



ALOE VERA STABILIZED NANO SILVER-REDUCED GRAPHENE OXIDE NANO COMPOSITES FOR FACILE CATALYTIC DEGRADATION OF PONCEAU 4R AND EOSIN-Y DYES IN VISIBLE LIGHT

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ABSTRACT

In this work nanocomposites comprising of reduced graphene oxide (rGO) and silver nanoparticles (AgNp) were prepared adopting eco friendlier components. Aloe vera plant extract was used as the stabilizing agent in the AgNp synthesis and graphite precursor being used in the rGO preparation. Size characterizations of AgNp-rGO nano composites were carried out from UV- Vis SPR, Powder XRD, HR-TEM and FE-SEM measurements. The catalytic ability of the fabricated green AgNp-rGO nano composites was confirmed by following the oxidative degradations of two popular dyes Ponceau 4R and Eosin-Y in aqueous medium under visible light irradiations at 25°C. Reaction kinetic parameters such as overall pseudo first order rate coefficients 'k', % mineralization of dyes and effect of oxidant sodium peroxomono sulfate ($\text{Na}_2\text{S}_2\text{O}_5$) were determined for the two dyes separately adopting visible light irradiation and nano composite catalyst inclusions. AgNp-rGO nano composites exhibited remarkable catalytic capacity under visible light irradiations of the dyes both in the presence and absence of oxidant. Among the dyes tested, Ponceau 4R degraded to a higher extent than Eosin-Y. The results point towards low cost advanced oxidation process and AgNp-rGO nano composites an efficient analytical tool for dye degradations.

Keywords: Green silver nanoparticles, Reduced graphene oxide nanocomposites, Visible light catalysis, Degradation of Ponceau 4R, Eosin-Y.

1. INTRODUCTION

Immobilizations of metal or metal oxide nano particles onto synergetic and appropriate carbaneous supports are exploited in sensing, reaction catalysis, photo activity and electronic conduction applications [1-6]. Recently research reports expose graphene and its related forms like graphene oxide (GO) and reduced graphene oxide (rGO) as suitable and robust supports for deposition of metal and metal oxide nano particles [7-10]. Among metals, silver nanoparticles (AgNp) are well known to exhibit excellent photo sensing and photo catalytic properties [11-15]. Hence forth, fabrication of AgNp-rGO nanocomposites and its utilization towards photo sensing and photo catalytic activities open up new opportunities in the development of novel and facile photo catalysis of complex organic substrates. In this work, preparation of AgNp adopting a greener pathway [16-17] using Aloe vera plant extract as the biostabiliser instead of synthetic stabilizer was attempted. Green

synthesis of AgNp using plant extract as the source of photo electron for the reduction of metals possess some advantages such as cost effectiveness, available in abundance, good stability, absence of hazardous chemicals, safe and easy operations. Bio molecules found in plant extracts function as both reducing and stabilizing agents during the synthesis of metal nanoparticles [18-21]. The as-synthesised AgNp are characterized using UV-Vis, SPR and Powder XRD measurements. GO was synthesized from graphite powder adopting mild and eco-friendlier process conditions, followed by sequential rGO formations and AgNp deposition. Here, reported procedures with slight modifications are adopted (22-23). The designed AgNp-rGO nanocomposites are appropriately characterized by HR-TEM and FE-SEM measurements.

The photo sensing and photo catalytic applications of AgNp-rGO nanocomposites are studied by following the photo oxidative degradations of two typical synthetic dye

substrates such as Ponceau 4R (P4) and Eosin Yellow (EY) in aqueous medium at 25°C, in the presence and absence of peroxomonosulfate ($S_2O_5^{2-}$) oxidant. Visible light irradiation was used, instead of UV light, ensuring eco-benign conditions. Ponceau 4R is called “E 124” or also 2-hydroxy-1-(4-sulfonate-1-naphthylazo)-6,8 naphthalene disulfonate trisodium ($C_{20}H_{11}N_2Na_3O_{10}S_3$) an azo dye $\lambda_{max} = 505\text{nm}$. Its chemical structure is represented in (Fig.1a) and profusely used in food, beverage, textile, paper and cosmetic industries due to the intense coloration, lower price, water solubility and high stability [24-26]. Likewise, Eosin yellow-2-(2,4,5,7-Tetrabromo 6-oxido-3oxo-3H-Xanthen-9yl) benzoate ($C_{20}H_8Br_4O_5$) an anionic dye of molecular weight 647.89 g mol⁻¹ with $\lambda_{max} = 517\text{nm}$. Its chemical structure (Fig.1b) is widely used as biological sample stains, and as flow water tracer, indicator and sensor extended applications [27-28]. However the chronic consumption in high concentrations leads to leakages and contaminations of environmental aquatic sources. Some of the side effects and hazards

