SOLAR LIGHT ACTIVE CeO₂/rGO HYBRID PHOTOCATALYST FOR DIRECT VIOLET 51 DEGRADATION

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ABSTRACT

A solar active hybrid photocatalyst is synthesized and applied for detoxification and degradation of dye molecules in an aqueous medium. Synthesis of rGO from GO using *carica papaya* leaf extract and nano-sized CeO₂ is coated over the rGO to make the hybrid photocatalyst. Prepared hybrids evaluated using SEM, XRD, EDX, IR, surface area (BET) and UV-DRS. Synthesized hybrid is used as photocatalyst for the degradation of Direct Violet 51 (DV 51) dye under both UV and solar irradiations. The surface area of the synthesized composite (CeO₂/rGO-HYBD) is 95 m²/g. The Langmuir kinetics for the reaction is also studied. The basic algorithm is used to fit the curves for the LH isotherm; deviations from the experimental values and the reaction order are enumerated for three different hypothetical conditions.

Keywords: Carica papaya, CeO₂/rGO Hybrid, Photocatalytic Degradation, Fractional Order, Direct Violet 51

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INTRODUCTION

Surface water bodies are highly demanded by the numerous activities of the growing population and industrialization over the past few decades expatiate to water scarcity. Plenty of water pollutants have threatened the availability and existence of pure water and makes various environmental issues to living beings. Predominantly dye effluents, due to their harmful nature, toxicological and deep coloring¹⁻³. So far various physico chemical and biological treatment technologies are adopted for the environmental remediation, protection and control of dye effluents. The photocatalyst is applied for the remediation of water pollution continuing from the mid of 19th century. Present investigations in dye effluent treatment show detoxification cum degradation occurred instantaneously with the help of catalysts results in innocuous final compounds.

TiO₂, ZnO, ZnS, Fe₂O₃ and SnO₂ photocatalysts are fabricated in the recent decade and made for the photocatalytic applications advantageously, in the dye degradation processes under UV irradiation.⁴⁻⁸ These semiconductor materials and chalcogenide catalysts are played a renowned role in degrading the organic dyes with the help of a UV light source. As the titania is active under UV rays, therefore it is essential to explore other catalysts that are active under visible light. Exploration of the visible light active photocatalyst is necessary and its band gap demands the required energy suitably absorbs from the incident visible light.⁹ The activity of photocatalysts can be improved on fixing metal¹⁰ or metaloxides¹¹ on the surface of host catalyst that can produce an interfacial electron and hole transfer between the catalyst and the host material after light absorption, effectively prevent the reunion of photo-generated electron and positive hole pairs^{12,13} on the surface of the catalyst. Photocatalyst size and morphological behaviours¹⁴ are the key factors that induce the photocatalysis through doping as well as extra phase coupling.

Most of the nanoscale materials impressed the scientific community as because of its physicochemical character distinct from the bulk materials owing to their high amount of active surface. This will improve the photocatalytic activity of a nanoscale semiconductor.¹⁵ Advanced materials of visible light active semiconductor photocatalysts such as Cu₂O nano particles,¹⁶ ZnO/CeO₂ solid solution nano wires,¹⁷ MoS₂/TiO₂ nanocomposite,¹⁸ nest-like Bi₂WO₆¹⁹ and hierarchical dendritic CdS²⁰ are prepared by choosing the method of preparation for the fabrication of a suitable morphology. Solar active photocatalyst harvests renewable energy and effectively degrade organic toxins in an environmentally efficient way.

Electron transferring applications of energy science and technology in the solid electrode and aqueous medium is performed in a remarkable way by the hybrid of nano architected carbon materials such as CNT along with semiconductor catalyst. Present investigations focused on the superior electrochemical behavior of CNT and its applications in energy storage²¹ and super capacitors.²² An allotropic, mono layer with an atomic thickness of sp² hybridized carbon formed in a two-dimensional honeycomb matrix, called as Graphene. Graphene assisted structural hybrid of 1D, 2D and 3D macroscopic architectures^{23,24} shows marked synergistic effects, by ion diffusion and charge transfer properties during electron transfer reactions. Graphene possesses very low resistance²⁵ results in enhanced conductivity. Graphene also has an extreme specific surface area²⁶ owing to its extremely thin nature. The synthetic methodology is vital in architecting the structure and shapes of graphene layers.²⁷

