



A NOVEL SYNTHESIS OF RGO@Ag NANOCOMPOSITES: AN EFFICIENT PHOTOCATALYST FOR DEGRADATION OF SUDAN – III AND SAFRANIN – O DYE IN CONTAMINATED WATER.

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Abstract

The accumulation of dyes in waste water is increasing every day, to increase the aesthetic value of products. The dyes though used in permissible limit are further leading to adverse effects. The Sudan – III which is a diazo dye, Safranin – O is a phenazine dye, used in textile and food industries is becoming a major concern as Sudan – III is characterised as grade – 3 carcinogenic agent and Safranin – O causes cancer. The partial degradation of Sudan – III produces secondary pollutants like Naphthylamine and aniline which cause adverse effect on humans and aquatic animals. The Photocatalytic degradation of Sudan – III and Safranin – O is very effective in presence of graphene based RGO@Ag nanocomposites. The morphology and structure were studied using spectroscopic and microscopic techniques such as UV-Visible spectroscopy, and powder XRD. The spectroscopy and microscopic results revealed the successfully formation of RGO@Ag nanocomposites. The photocatalytic degradation is carried in presence of Hg lamp and the degradation of dyes is confirmed by UV-Visible spectroscopy at 506 nm is 99.0% in acidic medium and 94.4% in neutral medium with catalyst having 6 cycles for Sudan – III and.

Keywords RGO@Ag nanocomposites (RGO@Ag NCs), Sewage water, Sudan – III dye, Safranin – O dye, Photolytic degradation.

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1. Introduction:

In present globalization colouring of materials has become a common method to increase aesthetic value to products. One of the common dyes used are azo and phenazine dyes for colouring of plastics, leather, wax, cellulose and synthetic lacquers, polishes, food products and paints. Among these azo dyes Sudan – III (S-3) dye is a diazo dye and Safranin – O (SO) of phenazine are used as colouring agent in textiles, oils, plastics, food products and biological stain in India. In 2003 S-3 was graded as group – 3 carcinogens, hence banned its usage in food products, but it is still used as colouring agents in textile, plastic industries and as biological stain in India.

S-3 and SO is a red coloured dye with molecular formula $C_{22}H_{16}N_4O$ and $C_{20}H_{19}N_4^+Cl^-$. S-3 and SO dyes are widely used in textile industry are resulting in causing water contamination through waste water produced from textile industries which is causing damage to aquatic life. Through water contamination it is causing hazardous impact on humans and seafood. The studies on S-3 and SO revealed that, S-3 releases secondary pollutants like naphthylamine and aniline during its partial degradation which may cause great risk to humans as they lead to carcinogenic impact. The permissible limit of S-3 dyes is in range of 0.1 mg/kg. The SO in high concentration as water contaminant is resulting in causing allergic dermatitis, skin irritation, cancer and mutation in human being. This addition of dye is resulting as contamination of water and researchers are searching for better qualitative method to irradiate these dyes from waste water contamination. Photocatalysis is a promising method for degradation of chemicals, as it converts the chemicals into less toxic or harmless minerals and gases. Photocatalysis is inspired from photosynthesis of plants, as it releases less toxic or harmless minerals and gases as by-products, it is considered as eco-friendly technique and plays a key role in green chemistry. In this paper we are focusing on degradation of S-3 and SO dyes by RGO@Ag nanocomposites (RGO@Ag NCs), which is water contaminant from textile and food industries [2]. The RGO is 2D material which is exfoliated from graphene with layer thickness is of 3.5 nm. The band gap of RGO varies from 1.00 to 1.69 eV based on reduction of graphene oxide. It acts as a good carrier of electrons and holes. It is not easily degraded by photo-excitation as it is known for its good optical, thermal, mechanical and physical properties. The silver nanoparticles (Ag NPs) are fused into RGO by one-pot synthesis (which helps in minimal usage of chemicals and

decreases toxicity) in presence of amino acids, as amino assisted synthesis is eco-friendly, it can maintain basic side chain in neutral pH, proper binding of RGO and silver nanoparticles. The Ag NPs in RGO@Ag NCs help in releasing the electrons in presence of light as they are readily photo-excited, these electrons reach from valence band (VB) to conduction band (CB) and helps in degradation of dyes in to minerals and gases. The photocatalysis is optimised by doing further changes in different parameters which are discussed in this paper.