faced by human being are eye irritation, nasal burning, skin rashes, chest pain, carcinogenicity, reproductive and developmental toxicity etc [29-30]. Therefore low cost, enviro-benign and efficient advanced oxidation analytical methods are needed in addition to many such existing in literature [31-32]. More so, data relating degradation processes are essential for food safety and human health factors. In the present work, the progress of the aerobic oxidations of P4R and EY in visible light, in the presence of AgNp-rGO nanocomposite catalyst was followed by absorbance variation with time measurements. The wave lengths with maximum absorbance in the visible region are 505nm and 517nm for P4R and EY dyes respectively. Maintaining pseudo first order conditions, the overall rate coefficient (k) and % mineralizations are determined for the dye substrates separately and the results are compared. Ponceau 4R degradations are more rapid than Eosin yellow and AgNp-rGO nanocomposite serves as an efficient visible light photo catalyst in aqueous medium for both sensing and dye degradation applications.

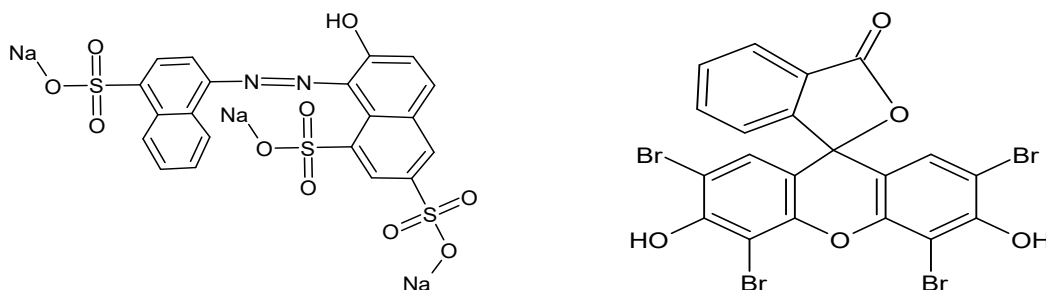


Fig. 1: Molecular structure of (a) Ponceau 4R and (b) Eosin-Y

2. EXPERIMENTAL

Silver nitrate ($AgNO_3$), sodium peroxomonosulfate, NaOH, graphite powder with particle size < 50 μm , 98% sulphuric acid, potassium permanganate and potassium nitrate were procured from Merck India. Ponceau 4R and Eosin-Y powders with 98%-99% purity were also purchased from Merck India. Fresh triply distilled water was used in all solution preparations.

2.1. Synthesis of Ag nano particles (AgNps)

Fresh and sliced Aloe vera slices (40gms) were ground to a fine paste adding 50 ml of NaOH solution at pH=5.0. The thick slimy solution was filtered and the clear filtrate was used as the stabilizing agent, 20 ml of 1 mM $AgNO_3$ solution prepared in 0.1M KNO_3 solution was taken and 50 ml of Aloe vera extract solution was added dropwise simultaneously maintaining 45°C as the medium temperature with constant stirring for 1 hr

period of time. Formation of a lemon yellow coloured solution indicated the completion of synthesis of AgNp. Repeated ultra centrifugations of this solution resulted in settling of AgNp in wet condition and the excess supernatant solution was siphoned out. This procedure was repeated several times and the AgNp suspension in dilute (0.01M) KNO_3 solution was stored for size characterizations [33]. UV-Visible, SPR recorded showed a prominent peak at 405 nm confirming the presence of AgNp. Solid AgNp were collected after vacuum drying and stored in N_2 purged dark container. Powder XRD of AgNp was taken.

Graphene oxide was synthesized from Graphite powder through improved Hummer's method [34, 35]. The typical procedure being 30ml of 9:1 (V/V) mixture of concentrated H_2SO_4 and H_3PO_4 was added to 1.5g of graphite powder and 9.0g of $KMnO_4$ with constant vigorous stirring for 12 hrs at 45°C. The reaction

mixture was cooled to 25°C and added 5ml of 30% H₂O₂ to convert MnO₂ residue to soluble sulfate form. Excess (250ml) triple distilled was added, stirred for 1hr at 80°C. After cooling, the mixture was ultra centrifuged several times with repeated washings. Final solid was coagulated with ether solvent and dark brown crystalline GO was vacuum dried and stored in dark and N₂ purged container.

