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PHOTODEGRADATION STUDY OF METHYLENE BLUE ON SILVER NANOPARTICLES AND GRAPHENE OXIDE

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ABSTRACT-Nowadays, plant mediated synthesis of nanoparticles has great interest and achievement due to its eco-benign and low time consuming properties. In this study, silver nanoparticles were successfully synthesized by using Terminalia Arjuna leaf extract and Graphene oxide produced using the simple Hummer's method. Synthesized nanoparticles were characterized by UV-Vis spectrophotometer. Dispersity and morphology was characterized by scanning electron microscope (SEM); crystalline nature and purity of synthesized nanoparticles were revealed by X-ray diffraction (XRD) and their FTIR spectra were examined to identify the effective functional groups responsible for the reduction and stabilization of nanoparticles.. The photocatalytic activity of the synthesized nanoparticles was examined by degradation of methylene blue under sunlight irradiation. The percentage of degradation of dye was compared.

Keywords- [Degradation of Dye, Terminalia Arjuna, Silver nanoparticles, Graphene oxide, methylene blue.]

1. INTRODUCTION

Nanoparticle changes in fundamental ways from the properties of both individual atoms/molecules and of the corresponding bulk materials. Their extremely large surface area permits the coordination of a vast number of ligands. The properties of silver nanoparticles applicable to human treatments are under investigation in laboratory and animal studies, assessing potential efficacy, toxicity, and costs [1]. Graphite oxide, formerly called graphitic oxide or graphitic acid, is a compound of carbon, oxygen, and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers.

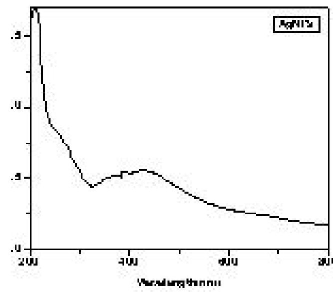
2. SYNTHESIS OF SILVER NANOPARTICLES

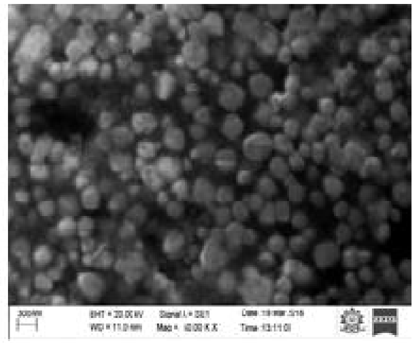
Terminalia arjuna leaves were collected from our College campus in the month of January. The fresh leaves were washed several times with running tap water and after that with distilled water. Around 20g of leave were weighted and boiled for 1h in 100ml double distilled water at 60^0C and then the extracts were filtered through whatman filter paper. Then the filtered extract was stored in refrigerator at 4^0C for further use in synthesis of silver nanoparticles.Graphene oxide[GO] was synthesized by modified Hummer's method [2,3]. The synthesized graphite oxide was then dispersed in water and sonicated for to get GO.

3. RESULTS AND DISCUSSION

3.1 CHARACTERISATION OF SILVER NANOPARTICLES

The UV-Visible spectrum was recorded in the wavelength range between 200nm and 800nm. Figure 3.1(a) displays an optical absorption band peak at about 440 nm which is of absorption for metallic Ag nano cluster. Leaf extracts potential in reducing silver nitrate to form silver nanoparticles. From the SEM image of biosynthesized silver nanoparticles, it is evident that the morphology of the biosynthesized silver nanoparticles is spherical in shape with the average size of 154nm.