2. Experimental section

2.1 Materials

Graphite flakes from Aldrich, Potassium Permanganate ($KMnO_4$), Hydrogen peroxide (H_2O_2), Sodium Nitrate ($NaNO_3$), Acetone, Sodium Hydroxide ($NaOH$), Sulphuric acid (H_2SO_4), Silver nitrate ($AgNO_3$), Hydrochloric acid (HCl), Ammonia solution (NH_3 , 25 %), Ascorbic acid (Vitamin – C), Isopropanol, Safranin – O and Sudan – III dye were purchased from Merck, India and used for synthesis without further purification. Deionised water was used throughout the process.

2.2 Synthesis of RGO@ Ag nanoparticles using Vitamin – C

0.2 gram of graphite oxide (GO) was added to a 250 mL round bottom flask containing 100 mL deionised water (2 mg/1 mL) under ultra-sonication. Then 100 mL of Silver Nitrate solution (0.005 M) was added and sonicated for 30 Min. Now the reaction is performed under nitrogen atmosphere at 80 °C for 1 hour at continuous constant stirring. Then 5 mL of 2 M Vitamin – C was added to the reaction mixture and after 30 min 5 mL ammonia solution (25%) was rapidly injected into a reaction mixture. The reaction was preceded for 2.5 hour at 80 °C under constant stirring. Then finally the blackish grey coloured precipitate was obtained which is filtered, washed repeatedly with deionised water and then dried under vacuum at room temperature.

2.3 Characterization

The UV – Visible absorption spectra were recorded using Shimadzu 2450 – SHIMADZU spectrometer. The sample was diluted with deionised water and it is introduced into UV-Visible Shimadzu 2450 – SHIMADZU spectrometer for characterization of sample. The X-ray diffraction (XRD) patterns were recorded using a PANalytical X'pert pro diffractometer at 0.02°/s scan rate with Cu- α radiation (1.5406 Å, 45 kV, 40 mA) and 2θ ranging from 10° to 90°.

2.4 Photocatalytic degradation of Sudan-III and Safranin – O using RGO@Ag nanocomposite:

The catalytic degradation efficiency of RGO@AgNCs experiments were carried out using S-3 solution (0.5 g of dye in 200 ml of Isopropanol, sonicated for 30 min. The filtrate is made up to 500 mL with deionised water) at room temperature (300 K) and normal pressure. The pH of solution was adjusted by NaOH (0.01 M) for basic and HCl (0.01 M) for acidic medium. 5 mg of RGO@AgNCs was suspended in 50 mL of dye solution. The sample initially was stirred in dark for 5 min with 400 rpm and then irradiated with 450 W Hg lamp for catalytic degradation. The samples from flask were withdrawn at the specified time of reaction until adsorption equilibrium was achieved. The sample was centrifuged and the clear solution with residual drug concentration was determined by UV – Visible spectrophotometer ranging from 200 nm to 800 nm. The reactions were monitored by observing the change in absorbance peak of S-3 at 507 nm in acidic, basic and neutral medium with different concentration ratio of dyes (2, 5, 10 and 50 ppm) and nanocomposites in (1.0, 2.5, 5.0 and 10.0 mg) respectively. The percentage of degradation was calculated by

$$Q = (C_0 - C) \times 100 / C_0$$

Where 'C₀' is the initial S-3 dye concentration (µg/L), 'C' is S-3 dye concentration (µg/L) in solution after degradation. Common absorption isotherms and kinetic models were used to demonstrate the degradation process [4].

The same procedure was followed for SO dye. The stock solution was prepared by dissolving 0.5 g of dye in 200 mL of deionised water, sonicated for 30 min. The filtrate is made up to 500 mL with deionised water. The absorbance of SO was noted at 520 nm .

3. Result and Discussion

UV-Visible spectroscopy: The UV – Visible spectra of RGO, Ag nanoparticles and RGO@Ag nanocomposites is shown in Figure-1. The characteristic peaks were observed for RGO at 260 nm, Ag nanoparticles at 400 nm and 430 nm and RGO@Ag nanocomposites at 260 nm, 400 nm, and 430 nm. The peak at 260 nm represents RGO, peak at 400 nm and 430 nm indicates Ag nanoparticles in individual materials and in RGO@Ag nanocomposites.

