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Enhancing catalytic efficiency of graphene in degradation of organic pollutants - Role of surface modification

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This research aims to protect freshwater resources from industrial effluents and reduce greenhouse gas emissions, addressing the issue of global warming. The study focuses on synthesizing smart non-metal functionalized graphene materials by converting saccharide units into graphene layers doped with oxygen, sulphur, and nitrogen (GO, S-GO, N-GO) for the primary treatment of various organic-based industrial effluents. The significant factors such as saccharides as precursor, heteroatom doping (O, N, S), pH, time, temperature, microstructure, surface functional groups, and morphology have been explored to enhance adsorption and photocatalytic efficiency. The study targeted less-explored pollutants like textile based azo, xanthenes, thiazine dyes and chlorophenols. Catalytic efficiency has been assessed via fluorescence properties, showing that S-GO exhibited superior photocatalytic performance compared to GO and N-GO. A linear correlation between fluorescence intensity, lifetime, and photocatalytic activity for degrading 2,6-dichlorophenol and organic dyes is observed using sample S-GO as the catalyst. The role play of Sulphur in the efficient catalytic activity of graphene structure is well analyzed. The research findings offer valuable insights for designing functionalized 2D Carbon materials, which could serve as effective catalysts for treating pollutants from textile, pharmaceutical, and petrochemical industries.

Keywords: Fluorescence, Graphene oxide, Hydrothermal, Nitrogen doped graphene oxide, Organic pollutants, Photocatalyst, Pyrolysis, Sulphur doped graphene oxide

Introduction

Water, a renewable natural resource is essential for all living beings in our environment. There is a global concern was mainly on the maintenance of quality of water. The present research work is focused on the management of the industrial water resources by the remediation of pollutants. The requirement of drinking water is the greatest challenge in the 21st century due to rapid population and industrialization which is causing tremendous threats to our ecosystem[1,2].

Among the textiles, pharmaceutical and petrochemical industries present in our country, the textile industry consumes large amounts of water, with huge wastewater discharge and high potential pollution that puts a high stress on the global water resource[3,4]. High consumption of water is seen in the stages like bleaching, dyeing, printing and finishing segments. The aqueous dyeing requires 100-180 L of water to dye 1 kg of fibers[5,6]. Nearly 1.6 million liters of water is required every day for an average-sized textile mill with processing capacity of about 8000 g of fabric per day. It is estimated that around 280,000 tons of textile dyes is being discharged as industrial effluent every year[7].

Taking the above factors into consideration, the current trend in research is to design catalyst from natural sources especially carbon and other non-metal atoms to remediate effluents from wastewater. In this context, smart 2D material of carbon from disaccharide (sucrose) and polysaccharides (starch and cellulose) with more non metal (O, S, N) functionalized materials are worthy of research. Graphene sheets are naturally hydrophobic; hence the functionalization of graphene sheets is important for their future applications to make graphene soluble in common solvents, thus avoiding stacking and making non-covalent organic functional groups exist on the surface[8].

Different units of saccharide being a carbon-rich material can provide the carbon backbone in the synthesis of micro and nanostructures. There are a few recent reports available on the synthesis of carbon-based nanomaterials using sucrose as a precursor[9-12]. Among these precursors, the polysaccharides have been mainly used as reducing reagents[13], as a binder with GO[14]. They are also explored as alternatives to conventional plastics[15]. In the case of graphene based nanomaterials (GBNs), the precursor of starch and cellulose have been widely used as polymers and nanocomposites for the remediation of pollutants[16] and also used as catalyst for biomass hydrolysis[17].

To date, the research on non-metal functionalized graphene-based nanomaterials (GBNs) derived from saccharides and processed via high-pressure hydrothermal methods remains unexplored. A key factor in this area is the efficiency of carbon atom conversion into smart nanomaterials, as it is crucial for the conservation of carbon in the atmosphere.

In this context, it is clear that the catalytic potential of 2D carbon materials has been underexplored. Therefore, it is essential to develop new, cost-effective methods to introduce covalent heteroatoms (O, S, N) for functionalizing carbon-based 2D materials. Utilizing simple carbohydrate precursors adds significant value to this research, as it allows for a deeper understanding of the conversion process. Moreover, investigating the surface-active properties of the resulting materials is vital for assessing their suitability for fluorescence and catalytic applications, while maintaining the structural integrity of graphene. This study addresses these factors and aims to provide foundational insights into the conversion of biomass into advanced carbon-based materials. The findings could significantly impact water resource management and the remediation of effluents from various textile and pharmaceutical industries.

Experimental Section

Materials required

The chemicals used in the present study for the preparation of carbon microspheres and graphene-based nanomaterials (GBNs) were sucrose (Merck chemicals), starch (Nice chemicals), cellulose (Merck chemicals), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) (Nice chemicals), Glacial acetic acid (Nice chemicals), 99.9% Ethanol (Analytical CS reagent), Ammonia (NH_3), Methylene blue (MB) stain (Merck chemicals), methyl orange (Nice Chemicals), rhodamine black (Merck chemicals), acid red -1 (TCI chemicals), p-chlorophenol (Nice chemicals) and 2,6 dichlorophenol (CDH chemicals).

Method of preparation of Carbon microspheres and non-metal doped Graphene materials

The nano scale carbon materials were prepared using di (sucrose) and poly- saccharide (starch) as precursor individually by changing the reaction parameters such as time, pH and temperature based on the greenish fluorescence using hydrothermal method and the precursor cellulose was processed through pyrolysis. The experimental conditions of pH, temperature and time were optimized on the basis of greenish emission of the product sample under UV-light. A black solid obtained under calcinations at 220°C for 4 h at neutral pH using di (sucrose) saccharide as precursor. The sample was labeled it as Carbon Microspheres (CMs).

