



# Preparation, Characterization of GO-SnO<sub>2</sub> Nanocomposite for the Electrochemical Dye Decoloration and Optimization of Operational Parameters

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## ABSTRACT

A facile one pot efficient synthetic approach has been adopted to prepare GO-SnO<sub>2</sub> nanocomposite material from the synthesized GO. The X-ray diffraction (XRD) analysis revealed the formation of GO-SnO<sub>2</sub> structure from the SnO<sub>2</sub> precursor during the synthesis. The surface characteristics and elemental composition of the nanocomposites have been studied by means of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS). The characterization of the GO-SnO<sub>2</sub> composites suggested that the metal is uniformly dispersed in the graphene matrix and gives evidence indicates the nanosheets are GO, which are formed and interface and we can see good compatibility between the graphite oxide and the tin matrix. Electrochemical decoloration of an aqueous solution of a textile dye Chrysophenine was investigated under different experimental conditions by using carbon electrodes. Our findings revealed that the electrodes evidenced great dye decoloration abilities to treat solutions containing this dye, in the presence of the synthesized nanocomposite. The influence of the synthesized nanocomposite was remarkable in the electrochemical dye decoloration process and ~100% color removal was found by the addition of 0.15g nano composite per 250 mL of the dye solution.

Keywords: carbon electrodes, electrochemical decoloration, nanocomposite, textile dye

## 1. Introduction:-

Recently the research interest revolved around Graphene-based materials, due to their unique thermal, mechanical, and electrical properties, which make them suitable to be used as fillers in the electrochemically prepared composite coatings [1-3]. Tin oxide, SnO<sub>2</sub> exhibits good photocatalytic properties for degrading dyes under UV light, particularly for SnO<sub>2</sub> nanocomposites due to electron transfer between SnO<sub>2</sub> and an additive [4]. Graphene is a best choice as an additive because it is an exciting two-dimensional material with a large specific surface area and perfect electrical properties [5]. The development of electrodeposited Sn-GO composites has shown promising electrochemical performance related to various industrial applications, such as corrosion protection, electronics fabrication or anode material for lithium-ion batteries [6]. In addition, the incorporation of graphene-related materials into Sn and Sn alloys acting as lead-free solders (i.e., SnAgCu, SnBi, SnZn and SnIn) facilitated an improvement of their wetting property, but an insignificant change in their melting point [7, 8].

The reported literature for the synthesis of tin-oxide nanoparticles need multiple steps with manipulation of process variables which is less efficient and time consuming [9, 10]. There are reports on growing SnO<sub>2</sub> nanorods onto the surface of graphene nanosheets that require some organic compounds for their synthesis process. During the synthesis process, these compounds strongly adsorbed over the surface of SnO<sub>2</sub> and the surface active sites are blocked resulting in poor performance of the system [11, 12].

Azo dyes constituting the largest class among the synthetic colors. Large amounts of different dyes are being used in the textile industries for dyeing purpose. Since dyes are carcinogenic and toxic, they imbalance the chemical and biological nature when they are discharged into the water bodies. About 10-15% of azo dyes are found to be unutilized and discharged to the environment via wastewaters leading to serious pollution, hence it is under considerable pressure to minimise the water consumption and to reduce the treatment cost. Conventionally textile wastewater is being treated through biological, physical and chemical methods [13, 14]. However, disadvantages such as high operating cost, incomplete azo dye degradation, possible secondary pollution, and high energy consumption, impede the practical applications of these methods in full-scale wastewater treatment methods. Electrochemical methods have been successfully tested [15] and it has certain significant advantages such as simple equipment, easy operation, lower operating temperature, etc. The process requires significantly less area and equipment than the conventional biological treatment processes [16, 17].

In the present work, we synthesized SnO<sub>2</sub>/GO composites using a simple, cost-effective method whereby all the reaction parameters were carefully optimized. The prepared nanocomposite material were characterized and reported in this study for better understanding the properties of nanohybrid material. The nanocomposite could be successfully used electrochemical decoloration of toxic textile dye. The present work focuses on the electrochemical decolorization/degradation treatment of the textile dye, using carbon electrodes, with the addition of the prepared nanocomposite to the

dye solution. The efficiencies of the electrochemical process is evaluated and various parameters are optimized for the electrochemical decolorization/degradation of the Chrysophenine dye. The existence of nanoparticles (MNPs) in the nanocomposite provides fast electrochemical decoloration of toxic dye on the carbon electrodes from aqueous media.