XRD: The phase structure and phase purity of prepared nanomaterials were confirmed by using XRD. The powder XRD patterns of RGO, Ag nanoparticles and RGO@Ag nanocomposites were presented in the Figure 2. The characteristic peaks centred at $2\theta = 22.6^\circ$ and 26.1° were corresponds to

lattice (002) and d – spacing 3.4 \AA indicates the presence of RGO [11]. The intense peaks centred at $2\theta = 38^\circ, 43.999^\circ, 64.1^\circ, 79.2^\circ$ and 81.8° corresponds to (111), (200), (220), (311) and (222) lattice indices of Ag nanoparticles which is well in agreement with standard JCPDS file No. 04-0783. In RGO@Ag nanocomposites, the characteristic peaks centred at 22.6° to 26.1° of RGO and the peaks at $38^\circ, 43.999^\circ, 64.1^\circ, 79.2^\circ$ and 81.8° corresponds to (111), (200), (220), (311) and (222) of Ag nanoparticles. Thus, XRD studies reveal the presence of RGO, Ag NPs and RGO@Ag nanocomposites [12].

Photocatalytic degradation of Sudan – III and Safranin – O using RGO@Ag nanocomposites:

In general, degradation efficiency is highly dependent on surface characteristics, size distribution and functional groups of adsorbent. The RGO@Ag NCs have shown better degradation of S-3 and SO. The degradation is carried out in constant conditions like normal room temperature, pressure and with variation in pH, Concentration of NCs and presence of H₂O₂.

Effect of pH: The degradation of S-3 and SO are studied at constant conditions like, concentration of dyes (5 ppm each) and weights of RGO@Ag NCs is same (5 mg each) with variation in pH from 3 to 12 for S-3 which is shown in Figure 3a and the degradation is good at pH – 7 and maximum at pH – 5 (Figure 3b), for SO the variation in pH from 3 to 10 (Figure 3d) and the degradation is good at pH – 7 and maximum from pH – 7.5.

Concentration of nanocomposites: The degradation of S-3 and SO were studied based on change in concentration of RGO@Ag NCs. The concentration of S-3 and SO is constant (5 ppm each) and the weight of NCs changes from 1 mg, 2.5 mg, 5 mg, 10 mg, 15 mg, 20 mg and 25 mg. The rate of degradation is good by the NCs concentration at 2.5 mg and maximum from the concentrations 5 mg for S-3 (Figure – 3c) and it is same for SO.

Effect of H₂O₂: The H₂O₂ with different percentages (1%, 2%, up to 10%) was added to the solution of S-3, SO and NCs at constant conditions, concentrations and equal weights. There is no significant effect on degradation rate of dyes in presence of NCs.

Mechanism: The degradation of S-3 and SO at optimum conditions like room temperature, normal pressure, 5 ppm of dye concentration and 5 mg of nanocomposites at pH – 5 for S-3 and pH – 7.5 for SO is explained as follows-

Acidic medium: In this RGO acts as binder and support for H^+ and electron transfer in acidic medium. The Ag NPs are good oxidative material, as it readily discharges electrons when exposed to light. The band gap of Ag NPs is 2.5 eV in acidic medium, this further helps in photo-excitation of electron from VB to CB. The conversion of Ag^+ to Ag^0 and Ag^0 to Ag^+ takes place rapidly in acidic medium, as Ag NPs have good repulsive force at surface of RGO. The higher wavelength helps in formation of photons, the photons in-turn produces more energetic electrons from Ag NPs (in presence of H^+ ions) due to excitation of surface Plasmon's which results in higher reaction rate in acidic medium, as H^+ ions concentration is high which accelerates the oxidation character of Ag NPs. The high electron hole ratio in acidic medium helps in ring expansion and converting Azo groups of S-3 in to amine groups, followed by breaking of \square bonds in benzene rings of S-3 [2]. Thus the conversions of azo to amine and ring breaking helps in discharging less toxic chemicals like $-NH_2$, CO_2 , O_2 , carboxylic acids and minerals from S-3 dye. This is not observed in SO as \square bonds in phenylphenazine compounds are stable in acidic medium, generally the phenazines are good at hydrogen bond acceptors but not hydrogen bond donor, which hinders the degradation of dye. Thus degradation of S-3 is maximum and minimum for SO dye in acidic medium.