The sample as obtained in the form of brown gel after calcinations at 190°C, neutral pH for 4 h using sucrose as precursor. The sample was labeled it as Graphene oxide-1 (GO-1). The brown crystalline sample obtained after calcined at 220°C, pH=9 for 5 h using starch as precursor and labeled it as Graphene oxide-2 (GO-2). The precursor cellulose was carbonized through pyrolysis for 6 h at 300°C. The brownish black crystalline sample was obtained and labeled it as Graphene oxide-3 (GO-3).

To introduce sulphur atom into the carbon moiety, the above obtained samples of GO-1, GO-2 and GO-3 treated with sulphuric acid in the proportion of 1:5 and calcined at 80°C individually. A black solid sample as obtained after drying at room temperature and the black solid samples was labelled Sulphur doped graphene oxide S-GO-1, S-GO-2 and S-GO-3 respectively[18].

The precursor sucrose and starch solution (0.1 mM) was hydrothermally heated at 220°C for 4 h with liquid ammonia in the ratio of 1:10 and a brownish-black solid samples was obtained and labeled Nitrogen doped graphene oxide-1&2 (N-GO-1 and N-GO-2), respectively[18]. The similar proposition of the precursor cellulose with ammonia carbonized through pyrolysis at 300°C for 6 h. Hence, here also brownish black crystalline sample as obtained and which is labeled it as sample-10 (Nitrogen doped graphene oxide -3 (N-GO-3).

All the ten products samples (GO-1, GO-2, GO-3, S-GO-1, S-GO-2, S-GO-3, N-GO-1, N-GO-2, N-GO-3 and CMs) were treated with ethanol to remove organic impurities and stored in a refrigerator for further characterization.

Material Characterization

The functional groups, bonding characteristics and structural defects in the prepared functionalized GBNs (graphene oxides (GO-1,2,3), sulphur doped graphene oxides (S-GO-1,2,3) and nitrogen doped graphene oxide (N-GO-1,2,3) and carbon microspheres (CMs) were analyzed using the FT-IR

(IR Affinity-1, SHIMADZU) and Micro- Raman spectrometer (BRUKER, RFS). The micro structural analysis was carried out using powder X-ray diffraction (PXRD) using Cu-Kα radiation (PAN analytical model Xpert pro). The surface morphology of the as-prepared samples was studied using the Field Emission Scanning Electron Microscope (FE-SEM) (FEI QUANTA) and High-resolution Transmission electron microscope (HR-TEM) (JOEL). The surface elemental composition and chemical state of the elements were identified using X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, Inc; Model: PHI5000 Version Probe III). The catalytic efficiency of the samples for the discoloration of dyes and degradation of Chlorophenols were studied under UV LED (365 nm), Sunlight and UV-visible spectrophotometer (UV - SHIMADZU 1601) respectively. The surface area and pore size analysis of the prepared sample was analyzed using Quanta Chrome instruments Autosorb IQ series**.**

Screening the catalytic efficiency of the prepared samples

The catalytic activity of the as-prepared samples was screened individually for the decolouration of dyes namely Methylene blue (MB), Methyl orange (MO) and, Rhodamine –Black (Rh-B) and Acid Red-1(AR-1) in the ratio (sample/dye) of 2mg/10mL (w/v). The discolouration reaction was followed at a pH of 3 for 2 h under dark, UV and sunlight respectively. The adsorption and photo catalytic efficiency of as-prepared sample S-GO-1 for the degradation p-Chlorophenol (p-CP) (0.001mM) and 2,6-Dichlorophenol (2,6-DCP) (0.5 mM) were also screened individually by taking the sample and the chlorophenol taken in the ratio of 1 mg/10 mL and degradation efficiency was calculated with respect to the blank.

Results and Discussion

Microstructural analysis

In general, the nature of bonding, intrinsic defects in 2D carbon structures play a key role in their surface activity and emission phenomena. The intrinsic and extrinsic defect arises in 2D material because of existing foreign atom. It is necessary to identify the type of defect from any of the two viz:- based on dimensionality, i.e. zero-dimensional defects. (Stone-Wales defects, vacancy, adatoms, and substitution impurities) or one-dimensional defects (line defect, GBs and edges). Hence it becomes imperative to screen and analyze the above aspects using powerful tools. The micro Raman spectra of the 2D materials provide wider coverage of the nature, intensity of structural uniformity and hybridization of Carbon atoms. The results of the study can be extrapolated to their catalytic application in the degradation of dyes and chlorophenols.

In the present study, graphene structures were doped with hetero atoms of O, N and S from the source of di and polysaccharides. The nature of bonding and defects if any in the structure of solid samples of GBNs (GO, S-GO, N-GO) and CMs were analyzed using micro Raman spectra as given in Fig. 1 (a, b, c). The bands due to sp^2 C (G Band) and sp^3 C (D band) were identified. The D-band denotes the disorderliness existing in the microstructure of prepared micro and nanomaterials. The type of defect