Isolation of grapheme,²⁸ unwrap outstanding research works, especially in the fields of energy conversion strategies like lithium batteries,²⁹ super-capacitors,²² gas diffusion for gas separation applications,³⁰ advanced optomechanics,³¹ as well as functionalized with biomolecules for imaging through labeling and targeted delivery via therapy^{32,33} in medical. Oxygen belonged functionalities in GO^{34,35} intervenes between the layers resulting in exfoliation of the oxidized graphene sheets into individual GO flakes in large quantities^{34,36} highly differs it from graphite. Furthermore, the charge transfer is prohibited in GO due to the strong localization of the oxygen functionalities,³⁷ but its reduction will produce a graphene-like molecule called rGO, which is a good conductor.

The electron excitation energy of a UV semiconductor photocatalyst can be effectively served from visible light by combining catalyst with graphene-based nano-carbon material as hybrid.³⁸ In our latest study we made a hybrid of a semiconductor CeO₂ with rGO prepared by green synthesis efficiently to harvest the visible light energy. Sun light is chosen as a visible light source as it provides renewable energy with a wide spectrum of visible and UV ranged light.

The metal oxide semiconductors are most ideal as role as catalyst because of their stability at a higher temperature, cost-effective, reusability and eco-friendly. In our investigation, we have reported several novel initiative studies and focused to study the synthesis of a novel hybrid metal oxide photocatalyst using semiconductor CeO₂ hybrid over the rGO.

It comprises the conversion of graphite to graphene oxide using modified Hummer's method followed by green reduction using *Carica papaya* leaf and doping with inner transition metal oxide. The resultant hybrid metal oxide is focused on the less photo-corrosive property. Synthesized materials characterization and its photocatalytic capability have to be examined scientifically.

Moreover, the prepared catalyst is employed for the degradation of dyes in their effluent, and the impact of pH and concentration on degradation efficiencies also investigated. Photodegradation is carried out under UV and solar lights. In the descending energy pattern, solar light holds nearly 5 % of UV and remaining equal parts of visible lights.

EXPERIMENTAL

Concentrated H₂SO₄, Concentrated HCl, KMnO₄, C₂H₅OH (99.9%), Ce(NO₃)₃.6H₂O, NaOH and Glycerol are procured from Sigma Aldrich and used without any purification. Direct Violet 51, M.W: 719.7 (C₃₂H₂₇N₅Na₂O₈S₂), CAS/CI No. 5489-77-0/27905, having the maximum abs wavelength of 549 nm and Graphite powder (Alpha Chemika, India) are also used. All the aqueous phase dilutions are performed using double distilled water.

Conversion of Graphite to GO

The synthesis of GO from graphite is carried out using the modified Hummer's method is the first step in the preparation of rGO. In this method, 1.0 g of graphite is taken in an RB flask and 23 ml of the con.

H₂SO₄ is added. The temperatures of the contents are brought down using ice for a temperature below 5°C with constant stirring. Along with this 3 g of powdered KMnO₄ is added carefully along with continuous shaking and the temperature of the flask is maintained constantly. After one hour the matters are cooled to ambient temperature then kept for another 2 h with stirring. Exactly 46 ml of double distilled water is mixed and the contents are heated to 95 °C for 30 min. The contents are quenched with the addition of 140 ml of double-distilled water. The so formed GO is filtered and washed two times with 10 % HCl solution and then finely with water.

Preparation of Green Extract

Matured papaya leaves are collected from well-grown papaya trees and thoroughly cleaned with water to remove the surface contaminants. The clean leaves are cut with a mean size of 2 to 3 cm², ground well and made into a paste with the help of mortar and pestle. The paste is mixed with a small quantity of double distilled water and again ground well. The contents are then filtered through Whatman 40 filter paper, the solid mass is discarded and the filtrate is used as a reductant for the synthesis of rGO. In order to avoid the preservation practices, every time the required quantity of leaf extract is prepared freshly.

Green Synthesis of rGO

About 30 mg of GO is sonicated for about 0.5 h with the addition of 50 ml of water. Followed by adding 30 ml of papaya leaf extract with constant stirring. The contents are heated to 95 °C for about 12 h with a condenser on the top of RB flask to avoid the evaporative loss of volatiles. After 12 h reflux, the black colored rGO is filtered, washed with plenty of distilled water and dried at 90°C using hot air oven and used for doping with cerium oxide.