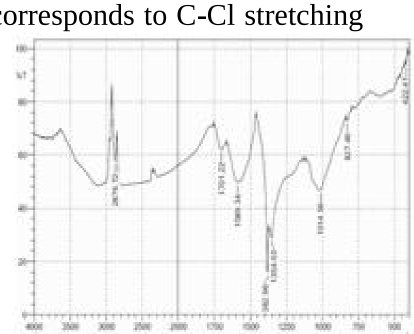


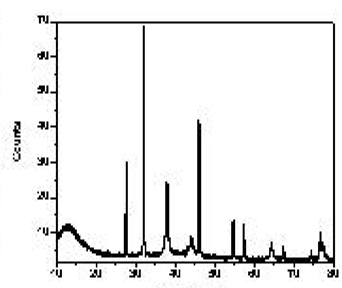
(a) (b)

Figure 3.1- (a) UV-visible Spectra Analysis of AgNPs (b) SEM images of silver nanoparticles

FTIR spectrum of biosynthesized Ag NPs shows different major peak positions at 2879.72, 1701.22, 1589.34, 1382.96, 1354.03, 1014.56, 827.46, 422.41 cm^{-1}. The peaks at 2879.72cm^{-1} corresponds to C-H bond stretching vibration of alkenes. The peak found around 1589.34cm^{-1} showed the band corresponds to the bending vibrations of the amide I and amide II bands of proteins respectively. The peaks at 1382.92 cm^{-1} and 1354.03 cm^{-1} assigned to nitro N-O bending. The peak at 1014.56 cm^{-1} corresponds to C–N stretching vibration of the amine. Silver Nanoparticles showed the band between 850-550 cm^{-1} corresponds to C-Cl stretching alkyl halides. The peaks at 422cm^{-1} are related to AgNPs bonding with hydroxyl groups. Therefore, it may be inferred that presence of biomolecules in leaf extract are responsible for capping and efficient stabilization of synthesized nanoparticles.

X-RD pattern of the plant derived AgNPs (Fig 3.2 (b)) shows four intense peaks in the whole spectrum of 2θ values ranging from 20° to 80° . All the reflections correspond to pure silver with cubic symmetry. The Observed peak for silver matches with the JCPDS values [(01-089-3722)], shows two prominent peaks having (2 2 0) (2 2 2).





(a) (b)

Figure 3.2- (a)FTIR spectrum of silver nanoparticles (b) X-RD spectrum of biosynthesized AgNPs

The average particle size of Ag-NPs can be calculated using the Debye – Scherrer's equation, $D = K \lambda / \beta \cos\theta$, where, K is the Scherrer's constant with value from 0.9 to 1 (shape factor), λ is the X-ray wavelength (1.5418 Å), β is the width of the X-RD peak at half-height and θ is the Bragg angle and D is the grain size. The grain size of the biosynthesized AgNPs is found to be around 38nm.

3.2 CHARACTERISATION OF GRAPHENE OXIDE

UV−Vis spectrum of GO is shown in Fig 3.3(a). The peaks at 216 nm and 294 nm (shoulder) could be ascribed to π−π* transition and n−π* transitions. The honeycomb structure of graphene and graphene oxide contains C=C which has sp^2 hybridized orbital with ($-2p_y$ and $-2p_y$ overlap or $-2p_z$ and $-2p_z$) overlapping to produce π bond between one carbon atom to another carbon atom. Hence, there is a possibility of π−π* transition at 216 nm. Figure 3.3(b) shows the SEM micrographs of graphene oxide at various magnification ranges. It is observed that the prepared Graphene oxide have like ultra-thin and homogeneous films of the layered structures.

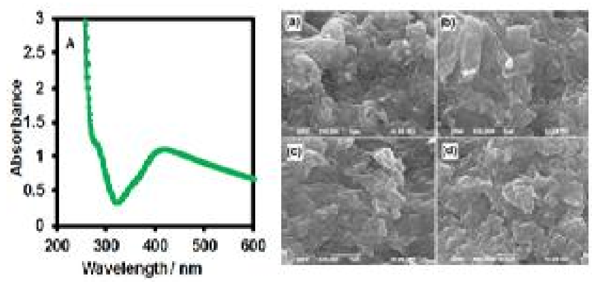
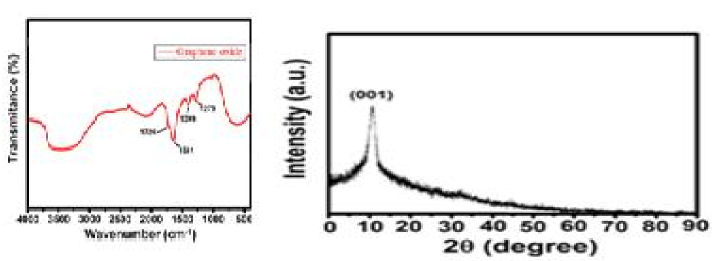