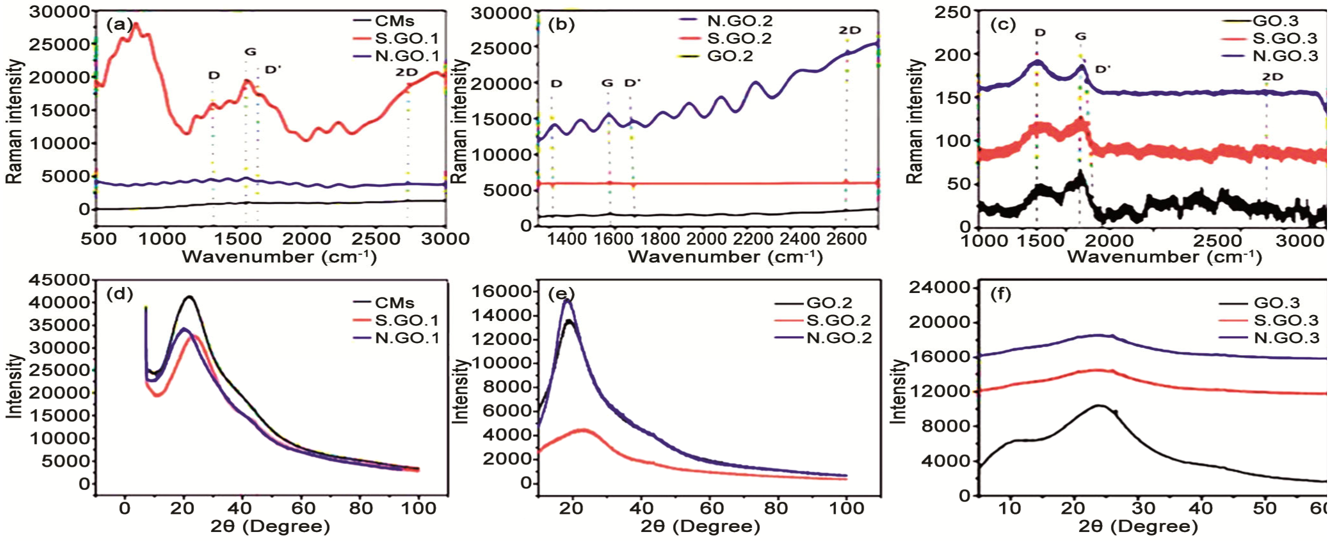

Fig. 1 — Micro Raman spectra and PXRD of prepared samples using (a, b) sucrose, (c, d) starch and (e, f) cellulose as precursor

was analyzed using $I_D/I_{D'}$ ratio obtained from this analysis. It is seen that the amount of defect density enhanced upon increasing number of saccharide units. The hetero atom of N (I_D/I_G=1.03) introduces more structural defects in the graphene oxides (I_D/I_G=0.89) than that of S atom (I_D/I_G= 1) which are indicative of the existence of covalent bonding in the structure of graphene. The number of layers in the microstructure of GBNs has been enhanced upon increasing saccharide units as precursor which was identified from I_{2D}/I_G value (<1). The defect structures in the form of grain boundaries (GBs) are indicated by the ratios of $I_D/I_{D'}$ value[19-21]. The result indicates the type and amount of defect in the structure can play an important role in the surface properties of the product samples.

The microstructure and crystal orientation of the prepared samples were analyzed using the PXRD spectrum as presented in Fig. 1 (d, e, f). The diffraction patterns confirm the formation C based micro and nanomaterials. The interplanar distance (d) value reduced with more heteroatom in the structure of the prepared sample of S-GO (0.38 nm) and N-GO (0.36 nm) with respect to GO (0.42 nm) suggesting the presence of the functional groups at the edges and not in the basal plane of graphene. There is a shift in diffraction angle with increased peak width suggesting the existence of defects in the form of grain boundaries and the observation correlates well with the micro Raman report. The role-play of the number of saccharide units as a precursor in the enhancement of the structural defects is well established when compared with the reports of monosaccharides as the precursor[18,22,23]. It also confirmed their eligibility of the as prepared samples for their surface activities.

Surface morphology analysis

A close look at the morphology of the samples is needed in order to validate the above reports. The presence of layer structure[52] is evident from the FESEM images (Fig. 2) of the as-prepared samples and correlated well with the reports of Sudhaparimala *et al.,* 2022[18].

All the carbon microspheres (CMs) are in perfect spherical morphologies and well-dispersed and have a high degree of uniformity as shown in Fig. 2(a). The layer with flakes were identified on the surface prepared graphene oxides (GO) and as given in the Fig. 2 (b, e, h). The spherical aggregates on the layer structure of S-GOs as in Fig. 2(c, f, i) is suggestive of enhanced catalytic property[18]. The amount of spherical aggregates reduced upon increasing number of saccharide units which may enhance the catalytic activity. The N-doped graphene oxide (N-GO) shows the perfect layer structure seen in Fig. 2 (d, g, j) when compared with the previous reports[23]. The strong positive influence of N and different saccharide units as precursor in the retention of the graphenic layer is confirmed. The surface morphology correlates well with PXRD analysis.

Surface functional group analysis

The wide scan X-ray photoelectron spectra of prepared samples (CMs, GO, S-GO, and N-GO) are given in Fig. 3(a-c). The C(1s) spectra of as-prepared samples show the binding energy value due to alkane (284.6 eV), alkene (285.9 eV) and hydroxyl (285.6 eV), epoxy (286.3 eV), carbonyl (287.3 eV), carboxyl (289.1eV) groups, suggesting the presence