AgNp-rGO nanocomposites were prepared by carrying out a procedure with minor modification to the reported one [34]. 50 mg powder of GO was dispersed into 100 ml of triple distilled water and ultrasonicated for 1 hr to form Yellowish brown exfoliated GO sheets. To the slurry, 30 mg of AgNps mixed in 50 ml of 0.01 M KNO₃ was added slowly under constant stirring at 60°C as the medium temperature of 1hr time period. The black precipitate (AgNp-rGO) obtained was washed several times to remove any unbounded AgNp and other impurities. Vacuum dried AgNp-rGO nano composites are stored for further use.

2.2. Spectra measurements and size characterization

All UV-visible spectra were recorded on a Shimadzu (UV-1650Pc) spectrometer fitted with thermostat for temperature control. Powder XRD patterns were obtained using Bruker diffractometer D8 Advance with CuK α radiation. HR-TEM measurements were carried out using TEM Hitachi Technai G20 and for FE-SEM, Hitachi FESEM S4800 microscopes respectively.

2.3. Reaction catalysis

A 50 ml of 1 mM colored dye solution was left in dark for 3hrs to reach equilibrium and loaded into Pyrex glass cylindrical photo reactor equipped with continuous N₂ or air purging, magnetic stirrer and a temperature controller. The photo reactor was irradiated by 20 series white light LEDs (nominal power 6W) with wavelength emission in the range 400-800 nm. 50ml of 0.1M Na₂S₂O₅ cool solution was added and N₂ purged after each addition of any component into the reaction vessel. After the addition of AgNp-rGO nanocomposite catalyst, small aliquots of the solution was drawn out at regular intervals of time and subjected to UV-visible spectra measurements. The completion of the reaction was known from the decrease in the absorbance of peak maximum to zero value and as well as complete decoloration of the dye solution. Pseudo first order conditions on the compositions of the dye, catalyst and

oxidant were maintained, and the pseudo first order rate coefficient values are determined from the absorbance-time variance data.

3. RESULTS AND DISCUSSION

The UV visible spectrum and Powder XRD of Aloe vera stabilized AgNp and AgNp-rGO is given in Fig. 2 & Fig. 3 along with SPR Spectrum (inset).