Synthesis of CeO₂ Doped rGO

Exactly 100 mg of Ce(NO₃)₃.6H₂O dissolved in 60 ml of glycerol. About 0.5 g of prepared rGO is for heated 24 h using RB flask under the N₂ atmosphere. Additional care is given during the process of this oxidation and the end of the reaction is achieved by quenching with an excess of water. The contents are filtered by centrifugation, washed with plenty of water than any residual glycerol is also removed by ethanol wash and finally dried at 110°C. The CeO₂/rGOs thus produced are labelled as CeO₂/rGO-HYBD.

Photocatalytic Study

Photocatalytic degradation study of DV 51 is carried out with prepared CeO₂/rGO-HYBD under the irradiation of UV and solar lights separately in the specified reactor setup. The % of dye removal by photocatalysis is measured after completion of adsorption processes, based on optimization studies required a quantity of catalyst is added in a selected concentration of dye solution and kept overnight. The residual dye concentration after the respective light irradiation is evaluated by separating the dye solution using a centrifuge. The filtered clear dye solution is tested at the λ_{max} of the selected dye using a double beam UV-Vis spectrometer (Elico make). Dilute HCl and aq. NaOH is used to adjust the solution pH of dye solution to study the pH effect of the degradation efficiency. The quantum of separate photocatalytic degradation processes is measured by deducting the individual components of photolysis and adsorption for ease of understanding. The stock solution of DV 51 dye is prepared based on the percentage purity of the dye sample using double distilled water as a solvent. Further, dilute solutions of DV 51 dye is prepared from the 1000 mg/l stock solutions through proper dilutions.

UV Photo Reactor Setup

Photocatalytic degradation studies are carried out using Philips India high-pressure UVB (having the cut off wavelength of 365 nm maximum) mercury vapor lamp model RDC-R17d with the 160 W and operating voltage of maximum 240 V. This UV lamp is positioned at the center of the photo-reactor and the pyrex tubes with samples are surrounded circularly. Each pyrex tubes are installed with a button type magnetic stirrer.

The Solar Photoreactor Assembly

The photodegradation by solar irradiation can be done by solar photoreactor assembly manufactured using Pyrex glass cooling jacketed beaker with a magnetic stirrer. In this process, the experimental dye

concentration solution with a known dosage of the photocatalyst is irradiated directly using sunlight without using any optical filters and devices. To minimize the evaporation loss of dye effluent and to maintain the reaction temperature, cooling water flow is given in the jacket side. Using distilled water the marginal volume loss is made up to the mark. All the photocatalytic dye degradation processes by solar irradiations are carried out in a clear sunny day between 11 AM to 03 PM only.

Characterizations

The morphological parameters carved with the Hitachi S-4800 scanning electron microscope (SEM) at 5kV accelerating voltage and Rigaku Ultima III is used to observe the X-ray diffraction (XRD) patterns of the powdered crystals (NIT, Trichy, India) with a monochromatic Copper $K\alpha = 1.54056 \text{ \AA}$ radiation. Observations are collected for 3 h at the rate of 20 readings/min. Energy dispersive X-ray's elemental analysis is performed by Ametek - Apollo X detector at 30 kV. Perkin Elmer- Spectrum RX is employed to elucidate the functionalities of the GO and various rGO using FT-IR spectroscopy (Fourier Transform Infrared). Band gap edges for the prepared semiconductors are calculated from the Reflectance Spectrum (DRS) using DB-20S and UV-visible Elico- BL-192 spectrophotometer is engaged to measure the aqueous dye solutions transmittance its λ_{max} for all concentrations used and its degradation studies.