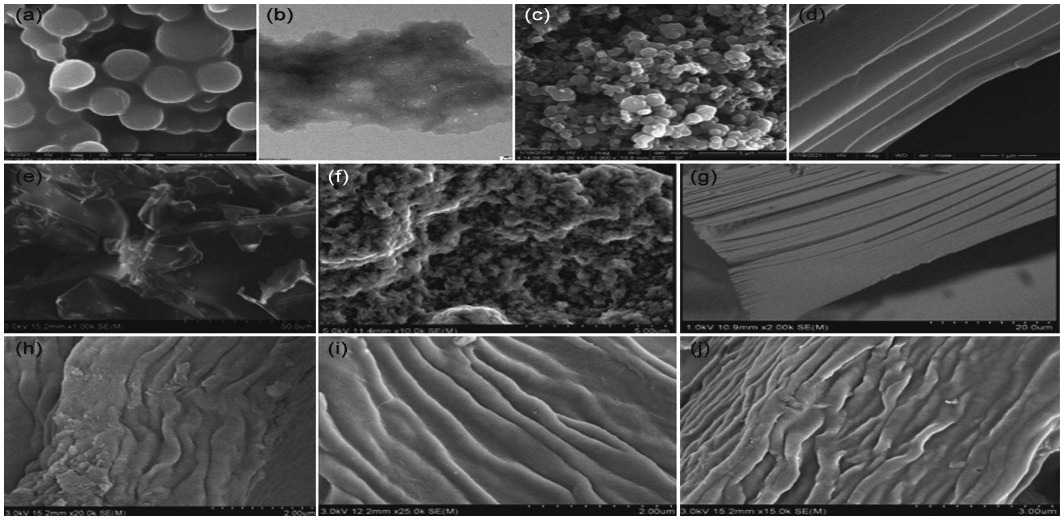

Fig. 2 — FE-SEM and HR-TEM images of prepared samples using (a-d) sucrose, (e-g) starch and (h-j) cellulose[52] as precursor

of the respective groups on the surface of the as-prepared samples. The additional binding energy peak corresponding to C-S was identified at 285.4 eV in the sample of S-GO and the C-N peak was identified at 287.7 eV in N-GO and their respective functional groups such as sulphonic acid, pyridinic, pyrrolinic and quaternary N observed from narrow scan XPS spectra of S(2p) and N(1s) [23-25]. They were existing only at the edges and not on the plane of graphene. The added N atom plays significant role in retaining the planarity, surface morphology and electrical neutrality due to replacement of C by N and which is not in the case of sample S-GO. The results correlate well with microscopic images of S-GO and N-GO, respectively. The C/O ratio from the EDX analysis which reflects the relative surface composition, it was decreased on doping graphene oxide (2.39) with S (2.02) and enhanced on doping with N (2.65) through hydrothermal process which was confirmed the replacement of C by N. These are all play a significant role in the catalytic activity of the prepared samples towards pollution treatment of contaminated water and protect various freshwater resources.

Similarly, the FT-IR spectra of the as-prepared samples indicated the functional groups corresponding to C-O, C=O, C=C, O-H, C-H were identified in the product sample and compared with the precursor. The more intense peaks due to O functionalities were identified in the sample GO. The functionality of S (C=S) and N (C=N) was identified at 792 cm^{-1} and 2230 cm^{-1} in S-GO and N-GO respectively[26], which confirmed the introduction of S and N on the structure of graphene oxide. It can be observed that the O is replaced more by N than S in the graphene oxide moiety as confirmed by the decrease in O functionality in GO through the transmittance value[18]. The amount of surface defects in the prepared samples can also be reviewed from sp^3/sp^2 ratio of C obtained from XPS analysis. The results consolidate the eligibility of the doped samples of graphene for the surface-active applications towards the remediation of organic pollutants.

The efficiency of retaining C atom in the samples during any process has become an important aspect as it indicates the amount of C given out to the atmosphere in the form of green gases. In today's context, the C cycle needs to be conserved. In the synthesis it depends on the surface and bulk composition of the product samples with respect to the precursor. The data related to the basics in the quantification of C atom economy is presented in the Table 1 which takes into account the report[27]. It can be seen from the table that the solid GBNs samples (GO, S-GO, N-GO) obtained from di and polysaccharides have retained more than 60% on the structure and 40% on the structure of CMs. The remaining percentage of C can be assumed to be involved in the evolution of gases of CO and CO_2 during the conversion of polymeric form of saccharides into GBNs upon aromatization. The amount of C content on the surface was calculated

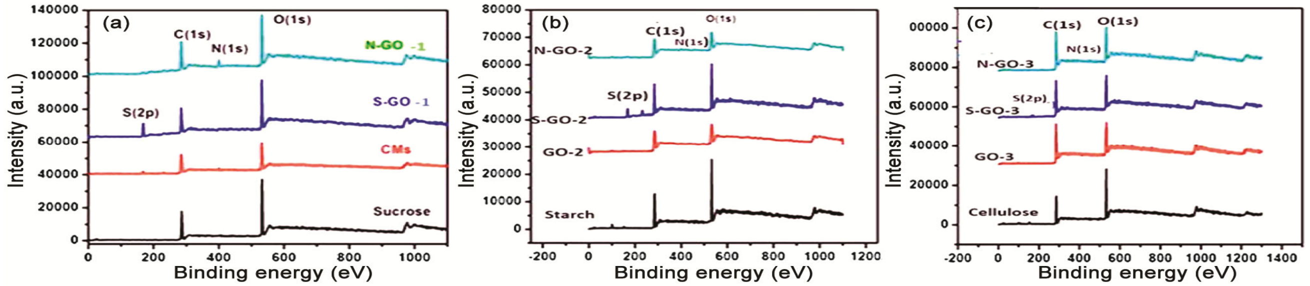

Fig. 3 — Wide scan XPS spectra of samples using (a) sucrose, (b) starch and (c) cellulose as precursor

Table 1 — Comparison of Carbon atom efficiency on the surface and bulk of the as-prepared samples using TGA and XPS analysis