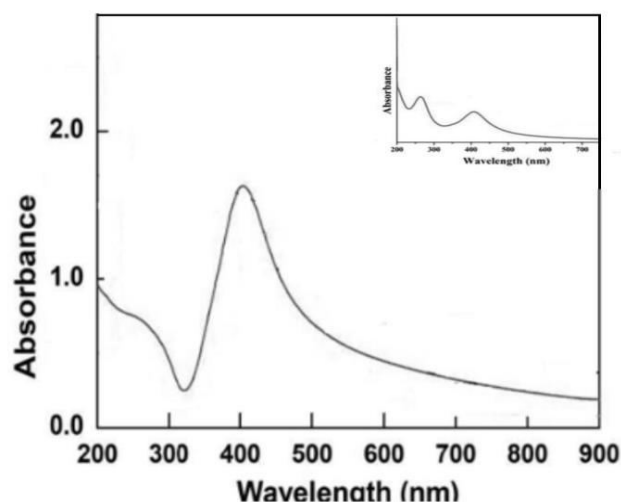


Fig 2: UV-visible Spectra of AgNp with inset figure of AgNp-rGO

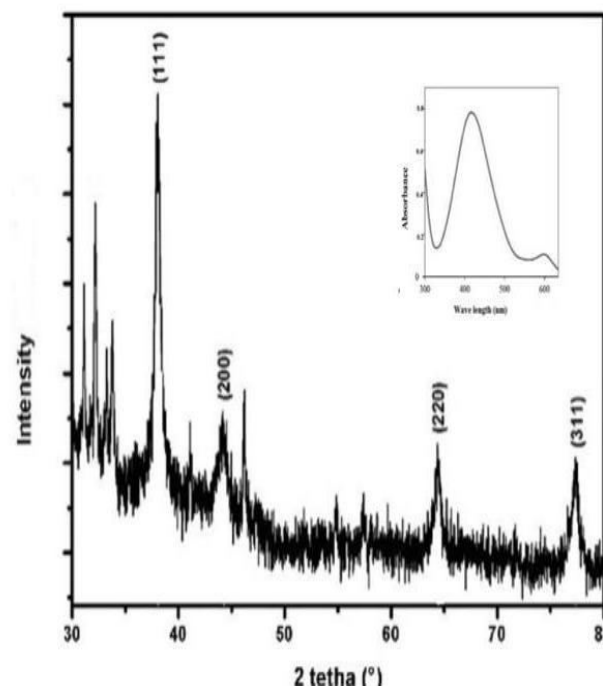


Fig. 3a: Powder XRD of Aloe vera AgNp with the inset figure SPR spectrum of AgNp

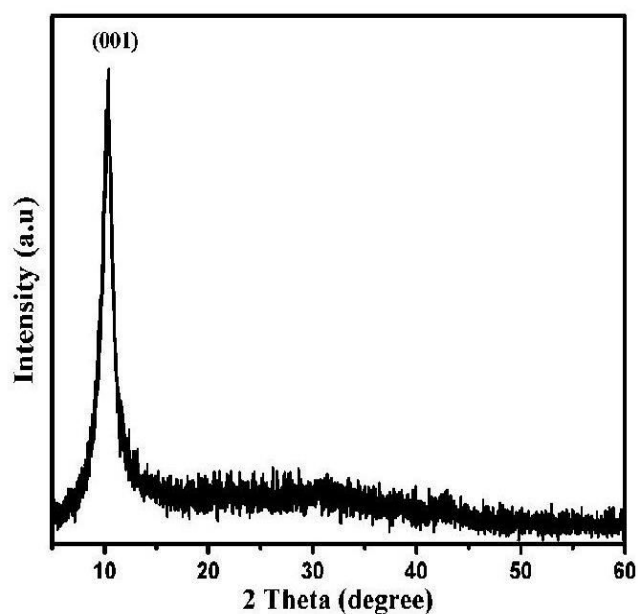


Fig. 3b: Powder XRD of rGO

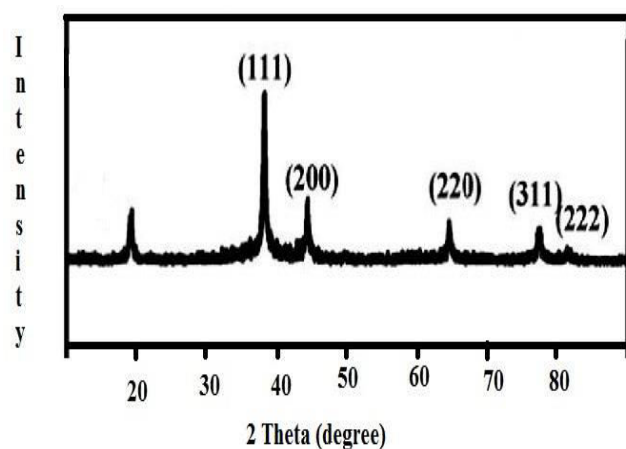


Fig. 3c: Powder XRD of Aloe vera AgNP-rGO

The PXRD patterns of AgNP confirm with the JCPDS file no 04-0783, using Scherrer equation, the size range of the AgNP has been found within 12 ± 2.0 nm. FE - SEM and HR - TEM micro images of AgNP- rGO nano composites are shown in Fig. 4 and Fig. 5 respectively. In the SEM image, layers of rGO and AgNP depositions on the surface are observed. Similar AgNP decoration on rGo surface are detected in HR - TEM images and the average size value of AgNP are found to be 16 ± 1.0 nm indicating a marginal increase in the average size of AgNP due to surface interactions with rGO nanocomposites could be a promising multifunctional material, such nano surfaces may be well suited for catalytic and photo electron transfer process.