## 2. Methods and Materials:-

### 2.1 Instrumentation:

- 2.1.1** Scanning Electron Microscopic studies: The surface morphologies of the composite samples were examined by scanning electron microscopy, using a ZEISS Supra 40 scanning electron microscope (SEM).
- 2.1.2** Transmission electron microscopic (TEM) analysis: The TEM offers excellent opportunities to study textural details in fine-grained aggregates. Like light microscopy, the TEM not only provides information about orientation but also about grain shape and, more importantly, about dislocation microstructures indicative of active deformation mechanisms. Transmission Electron Microscope (TEM) images were taken using High Resolution (HR) TEM images was taken with HITACHI H9500.
- 2.1.3** EDAX analysis: The weight percentage of elements in the metal nanocomposite coatings were verified by using energy dispersive X-ray analysis using FEI ESEM Quanta (EDAX) machine.
- 2.1.4** XRD studies: XRD analyses of the powdered samples were performed using an X-ray power diffractometer with Cu anode (PAN Analytical Co., X'pert PRO, Almelo, The Netherlands), running at 40 kV and 30 mA, scanning from 4 to 80° at 3/min, for data including particle size or crystallinity measurement.
- 2.1.5** UV-visible studies: A UV-Vis Spectrophotometer (ELICO, SL-159) was employed to measure the optical density of (at  $\lambda_{\max}$ ) dye effluent before and after electrolysis. The decolourisation efficiency was calculated using the relation:

$$\%E = \left\{ \frac{(A_i - A_e)}{A_i} \right\} \times 100$$

where,  $A_i$  and  $A_e$  are absorbance values of dyes solutions before and after treatment with respect to their  $\lambda_{\max}$ , respectively

**2.1.6** pH and conductivity measurement: A water analyser (Systronics, Model-371) was used to measure the pH and conductivity of the dye effluent before and after electrolysis under different electrolysis conditions.

**2.1.7** Electrochemical degradation of textile dyes: Graphite carbon electrodes of 4.5 cm length and 0.8 cm diameter were used as anode and cathode for electrochemical degradation studies. [18] The supporting electrolytes such as NaCl were added to the electrolytic solution, which increases the conductivity of the solution and reduces the electrolysis time.

### 2.2 Batch Studies:

Few batch studies were carried out in 250-mL of dye solution. A weighed amount (0 to 0.25g) of nanocomposites was added to the dye solution in flasks. The flasks were agitated at a speed of 140 rpm in an incubator shaker at 308 K. The influence of pH (2.0-14.0), initial dye concentration (0.01 – 0.04 mg L<sup>-1</sup>), nanocomposite dosage (0-0.25 g L<sup>-1</sup>), current density (0.04-0.16 Amps) and temperatures (298, 303, 310, 313, 318 K) were evaluated. At regular time intervals samples were collected for measuring the residual dye concentration in the solutions.

Now at a time interval of 2 minutes, 5 minutes, 8 minutes, 12 minutes and 15 minutes samples were taken out, centrifuged at 10000 rpm for 15 minutes and the amount of dye removed from the solution and the residual amount of dye in each flask was explored was measured using a spectrophotometer. The same process was carried out for nanocomposites.

### 2.3 Chemicals and Reagents:

All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in double distilled water. Toxic textile dyes, Chrysophenine was purchased from Molakalmur textile industries.

### 2.4. Preparation of GO-SnO<sub>2</sub> Nanocomposite:

GO-SnO<sub>2</sub> nanocomposite was synthesized by homogeneous coprecipitation method. Urea and hydrazine hydrate were reduced under refluxion method. Initially 2 m mol. of 25 ml SnCl<sub>2</sub>.2H<sub>2</sub>O (Merck 98%) was dissolved in 50 ml of GO solution (2 mg/ml) under stirring. Then 4 m mol of 25 ml urea was dissolved into the above solution. After adding the urea, the mixed solution was treated in an ultrasonic bath for 1 h and then refluxed for 2 hours. The solution was then cooled down to room temperature and then 1 ml of H<sub>2</sub>N<sub>2</sub>O (Hydrazine hydrate, MERCK, 80%) was added with continuously stirring for 5 h. The mixed solution was slowly heated for 5 min. Then the solution became black. Then the solution was cooled down to room temperature followed by filtering and washing for several times. The obtained solid product was dried at 60 °C under vacuum for 5 h. The as-synthesized composite material was dried under vacuum in order to improve the crystallinity of SnO<sub>2</sub>. Finally homogeneous G-SnO<sub>2</sub> composite was obtained.