Structural properties	Instrumental tool used	Carbon microspheres	Graphene oxide	Sulphur doped graphene oxide	Nitrogen doped graphene oxide
Total percentage of Carbon content	TGA analysis = Sum of volatile matter + Fixed Carbon + Ash content	40.16	GO-2=55.40 GO-3=61.12	S-GO-1=52.23 S-GO-2=71.1 S-GO-3=66.89	N-GO-1= 65.27 N-GO-2=36.16 N-GO-3=57.83
Percentage Carbon content on the bulk	= Total Carbon content – amount of Carbon on the surface	16.36	GO-2=19.44 GO-3=20.01	S-GO-1= 23.61 S-GO-2=31.29 S-GO-3=65.96	N-GO-1= 33.67 N-GO-2=14.13 N-GO-3=22.56
Percentage Carbon content on the surface	XPS = (Total Carbon × Percentage Carbon from XPS analysis) ÷ 100	23.80	GO-2=35.96 GO-3=41.11	S-GO-1= 25.82 S-GO-2=39.81 S-GO-3=44.21	N-GO-1=31.60 N-GO-2=22.03 N-GO-3=35.27

using XPS analysis. Upon comparing the GBNs, the Sample N-GO has less carbon with respect to precursor and GO due to replacement of carbon by nitrogen during conversion of GO into N-GO. The percentage of carbon present equally on the bulk and surface of sample S-GO. The carbon content on the surface due to the presence -SO_3H, COOH, C-OH , C=O functional groups were around 50% which may be utilized more towards fluorescence and catalytic activity. The discussion presents a novel approach in the assessment of C atom efficiency in the processing of carbon resources. It also suggests the approach towards conversion of Carbon atom into graphene-based nanomaterials as the available literature reports are very limited[28].

Band gap, Surface area and pore size analysis

In order to analyze the emission especially fluorescence property of the samples, the value of the band gap energy is very important. In the study, the direct gap energy calculated using *Tauc* plot for sample S-GO-1, S-GO-2, S-GO-3 and it was found to be 4.4eV, 4.3eV, 4.15eV, respectively as seen in the Fig. 4 (a-c). It can be suggested that the doping of Sulphur atom reduced the band gap energy more with respect to GO than N-GO due to less electronegative difference between the heteroatom of Sulphur and Carbon. The band gap energy of prepared GBNs was correlated with reported GBNs[29,30]. Further, it can be seen that surface active centers responsible for the fluorescence and catalytic property are seen to be enhanced in S-GO due to less band gap, large structural defects with high Oxygen containing functionalities.

The above factors with respect to S-GO can be correlated by the results of BET and BJH pore analysis of sample S-GO as represented in the Fig. 4 (d-f). The total surface area of samples S-GO-1, S-GO-2 and S-GO-3 from BET analysis was found to be 1532.987 m^2/g, 5445.56 m^2/g and 529.47 m^2/g, respectively[52]. Among the three samples of S-GO, the sample S-GO-2 prepared from starch has relatively large surface area which may contribute more catalytic activity for removal of organic pollutants in industrial wastewater. From BJH pore analysis, the pore diameter of the samples S-GO was found to be less than 2 nm (S-GO-1=1.55 nm, S-GO-2=1.55 nm, and S-GO-3=1.85 nm) which confirms the micro porous nature existing on the surface of the sample[31,32]. The sample S-GO-3 has got large pore diameter which may enhance the catalytic activity.

Screening the catalytic (adsorption and photo) efficiency

The microstructure and surface property of graphene-based nanomaterials discussed above clearly indicated their suitability for the catalytic activity. The study focused on the less explored areas of the decolouration of organic dyes and degradation of chlorophenols by the non-metal atom passivated layer structure of graphene (product samples) through their fluorescence. The correlation between the fluorescence intensity of the samples and the photo catalytic activity are quantified with precision.

Tunable luminescence spectra

It is observed that the fluorescence properties of layer structure of carbon depend on intrinsic inner structure and surface functional groups in the carbon core of graphene structure where the contribution is from the π-π* transition of aromatic sp^2 carbon and n-π* from C=O functional groups exist on the 2D

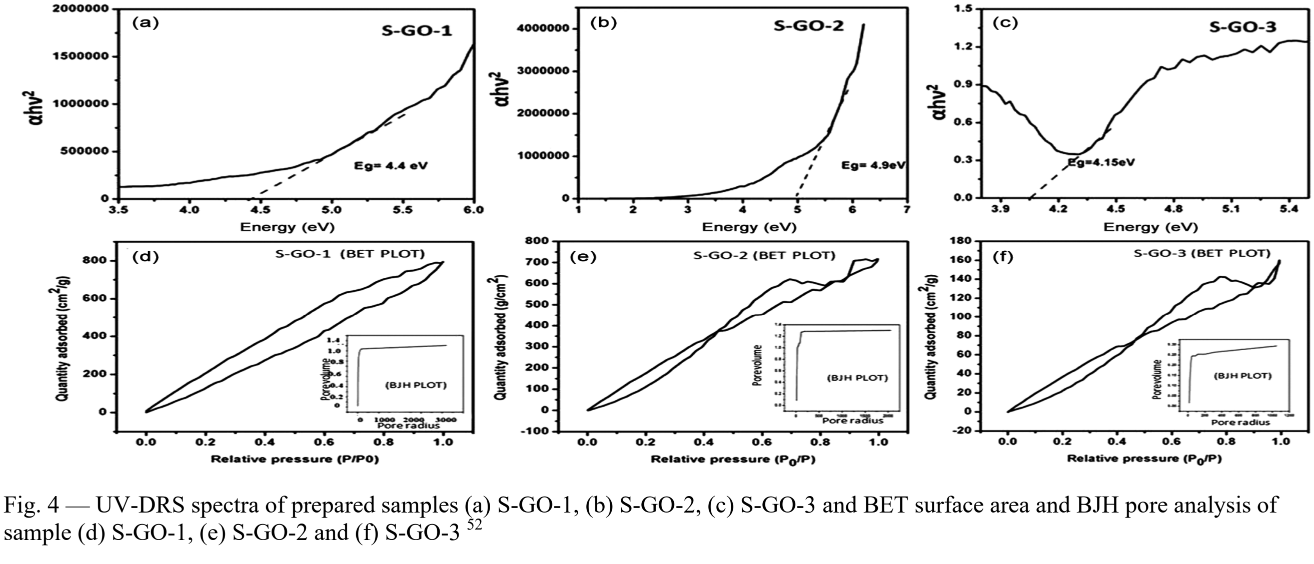

Fig. 4 — UV-DRS spectra of prepared samples (a) S-GO-1, (b) S-GO-2, (c) S-GO-3 and BET surface area and BJH pore analysis of sample (d) S-GO-1, (e) S-GO-2 and (f) S-GO-3 [52]

structure[33]. The photoluminescence mechanism can arise in two different ways of emissions i.e., Stoke's and anti-stoke's shift[34].