RESULTS AND DISCUSSION

Characteristics of rGO and CeO₂ Doped rGO

Vibrational spectrum intern explicit to explore the functionalities of a molecule, and further the changes occur in them due to the chemical treatments. The efficiency of chemical treatment can be clearly observed by careful analysis of the FT-IR spectrum. The FT-IR spectrum of rGO and CeO₂/rGO-HYBD prepared, are shown collectively in Fig.-1(a). The peaks at 1096 cm^{-1} and 1390 cm^{-1} in rGO correspond to C–O and epoxide functional group vibrations respectively. Furthermore, the absorption peak at 1680 cm^{-1} is due to the backbone vibrations of remaining sp^2 hybridized carbon skeleton which is unaffected by oxidation³⁹ and a wide band like a peak at 3450 cm^{-1} belongs to OH group.⁴⁰ CeO₂/rGO-HYBD shows diminished peaks for the hydroxyl and C–O stretching frequencies. Moreover the absorption peaks intensity increased for CeO₂/rGO-HYBD in 1585 and 1735 cm^{-1} due to the graphitised C=C and C=O functional groups. The epoxide stretching is relatively retarded when doping with ceria and also explains the replacement of ceria over the rGO surface. Acid-base interactions make the Ce^{4+} effectively placed over rGO surface through Ce–O linkage. The Ce–O stretching show as a minor peak at 450 cm^{-1} on the increasing concentration.⁴¹ Research reports conclude total reduction of GO may be difficult⁴². These results indicate the rGO present in the CeO₂/rGO-HYBD has been reduced in a better way.

XRD plot observed for rGO and CeO₂/rGO-HYBD samples prepared from GO by papaya leaf extract as a reducing agent are shown in Fig.-1(b). In contrast, to GO, the rGO and CeO₂/rGO-HYBDS are exhibits their reflection peak (002) at 25° and 26.2° ^{43,44} respectively with the d spacing values of nearly 0.36 nm , uniformly in all concentrations of doping. The increased d spacing represents the restacking in rGO as well as internal sandwiched CeO₂. The broadness of the peaks surpassingly sharpens from rGO to CeO₂/rGO-HYBD sample implies the amorphous to crystalline nature as well as the particle size of the CeO₂/rGO-HYBD is showing lesser. Diffracting angles for the ceria equivalent to the lattice plane are observed at 29.46 (111), 33.44 (200), 48.68 (220), ensured from the ICDD number 01-075-9470 for face-centered cubic ceria.

The UV-visible DRS of CeO₂/rGO-HYBD is shown in Fig.-2. The band gap (E_g) of the sample is evaluated from the energy equation, $E_g = 1239.8 / \lambda$. Where, 1239.8 correspond to a multiplication factor of Plank's constant and speed of light. The corresponding wavelength of light employed is λ . The band gap 2.91 eV is calculated from the observed absorption λ_{max} edge at 426 nm .

The obtained band gap of the CeO₂/rGO-HYBD shows a reduction in band gap of CeO₂ (3.19 eV) and the result is comparable with the results of bismuth oxide-graphene nano composites.⁴⁵ The CeO₂/rGO-HYBD sample synthesized by green reduction process shows the surface area of $95 \text{ m}^2/\text{g}$ (BET) and shows a narrowed band gap, optimum to utilize visible light energy. The CeO₂/rGO-HYBD sample has been used for further photocatalytic studies.

SEM image at different magnifications of the GO sample is shown in Fig.-3(a) & (b) and CeO_2/rGO -HYBD sample is shown Fig.-3(c) and (d). The GO image describes the multi-layers of graphene are separated spectacularly and it is obviously in agreement with the XRD d-space values of 002 lattice plane. The smooth surface morphology of GO also pictured along with the EDAX of the GO as an insert in Fig.-3(b). From the EDAX values, it is observed that a considerable amount of oxygen content substantiates the presences of C-O functionalities that ensure the good oxidation in the first step of the preparation. Figure-3(c) presents the morphological behaviours of CeO_2 doped rGO. rGO layer is coated with nano-sized CeO_2 uniformly over the surface and in all the rGO layers consistently. The EDAX insert in Fig.-3(d) also validates the presence of Cerium dopant quantitatively. Presence of least quantity of non-metals and minerals of alkaline and alkaline earth metals may be due to the traces of reducing agent and the chemicals applied in the reaction process respectively.