### 3. Results and Discussions:

#### 3.1. Characterization of Sn/GO nanocomposite:

##### 3.1.1 Powder X-ray diffraction Studies:

Powder X-ray diffraction (XRD) patterns of graphene-SnO<sub>2</sub> nanocomposite are shown in figure 1. The diffraction peaks of graphene-SnO<sub>2</sub> composite clearly show the tetragonal rutile structure (JCPDS No. 41-1445) confirming that the synthesized and thermally treated samples retain the tetragonal SnO<sub>2</sub> structure. The strong intensity can be attributed to the good crystallinity of SnO<sub>2</sub> particles. The diffraction peaks of graphene-SnO<sub>2</sub> nanocomposite are indexed with (100), (101), (111), (211), (002), (310), and (321) planes. The absence of specific diffraction peaks of graphene may be due to (i) the disordered interfacial structure produced by the interfacial bonds between SnO<sub>2</sub> nanocrystals and graphene sheets; (ii) the SnO<sub>2</sub> is highly crystalline than graphene (iii) the disordered stack nature of graphene sheets in the composite. The results reveal the presence of the (002) plane of graphitic carbon in the SnO<sub>2</sub>-GO nanocomposites [19, 20].

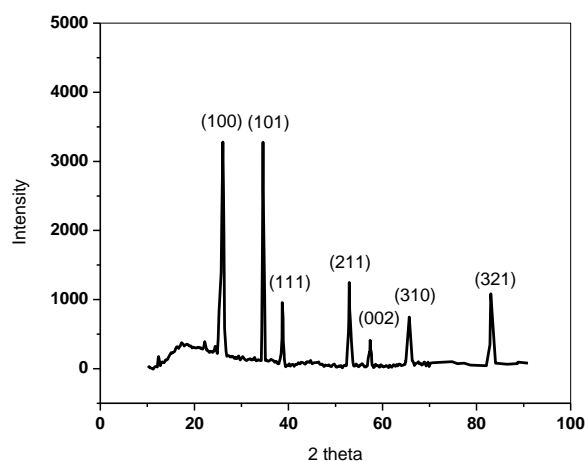


Figure 1.: XRD patterns of Sn/GO composites

##### 3.1.2. SEM and TEM analysis of the nanoparticles:

The morphology of graphene by SEM (Figure 2) shows wrinkled paper like structure. The graphene-SnO<sub>2</sub> nanocomposite reveals platelet like structure and or very thin sheet like structure [21]. SEM images of GO-SnO<sub>2</sub> show the presence of SnO<sub>2</sub> nanoparticles in the GO crumbled layer by layer sheets. The nanosized SnO<sub>2</sub> particles were observed on the graphene sheets. The average size distribution of SnO<sub>2</sub> nanoparticle was around 100 nm as shown in Figure. The sheet-like morphology was retained even after covering the surface of the graphene with an interconnected network of graphene-SnO<sub>2</sub> nanocomposite [22].

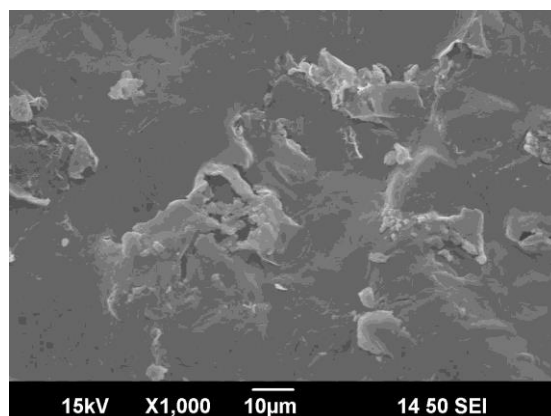
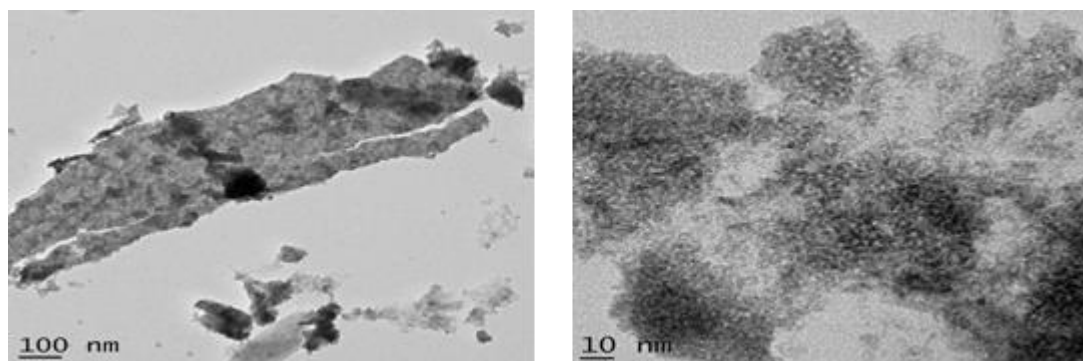


