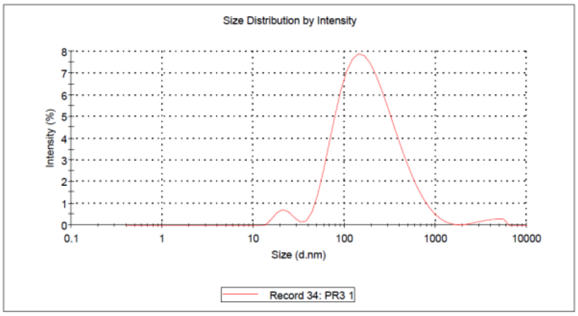

Fig. 4: Particle size of rGO@AgNCs

Dye degradations

The dye degradation using rGO@AgNCs has shown that both MG and MB almost degraded completely within 40 minutes in the presence of 5 mg rGO@AgNCs (Fig. 5). The rGO@AgNCs showed optimum dye degradation may be due to the loading of 24.53% of Ag ions.

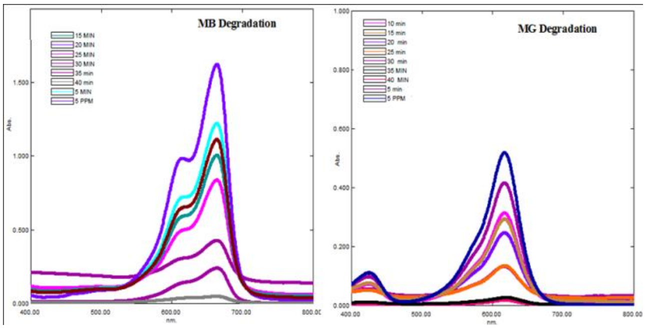

Fig. 5: MB and MG degradation using rGO@AgNCs.

Conclusion

We have reported a single step and simple green *in situ* synthesis method for fabrication of the rGO@AgNCs using peanut skin extract. Therefore, the exploration of agro-waste is believed as a promising strategy to prepare diverse kinds of graphene based metal nanocomposites for various environmental applications.

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None.

Conflict of Interest

None.

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