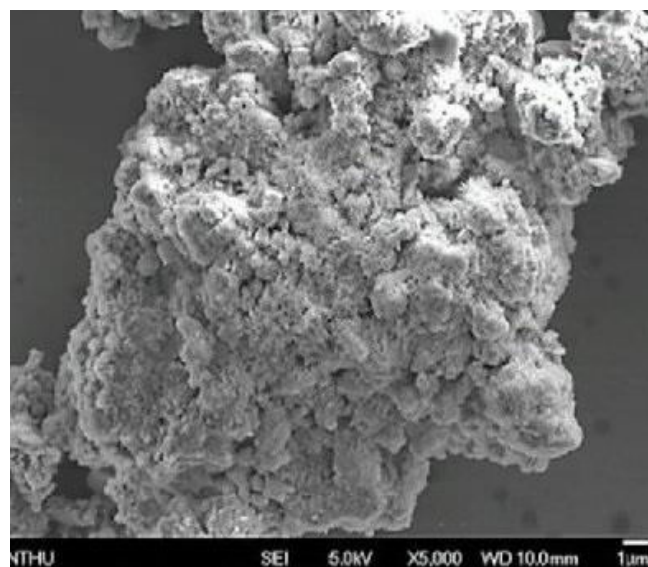


Fig. 4: FE-SEM images of AgNP-rGO nano composites

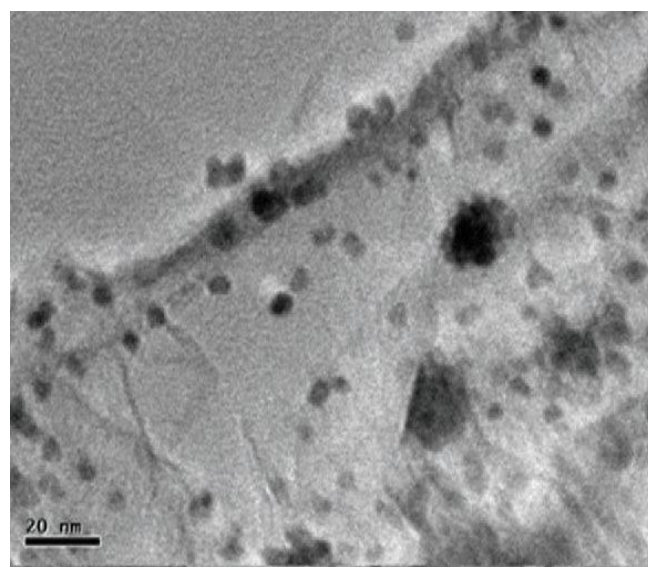


Fig. 5: HR-TEM microphoto of AgNP-rGO nano composites

To confirm, the photo catalytic behavior of the fabricated AgNP-rGO nano composites, degradations of P4 and EY dyes were studied separately and the following salient observations are found. The decoloration of the dye started only upon the start of visible light irradiation in the presence of oxidant. Also, the dye decoloration was extremely slow in the absence of light but even in the presence of AgNPs, rGO nanocomposite and the oxidant. The progress of the oxidant reaction was nearly the same whether aerobic (air purge) or anaerobic (N_2 purge) conditions are

maintained. In the absence of the oxidant but in the presence of nano composites and visible light, the dye decoloration was slow and took more than 8 hrs for complete decoloration.

The absorbance of the wavelength maximum peak in the visible region of spectra for each of the dye decreased with increase in the time of progress of the oxidation. In Fig. 6 and Fig. 7, such time variance in the spectra is shown for dyes P4 and EY respectively. The corresponding absorbance versus time plots for the two dyes are shown in fig. 8(a) and 8(b). The extent of absorbance decreases with time has been found to be more for P4 than EY dye degradations. These data are

used for the kinetic plots from which the overall pseudo first order rate coefficient values are determined. These are shown in Fig. 9(a) and 9(b). The completion of the reaction was indicated from the absorbance values reaching zero value and as well as by complete decoloration of the reaction. The nano composite catalysts were recovered by filtration and washed repeatedly followed by ultra centrifugation. The catalyst residue was vacuum dried and as well as stored in dark for 24 hrs to attain equilibrium. The catalyst activity of AgNp-rGO nanocomposite was tested by repeating, the dye degradation procedures.

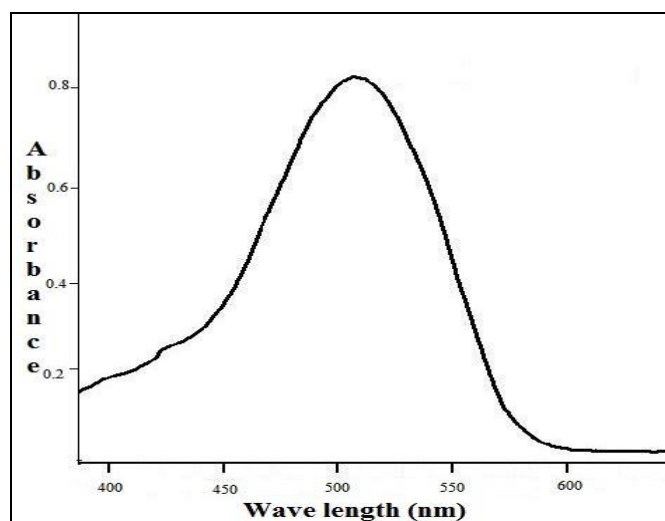
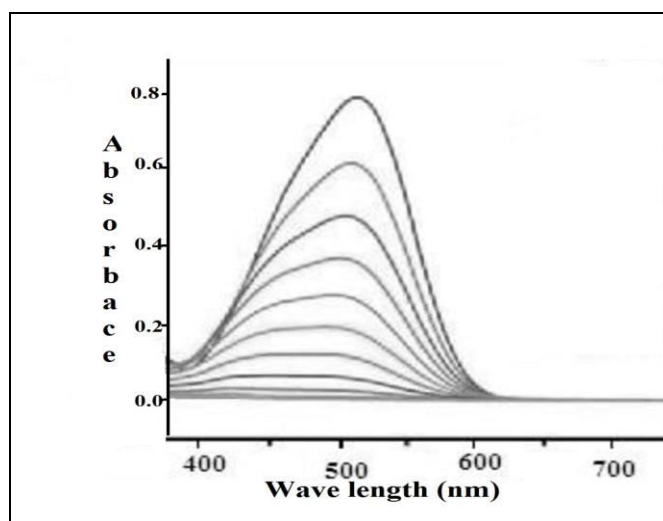