Figure 2. Scanning electron microscopy (SEM) image of Sn- GO hybrid structures.



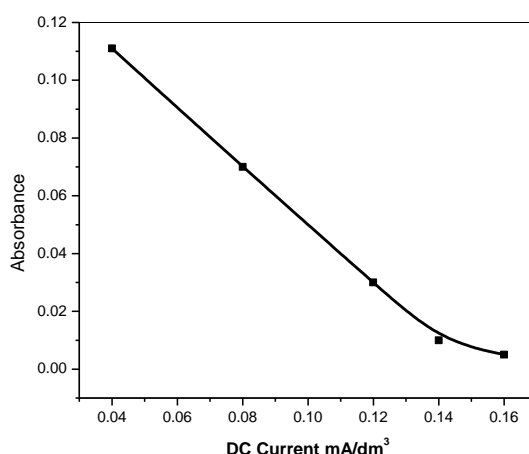
**Figure 3. TEM image of Sn- GO hybrid structures.**

The HR-TEM image of the folded and transparent 2D graphene-SnO<sub>2</sub> nanocomposite and its higher magnification images are shown in Figure 3 respectively. The uniform distribution of SnO<sub>2</sub> nanoparticle on the graphene sheets and interlayer of the graphene sheets has been observed from the HR-TEM image as shown in Figure 4.7.3. The higher magnification image clearly confirms the presence of the layered structure of graphene and SnO<sub>2</sub> nanoparticle as shown in the Figure. The size of the SnO<sub>2</sub> nanoparticle have been measured and are in the range of 50-100 nm [23].

### 3.2 Application of Sn-GO nano composite for the electrochemical degradation of Chrysophenine dye ( $\lambda_{max}=400nm$ ):

**3.2.1 Effect of initial pH:** Solution pH is one of the important factors that affect the performance of electrochemical process. Hence experiments were conducted to study the effect of pH on the degradation efficiency of textile effluent. A significant difference in the extent of decolourisation was noted when concentration of NaCl was at 0.25 g /250mL. The initial pH of the solution (3-11) was adjusted using 1N H<sub>2</sub>SO<sub>4</sub> or NaOH. The electrolysis was carried out at the current density of 0.03 Acm<sup>-2</sup> for 10 mins with a textile effluent and at room temperature (308K). After electrolysis the results indicate that final pH was slight varied from acidic condition and decreased from basic conditions. The decolouration efficiency of dye effluent was found percentage of 99.54 % in acidic pH-8 It indicated that the degradation of dye effluent in acidic solution is higher than that of in the basic media. Therefore the optimum pH 8 was maintained in subsequent experiments [24].

**3.2.2 Effect of current density:** Current density is a very important variable in electrochemical engineering. As shown in the Figure 4, both the colour and COD removal efficiency was increased by increasing the applied current density (0.04to 0.16 A/cm<sup>2</sup>) the results may attributed to the increased oxidant such as: chlorine/hypochlorite, hydroxyl radicals at higher current densities. The hydroxyl radical adsorbed on the active sites at the anodic surface of the graphite carbon increases with current density, which in turn would enhance the rate of electro-oxidation of dye molecule present in the effluent. Further increase in the current density did not have much effect on decolourisation, which can be attributed to the fact that increasing current density increases over potential required for the generation of oxidants [25]. At the same time, more energy will be consumed at higher current density applied. Therefore, the optimal current density for the successive electrochemical degradation of dye effluent was 0.14A/cm<sup>2</sup>.