Neutral medium: RGO plays the same role, it acts as good binder and transfers electron-holes due to

its good optical, physical and mechanical properties. The Ag NPs acts as good oxidative material, the discharge of electron takes place due to surface Plasmon resonance but H^+ ion concentration is not high as in acidic medium and also OH^- ions that are present in water suppress the oxidation of Ag NPs. This suppression the degradation rate in S-3 dye when compared to acidic medium, still it has good degradation rate of S-3 and SO dye in neutral medium.

Basic medium: RGO acts as good binder of electron-hole pair, but the Ag NPs does not show good oxidation phenomenon. The oxidation phenomenon is suppressed by OH^- ions that are present in basic medium. These OH^- ions release electrons and neutralise Ag^+ back to Ag NPs, thus the degradation in basic is 52% which indicates partial degradation of S-3 dye. In SO dye the degradation is good in basic medium, as SO contains phenazines which acts as good hydrogen bond acceptors but not hydrogen bond donor, this results in SO carrying negative charge in basic medium, this in turn helps in accelerating degradation phenomenon of dye. The primary and secondary amines in SO easily dissociate in basic medium by absorbing OH^- ions, this results in breaking of organic compound into smaller compounds, these smaller compounds are further converted into amines to ammonia in presence of electrons transferred by the hydroxide ions which are present on the surface of nanocomposites. Thus the degradation of S-3 is good in acidic medium is 99.0% and better in neutral medium is 94.4 %.

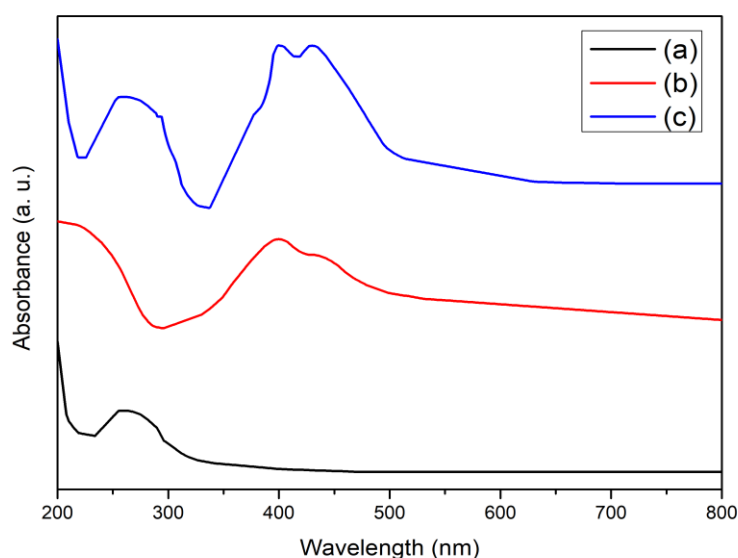


Fig. 1. UV-Visible absorption spectra of (a) RGO, (b) Ag nanoparticles, (c) RGO@Ag nanocomposites