The tunable luminescence of the prepared samples from the precursors of di and polysaccharides was analyzed based on excitation dependent emission and represented in the Fig. 5(a-c) [18]. The prepared sample exhibits emission due to Stoke's shift which may correlated well with disorderliness or defects in the structure and exhibit emission towards visible region. Upon comparing the emission nature of microsphere of carbon with other prepared GBNs, it is noted that the lower dimension and the hetero atom of sulphur contribute more towards intense green emission among the GBNs. It may be due to reduced band gap of poly aromatic structures as suggested in this report[37]. The green emission arises due to the emission of photon from Fermi energy levels through internal conversion from π*-n (-C=O group) existing on the surface.

The comparison of fluorescence intensity of prepared GBNs with respect to the precursor indicated that the number of saccharide units contributes inversely towards the fluorescence intensity. It may be due to enhancement in the layered carbon as observed from PXRD analysis. The reduction in the fluorescence intensity indicated less recombination of electron–hole pair in the microstructure of GBNs and it is clearly seen in the S-GO prepared from cellulose. The results also suggest that the precursor of cellulose is more suitable for the enhanced photocatalytic activity for remediation of organic pollutants among the precursors considered in the study. Based on the above factors, a simple mechanistic pathway has been suggested and presented in the Fig. 5 (d)[35-37].

In the context of fluorescence of GBNs, lifetime measurement adds value for the better assessment of photocatalytic activity of the GBNs. The fluorescence lifetime values of the samples S-GO-1, S-GO-2, S-GO-3 were found to be 2.46 ns, 1.73 ns and 9.02 ns, respectively. The observed higher fluorescence life time of sample of S-GO-3 indicated that the recombination of electron-hole pair takes place very slowly. The property can be tailored for better photocatalytic activity for the degradation of organic moieties.

Treatment of industrial effluents

Adsorption and UV- Visible assisted catalytic decolouration of organic dyes

The anti-recombination phenomenon of electron-hole pairs in the heterogeneous photocatalytic activity of 2D carbon materials is significant and is attributed to their nanometric thickness and high surface area. Few studies have focused on tuning Carbon-based nanomaterials, particularly 2D layer structures, as shown in Table 2[46,47].

This study screened the prepared samples (CMs, S-GO, N-GO) as catalysts for the degradation of

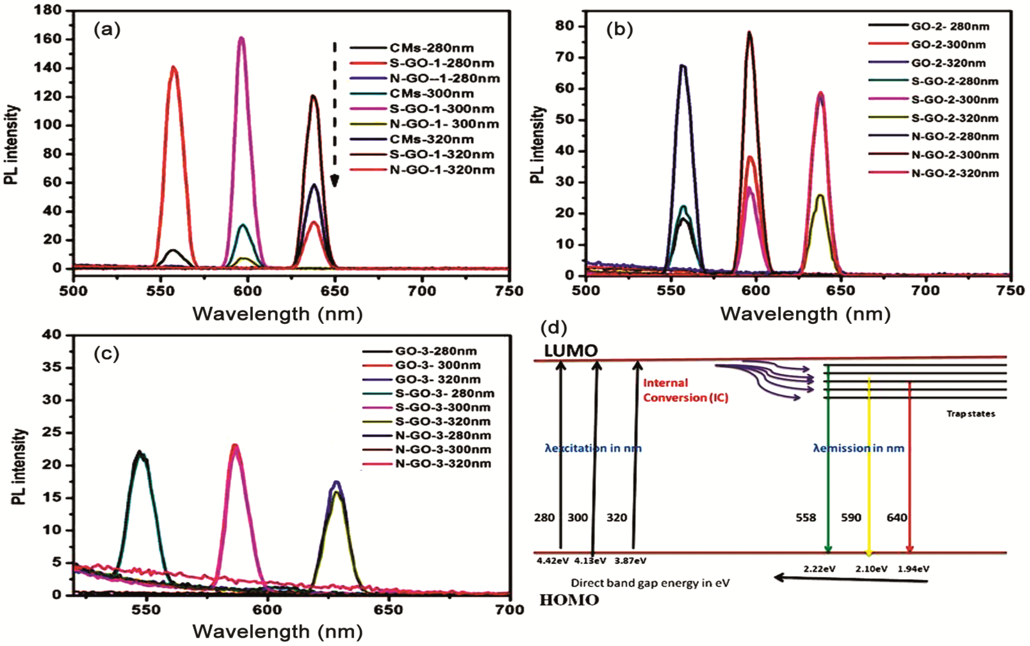

Fig. 5— Tunable luminescence spectra of prepared samples using (a) sucrose, (b) starch, (c) cellulose as precursor, and (d) energy level diagram for the excitation dependent emission

organic pollutants in water, including textile industry dyes (MB, Rh.B, MO, AR-1), and petrochemical and pharmaceutical pollutants such as p-chlorophenol (p-CP) (0.001 mM) and 2,6-dichlorophenol (2,6-DCP) (0.5 mM). Experimental conditions were optimized at an acidic pH of 3, with pollutant concentrations of 2 mg/10 mL and 1 mg/10 mL, respectively, for 2 h, under both UV-light and dark conditions.