Fig. 6: Visible spectra with time variance of Ponceau 4R in aqueous medium in the presence of AgNp-rGO nano composites and peroxomono sulfates under visible light irradiation at 25°C

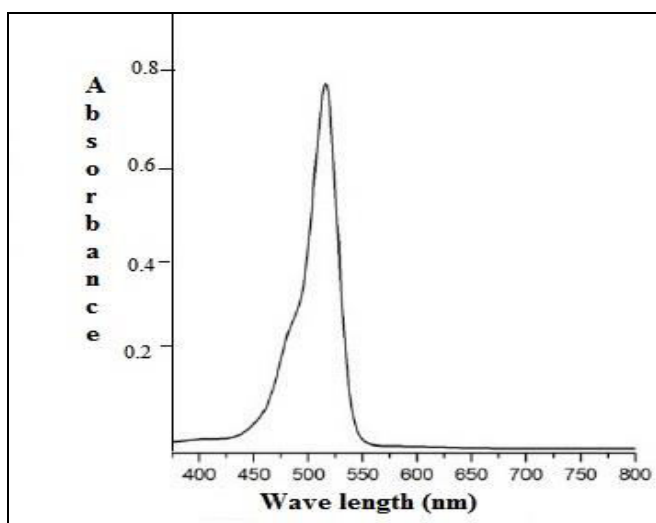
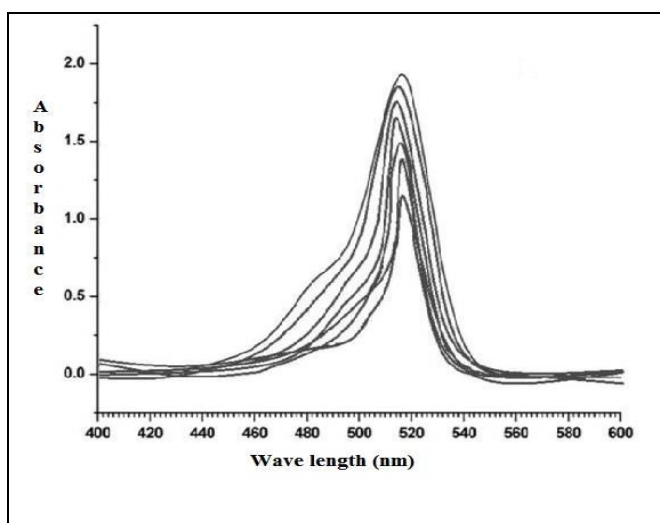


Fig. 7: Visible spectra with the time variance of Eosin-Y in aqueous medium in presence of AgNp-rGO nanocomposites and $S_2O_5^{2-}$ under visible light irradiation at 25°C.