Figure 3.3(a)- UV-Visible spectrum of Graphene oxide (b) SEM Image of Graphene oxide

The FTIR spectrum of Graphene oxide is presented in the figure 3.4(a). In the case of GO, a broad band is observed in the range from 3200–3500 cm^{-1} which was ascribed to the hydroxyl (–OH) group, possible from COOH group present in GO. The characteristic band observed at ~1726 cm^{-1} may be assigned to C=O group present in the graphene oxide and C=C bending vibrations exhibited at 1641cm^{-1} and the vibration frequency found at 1273cm^{-1} is corresponding to C–O–C group. In addition to that, the band at 1399 cm^{-1} may be due to O–H deformation vibrations of tertiary C–OH. The X-RD Spectrum for GO is displayed in figure 3.4(b). The peak at 2θ = 11.8^o with (hkl) value (001), suggesting the successful oxidation of the graphite material. The XRD Pattern suggest that GO particles are homogeneous, well defined crystalline structure and having high purity



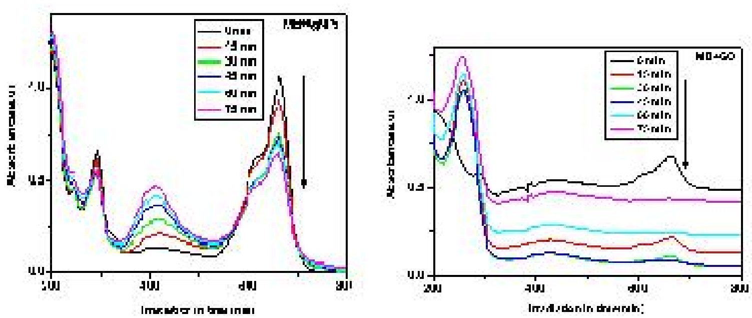
(a) (b)

Figure.3.4- (a) FTIR Spectrum and (b)X-ray spectrum of Graphene oxide

3.3 DEGRADATION STUDY OF MB

Silver nanoparticles (AgNPs) and Graphene oxide (GO) on degradation of dye were demonstrated by using methylene blue dye. The degradation of methylene blue was carried out in the presence of these solutions at different time in the visible region. The absorption peak at 664nm for methylene blue dye was decreased gradually with the increase in the exposure time under irradiation and that indicates the degradation reaction of methylene blue.

Figure 3.5(a) and (b) shows the degradation of MB on AgNPs and on GO. As the exposure time was increased, the absorption peak of methylene blue dye was decreased whereas absorption band for AgNPs and GO were increased. The completion of the degradation of the dyes is known from the gradual decrease of the absorbance value of dye approaching the base line and increased peak for AgNPs and GO. In figure 3.5(a), while decreasing the concentration of the dye, UV spectra show typical SPR band for silver nanoparticles. The percentage of degradation was calculated as 91% at 75 minutes [4]. As increasing the time of contact between GO and MB, there was an electrostatic attraction of MB molecules and H^+ ions in the functional groups on the GO's surface. The percentage of degradation of MB on GO was calculated as 99% at 75 minutes.



(a) **(b)**

Figure 3.5- UV-Vis spectra of MB on (a) AgNPs and (b) GO recorded at different time

CONCLUSION

Silver nanoparticle was biologically synthesized using Terminalia Arjuna leaf extract. FTIR spectrum was examined to identify the effective functional groups responsible for the reduction and stabilization of silver nanoparticles synthesized by leaf extract. Graphene oxide was successfully prepared through Hummer's method and it was characterized by using X-RD, SEM, UV-Vis spectrometer, and FTIR Spectrometer. The absorbance of silver nanoparticles and Graphene oxide was evaluated by choosing methylene blue dye. The main absorption peak at 664nm decreased gradually with the extension of the exposure time. The photodegradation of methylene blue (MB) dye showed that the synthesized GO exhibits maximum adsorption efficiency than AgNPs. This may due to the interaction of aromatic dye with aromatic graphene.

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