The comparison of adsorption and photocatalytic efficiency for organic dye decolouration is shown in Fig. 6(a-d). The catalytic efficiency of S-GO was notably higher under both dark and UV-light conditions compared to other GBNs and CMs, likely due to electrostatic interactions between surface functional groups and the adsorbates. With respect to the precursor, the catalytic efficiency of sample S-GO from polysaccharides showed better performance than from monosaccharides.

An enhanced photocatalytic activity was observed for S-GO-3, prepared from cellulose, likely due to its high fluorescence time, pore diameter (1.85 nm) and acidic functional groups on the surface. While previous studies reported that GO materials are not photoactive enough to degrade methyl orange[48-49]. This study found that S-doped GO (S-GO-3) demonstrated excellent photocatalytic activity, achieving 78% decolouration of azo dyes especially methyl orange. Similar results were observed for the decoloration of methylene blue and rhodamine B when S-GO-3 was used as the catalyst, aligning with previous reports on S-GO or S-rGO/Ag_3VO_4 composites[45].

For N-GO, the decolourization of rhodamine B increased from 15% to 30% when the precursor was changed from glucose to sucrose. This indicates that N-GO, derived from sucrose (disaccharide), showed superior photocatalytic performance compared to monosaccharide-based (aldose and ketose) samples for the decolouration of organic dyes[18,43].

The reaction kinetics of prepared samples for dye decolouration under dark and UV-light were analyzed, revealing that the reaction follows pseudo-first-order kinetics under both conditions. The reaction rate was higher for rhodamine B and methyl orange under dark conditions. These findings are significant as S-functionalized graphene materials

Table 2 — Comparison of photocatalytic degradation of chlorophenols using various catalyst reported from literature

S. No.	Sample	Reported direct bandgap (eV)	Pollutant	Reaction time (min)	Photocatalytic degradation (%)	Reference
1	Graphite oxide	2-4.7	4-Chlorophenol	100	92	50
2	Graphene oxide	1.8-4	4-Chlorophenol	100	97	50
3	Titanium oxide g-C_3N_4	2.89	4-Chlorophenol	60	64	51
4	Sulphur doped graphene oxide (S-GO)	3.57	2,6-Dichlorophenol	120	23	43
5	Sulphur doped graphene oxide-1 (S-GO-1)	4.4	2,6 – Dichlorophenol, p-Chlorophenol	60 60	67(sunlight), 61(UV-light) 17(Sunlight) 8(UV-light)	Present study

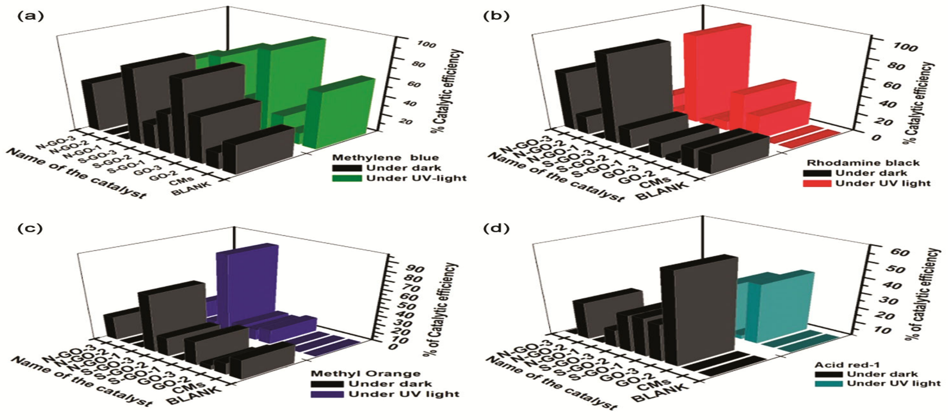

Fig.6 — Comparison of percentage adsorption and photo catalytic discoloration of organic dyes using as-prepared samples (CMs, GOs, N-GOs, S-GOs) (a) Methylene blue (MB), (b) Rhodamine black (Rh.B), (c) Methyl orange (MO) and (d) Acid red-1(AR-1)

have been explored more in electrical applications than in water pollution management.

Adsorption and UV- visible assisted catalytic degradation of chlorophenols

Further, the research study extended for prove the prepared materials as the efficient catalyst for the treatment of effluents obtained from pharmaceutical and petrochemical industries consisting of chlorophenols as the major toxicants. The catalytic efficiency of the prepared samples was screened under dark and UV-light for the degradation of chlorophenols namely p-chlorophenol (p-CP) and 2,6-dichlorophenol (2,6-DCP).

From the result, it is found that CMs and N-GOs derived from di and polysaccharides showed negative catalytic activity in the dark and UV-light for the degradation of p-CP and 2,6-DCP. Among the prepared samples of S-GO, the sample S-GO-1 exhibit better catalytic efficiency for the degradation of chlorophenol under dark and light medium. This may attributed due to the presence of higher percentage of Sulphur containing functional groups exist of surface calculated from wide scan XPS spectra. The direct band gap energy of the prepared sample S-GO-1 (4.4 eV) was overlaps well with band gap energy of chlorophenols (4.4 eV).