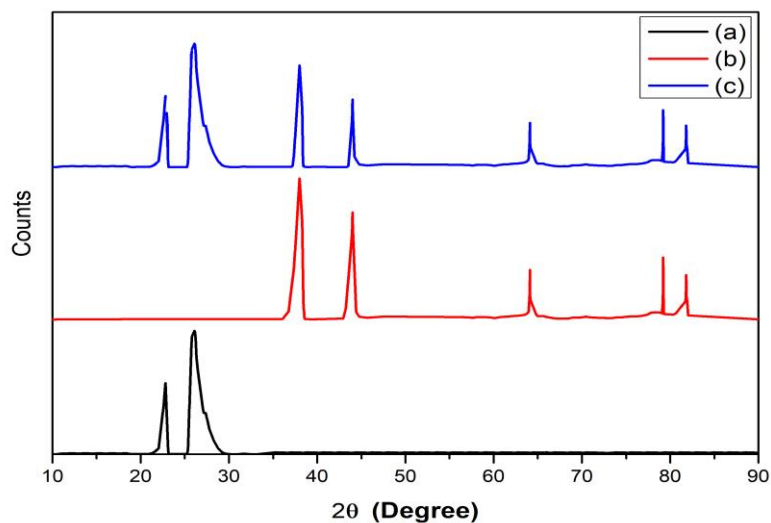


Fig. 2. XRD of (a) RGO, (b) Ag nanoparticles, (c) RGO@Ag nanocomposites

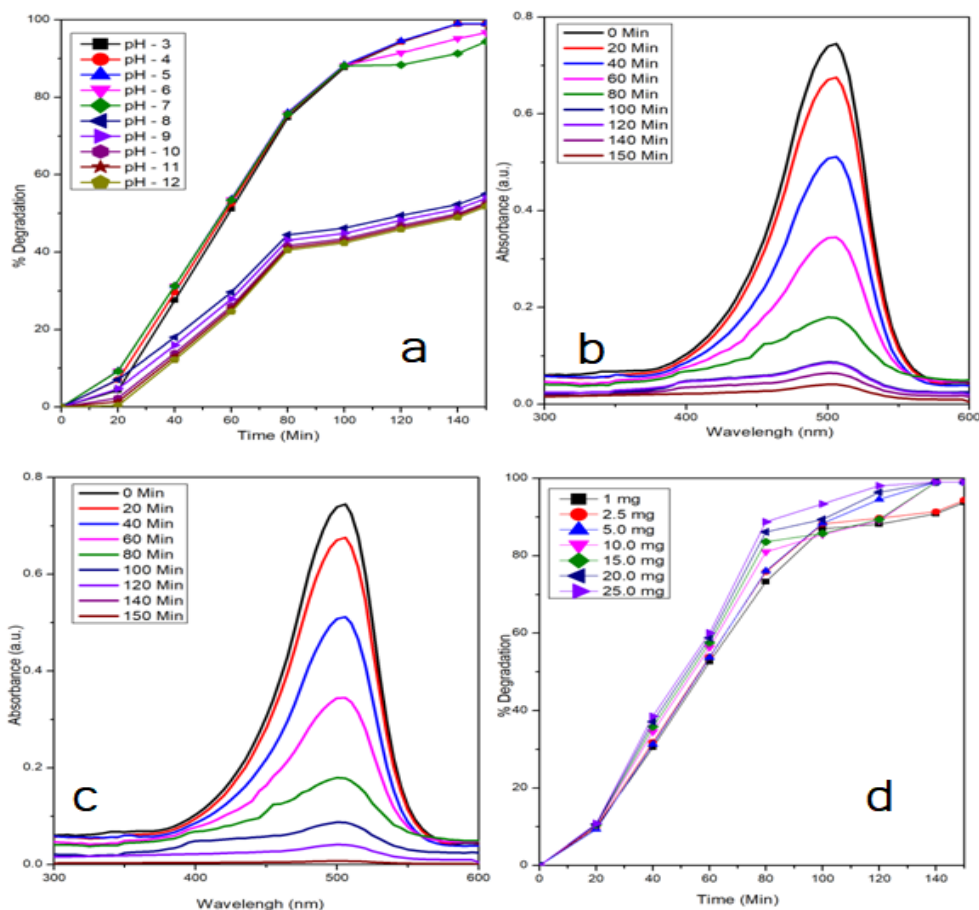


Figure 3: Degradation of S-3 (a) at different pH, (b) RGO@Ag Nanocomposites (5 mg) at pH – 5, (c) RGO@Ag Nanocomposites (5 mg) at pH – 7 and (d) different weights of RGO@Ag Nanocomposites at pH – 5.

Conclusion

The 5 ppm aqueous solution of Sudan – III (S–3) is subject to photolytic degradation with RGO@Ag nanocomposites. The degradation of S–3 is 99.0 % in acidic medium at optimum conditions like room temperature (300 K), normal

pressure, in acidic medium (pH – 5.0) with concentration nanocomposites is 5 mg. In neutral medium (pH – 7.0) with same conditions the degradation of S–3 is 94.4%. The formation of RGO@Ag nanocomposites was confirmed by UV-Vis spectroscopy and XRD. The silver

nanoparticles formed individually and in nanocomposite are in good agreement with JCPDS file. The degradation of S-3 follows first order pseudo reaction which is confirmed by the decrease in the intensity graph in UV-Vis spectroscopy at 554nm. The degradation of S-3 (5 ppm) is 94.4% in basic medium (pH – 9.0) at optimum conditions like room temperature (300 K), normal pressure and with concentration nanocomposites is 5 mg with a time period of 120 min. In neutral medium (pH – 7.0) with same conditions the degradation of SO is 89.5% and the catalyst has 4 cycles with same efficiency.

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