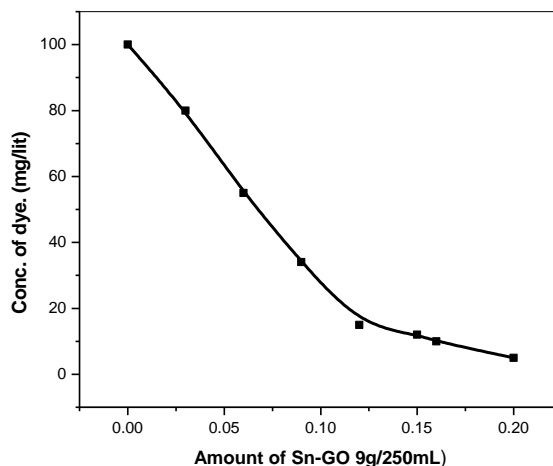


**Figure: 4. Effect of current density**

When NaCl is added, the decolourisation efficiency increased with a subsequent decrease in the applied voltage. From this observation it concluded that the introduction of NaCl increases efficiency of decoloration and obtained maximum efficiency at 0.20g/250mL.

### 3.2.3 Effect of Sn-GO nanocomposite:

Figure 5. shows the effect of Sn-GO nano particle concentration on the decoloration of Chrysophenine. In these conditions, the removal of ions in dye from wastewater is mainly due to the combination of the electro-adsorption of particle electrodes and anodes and the enrichment of ions in the solution. The concentration of Sn-GO nanoparticle is increased from 0 to 0.25g/250mL.



**Figure 5: Effect of Sn-GO nano composite on the electrochemical degradation of Chrysophenine**

In dye decoloration process, the electrons on the GO sheets react with the adsorbed oxygen ( $O_2$ ) to form superoxide radicals ( $O_2^{\cdot -}$ ) [26]. These reactive oxygen species may degrade the dye present in the solution.

### 3.2.4 Electric energy consumption:

The electrical energy consumption is the major operating cost is associated with the electrochemical degradation process. The electrical energy consumption (E) is required to decompose diluted dye solution at various current densities was calculated using the relation:

$$E = (VIt_E/V_s) \times 10^{-3}$$

where E is the electrical energy consumption ( $kWhm^{-3}$ ), V is the applied voltage (V), I is the applied current (A),  $t_E$  is the electrolysis time (h) and  $V_s$  is the volume of dye effluent ( $m^3$ ).

**Table 1: The electric energy consumed during the degradation of 50 ppm (w/v) Chrysophenine dye solution (pH 8) at various current densities**

Current (A)	Current density ( $Am^{-2}$ )	Electrolysis time (min)	Energy Consumption ( $kWhm^{-3}$ )
0.01	10	20	2.0
0.02	20	15	2.6
0.04	40	10	3.3
0.06	60	5	2.9

As per the results, shown in Table-1, the minimum electrical energy consumption was  $2.0 k Wh m^{-3}$  for dye solution at  $10Am^{-2}$  current density. At higher current densities, the energy consumption was found to be increased, which may be attributed to the increased hydrogen and oxygen evolution reactions.

## Conclusion:

We successfully synthesized the metal  $SnO_2$ -GO nanocomposite by a facile one-pot preparation approach. The characterization of the  $SnO_2$ /GO composites suggested that the metal is uniformly dispersed in the graphene matrix and gives evidence indicates that the flake-like nanosheets are GO, which are formed and interface and we can see good compatibility between the graphite oxide and the  $SnO_2$  matrix. Electrochemical decoloration of an aqueous solution of Chrysophenine dye was investigated under different experimental conditions by using carbon electrodes. Our findings revealed that the electrodes evidenced great dye decoloration abilities to treat solutions containing this dye, in the presence of the synthesized nanocomposite. The influence of the synthesized nanocomposite was remarkable in the electrochemical dye decoloration process and almost 100% color removal was found by the addition of 0.2g nano composite per 250 mL of the dye solution at a pH =8, under a current density of  $0.14 A cm^{-2}$  on electrode and NaCl supporting electrolyte at 0.2 g/250mL . Our results showed the applicability of electrochemical technology with the application of the nanocomposite proposes, an

alternative for dye removal from textile wastewater, eliminating their strong color by reducing their eco-toxicological consequences for the aquatic environment.

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