The screening of the adsorption and photocatalytic efficiency of the as-prepared sample of S-GO-1 as a catalyst for the degradation of chlorophenols was encouraging and given in the Fig. 7(a-e). The reaction kinetics was followed for every 10 min under UV-light and sunlight using S-GO-1 as catalyst catalyst for degradation of p-chlorophenol as represented in Fig. 7(a) and Fig. 7(b), respectively. The photocatalytic efficiency of S-GO-1 was relatively high under sunlight (17%) than UV-light (8%) for p-chlorophenol[18]. There was an effective adsorption and photo catalytic activity observed under dark (21%), sunlight (67%), UV-light (61%) for the degradation of 2,6-DCP Fig. 7(c,d,e).

The study also examined the influence of precursors on the photocatalytic efficiency of S-doped GOs. It was found that the photocatalytic efficiency of S-GO-1, prepared from sucrose, was 8% higher under UV light than the S-GO sample prepared from glucose (0%), which had been reported for p-chlorophenol degradation. This improvement may be due to a higher precentage of S-containing functional groups and surface defects. Additionally, the adsorption and photocatalytic activity of S-GO (under UV light) increased by nearly 15% and 38%, respectively, compared to the S-GO prepared from glucose[18]. Finally, the photocatalytic activity of

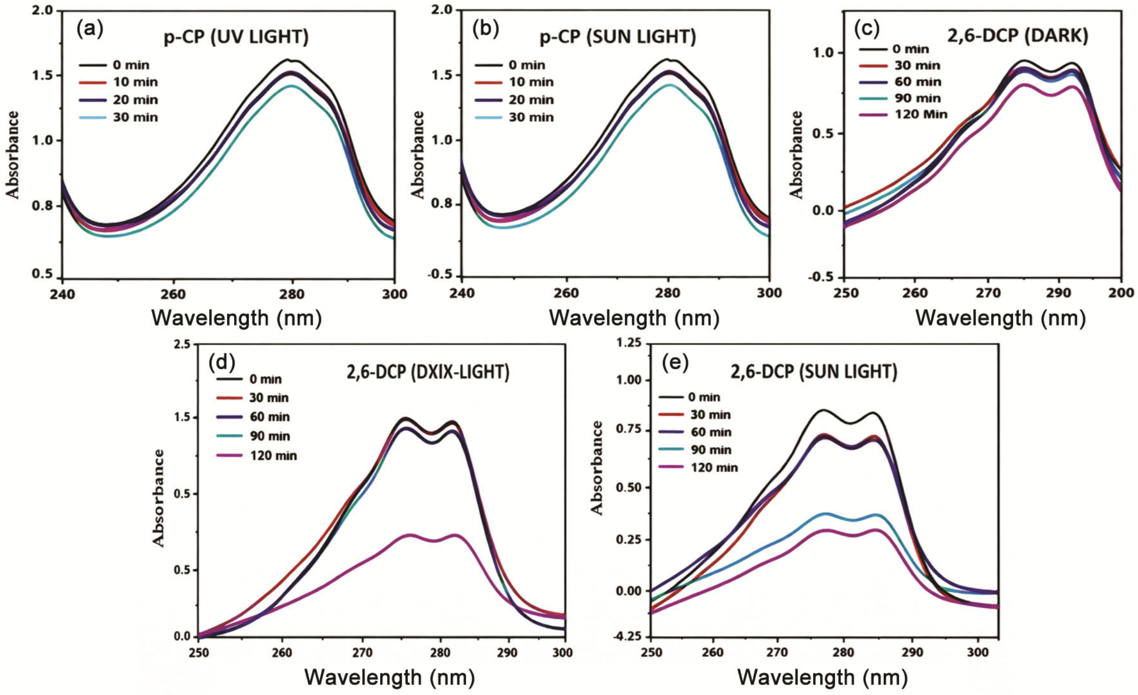

Fig.7 (a-e) — Comparison of adsorption and photo catalytic degradation of p-chlorophenol (p-CP) and 2,6-dichlorophenol (2,6-DCP) using S-GO-1 as catalyst; (a) p-CP- under UV-ight, (b) p-CP- under sunlight, (c) 2,6-DCP under dark, (d) 2,6-DCP under UV-light and (e) 2, 6- DCP under sunlight

S-GO-1 was found to be effective for the degradation of 2,6-DCP compared with existing reports as given in the Table 2.

Based on these observations, it can be concluded that S-GO-1, derived from sucrose, is an effective heterogeneous photocatalyst for removing organic pollutants, including dyes and chlorophenols. Photocatalytic activity is a process of advanced oxidation, depending on optical and surface properties such as bandgap (E_g), surface area, morphology, and the functional groups present on the microstructure. The S-GO-1 sample demonstrated a large surface area and sulphur functionality on the surface, as confirmed by BET and XPS analysis.

Conclusion

Graphene-based nanomaterials have been explored due to their chemical stability, large surface area, and ability to adsorb chemicals and biomolecules, with size-dependent optical properties. The study found efficient retention of solid carbon material and reduced carbon emission (40%-70%) depending on heteroatom doping. The experimental conditions were optimized in such a way as to design the carbon structures with enhanced catalytic activity for the degradation of toxic organic pollutants chlorophenols (mono, di and poly) and amino dyes present in the industrial wastewater. It was found that the structural defect created by covalent atoms on the surface in terms of grain boundaries and functional groups (hydroxyl, carboxyl, epoxy, carbonyl) influences the catalytic activity both by UV-light and adsorption. The oxygen and sulphur containing acidic functional groups played major role in the enhanced photo catalytic activity upon increasing number of saccharide units for the removal of organic pollutants with less intense green fluorescence. From the outcome of the study, the correlation between precursor, microstructure, surface morphology and surface activity of the functionalized graphene structures are well established with the help of spectroscopic and microscopic data and suggested reaction mechanism. The study concludes that optimizing saccharide unit conversion into Carbon-based materials can effectively treat polluted industrial water.

Conflict of interest

The authors declare that they have no conflict of interest.

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