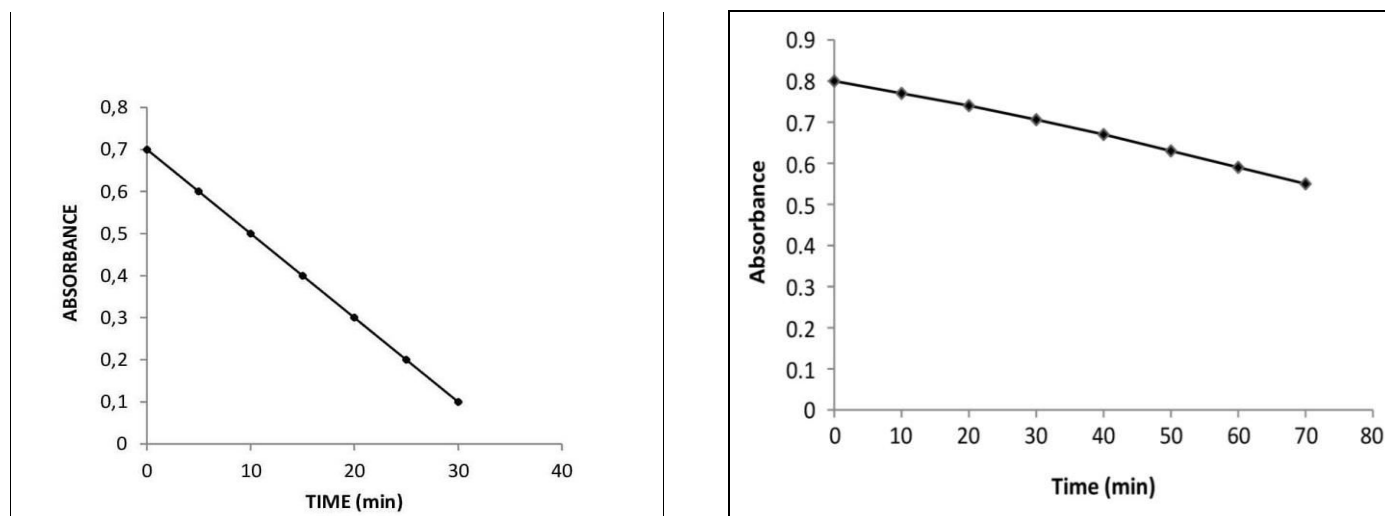


Fig. 8: Absorbance variation with time plots for (a) Ponceau 4R and (b) Eosin-Y photo degradation under visible light irradiations and AgNp-rGO nanocomposite catalyst with $S_2O_5^{2-}$ oxidant at 25°C

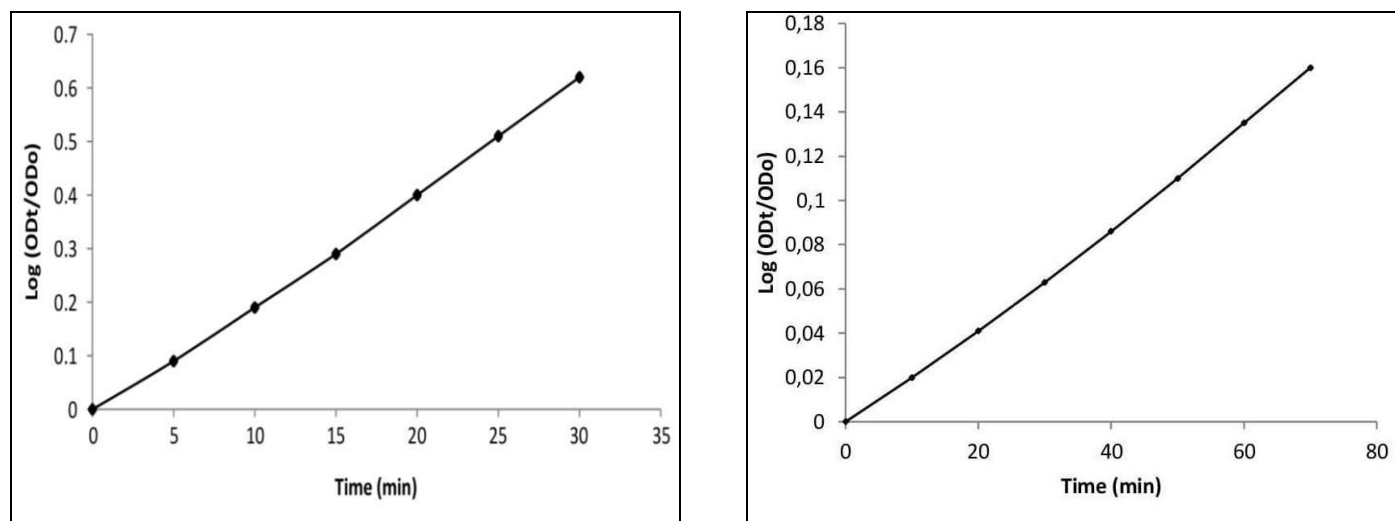


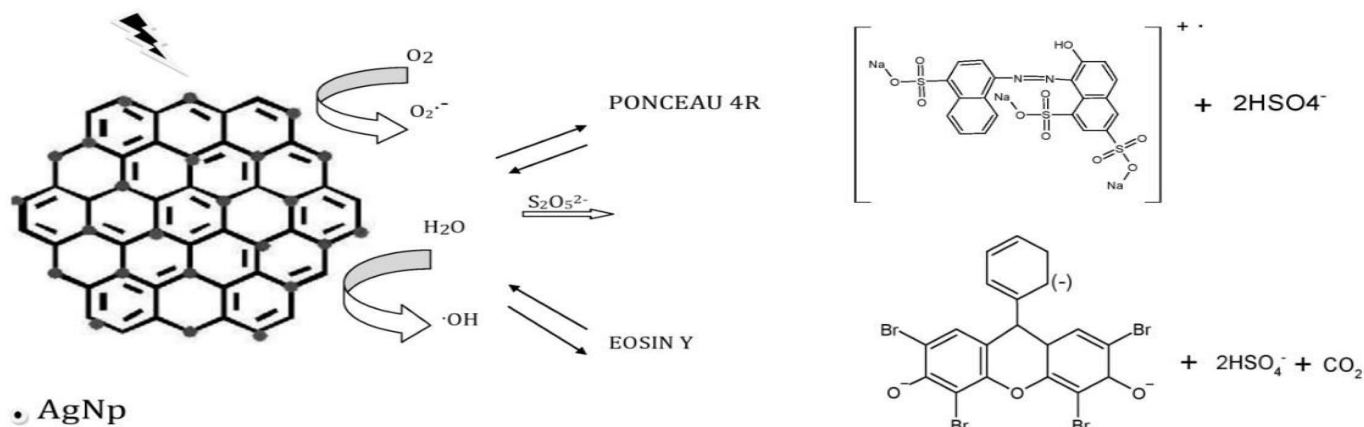
Fig. 9: Pseudo first order kinetic plots for rate coefficient determination of (a) Ponceau 4R and (b) Eosin-Y photo degradations under visible light and AgNp-rGO nanocomposite catalyst and $S_2O_5^{2-}$ oxidant at 25°C

However, the dye decoloration took longer hours, indicating that the nano composites have lost the catalytic activity significantly. This may be attributed to the tarnishing of Ag metal surfaces by air oxygen. The filtrate was analyzed for the dye mineralization. In Table 1, the kinetic parameters including the overall rate coefficient values for the pseudo first order condition and % mineralization of the dyes are put forth. The data indicate that P4 degraded faster than EY dye in the visible irradiation and AgNp-rGO nano composite surface catalyses P4 molecules more rapidly than EY molecules in the presence of $S_2O_5^{2-}$ oxidations. The plausible oxidation mechanisms of the two dyes are

given in Fig 10. Presence of Ag nano particles on the GO matrix enhance the absorption of UV light, due to the strong SPR and facilitates the electron transfers as well as the H atoms transfers from the dye and the oxidant molecules. The rGO being a good electron acceptor and excellent charge transporter with excess π electrons, facilitates the anchoring of the dye molecules suitable for e- and H transfers. This contributes to the rate determining step. In consequence, cascading mineralization of the dyes with CO_2 evolution wherever necessary occur. These steps are essential in the water treatment by AOP during dye leakages in to aquatic sources.

Table 1: The overall pseudo first order rate coefficient ($k \times 10^{-2} \text{ sec}^{-1}$) values for the oxidation reactions of Ponceau 4R and Eosin-Y using peroxomonosulfate and AgNp-rGO as catalyst at 25°C

Substrate	k	$t_{1/2}$ (min)	% mineralisation
Ponceau 4R	5.98	0.19	92
Eosin-Y	0.46	2.50	89

**Fig. 10: Plausible mechanism of oxidation of (a) Ponceau 4R and (b) Eosin-Y with $\text{S}_2\text{O}_5^{2-}$ oxidant under visible light irradiation**

4. CONCLUSION

AgNps synthesized by green method using Aloe vera extract resulted in stable nano particles which are conveniently deposited on to rGO surface resting in AgNp-rGO nano composite material. When the fabricated nanocomposite material is used as a photocatalyst for the oxidative degradation of the two popular dyes Ponceau 4R and Eosin-Y under visible irradiation in the presence of peroxomonosulfate oxidant, remarkable dye degradations took place. Ponceau 4R degraded more rapidly than Eosin-Y, along with % mineralisations occurred in larger extents for Ponceau 4R compared to Eosin-Y. These results point the utility of the designed nano composites as nano sensors and initiators of destruction of the aqueous dye molecules.

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Conflict of interest

None declared

6. REFERENCES

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