Fig.-1(a): FT-IR Spectrum and (b) XRD Pattern of GO and CeO_2/rGO

Fig.-2: UV-DRS Spectrum of CeO_2/rGO -HYBD Absorption Cutoff Wavelengths

Photocatalytic Degradation Studies of DV 51 Dye Using CeO_2/rGO -HYBD

Photocatalytic degradation of DV 51 dye is studied with the help of CeO_2/rGO -HYBD catalyst in two different lights, UV and solar lights. Results are presented graphically in Fig.-4 respectively. It is necessary to omit the adsorption of dye on the catalyst-composite surface for the calculation of net photocatalytic degradation. As seen from the Fig.-4, the percentage of dye removal is gradually decreased from lower to higher dye concentrations for a specific catalyst dosage of 40 mg/L in both UV and solar irradiations. A considerable decline in adsorption is observed before and after ceria dope with rGO. As the semiconductor surface covers the graphitic area and hinders the dye adsorption over the surface of the carbon.

Effect of pH

A pH of the solution is a necessary tool in determining the environmental impact and also determines the extent of photodegradation using catalysts⁴⁶. Among the many factors which are responsible for the adsorption of a solute on a solid surface, pH is a dominant factor that has a great influence on the

adsorption. The DV 51 dye degradation is performed with a pH range of 2.0 to 11.0 as presented in Fig.-5. The graph shows the acidic pH is suitable for effective dye degradation may be due to the following specifics,

There are two factors needs to be considered while analyzing the mechanism of variation of adsorption with respect to pH. One is the changes occurring on the surface of the catalyst and another one is the ionization of dye molecules. Graphical observations conclude the following facts regarding the photodegradation of DV 51 over $\text{CeO}_2/\text{rGO-HYBD}$ catalyst, DV 51 dye adsorption over the catalytic surface is smoothly increased in the acidic range.

Fig.-3: SEM Image at Two Different Magnifications of GO (a and b) and $\text{CeO}_2/\text{rGO-HYBD}$ Sample (c and d). The inset in Figures 3(a) and 3(d) are the corresponding EDAX

Fig.-4: Photocatalytic Degradation of Various Concentration of DV 51 dye Under UV and Solar Light Irradiations

Acidic condition increases the active sites over the catalytic surface results in more adsorption of DV 51. Earlier transfer of the excited electron⁴⁷ through all over the area of rGO delay the recombination and produce $\text{HO}^\bullet$ radicals and a huge number of super oxide anions, which will easily oxidize the dye molecules. Further increase in pH produces more hydroxyl ions and competes with the anionic component of the direct dye molecules during the adsorption process, results in minimum activation sites for dye degradation.

Impact of Catalyst Dosage

Optimization of catalyst dosage is important for the economic and environmental feasibility studies. We carried out the $\text{CeO}_2/\text{rGO-HYBD}$ optimization for the photocatalytic degradation of DV 51. Optimization is performed by gradually increasing the quantity of $\text{CeO}_2/\text{rGO-HYBD}$ in a constant volume of DV 51 dye solution. Practically the catalyst quantity started from 10 mg, and then it is added by 10 mg increments for the next study up to the maximum of 50 mg per 100 ml of 100 mg/L concentrated DV 51 solution. Photodegradation study is undergone for a maximum time of 100 min with its natural pH under UV and solar lights individually. Practical observations are presented as a graph in Fig.-6.

Fig.-5: Influence of Solution pH for the DV 51 Degradation

On increasing the quantity of $\text{CeO}_2/\text{rGO-HYBD}$ from 10 to 40 mg, the dye removal increases slowly and on later it showing a down-trend. When the quantity of $\text{CeO}_2/\text{rGO-HYBD}$ exceeds 40 mg, there is a reduction in the number of quanta's of radiation reaching the catalyst surface, ultimately the degradation efficiency decreases. Based on this result, 40 mg of $\text{CeO}_2/\text{rGO-HYBD}$ is fixed for further studies. The quantity of catalyst requirement depends upon the physicochemical parameters like band gap, grain size, morphology, crystallinity, defects in the lattice, surface area and size of the crystallites.⁴⁸

Fig.-6: Influence of Catalyst Load on the Photodegradation of DV 51 Dye

Influence of DV 51 Concentration

The influence of initial DV 51 concentration on the photodegradation by $\text{CeO}_2/\text{rGO-HYBD}$ is evaluated by changing the DV 51 concentration from 50 to 250 mg/l. The volume of test solution fixed as 100 ml and catalyst quantity of 40 mg under UV and solar irradiations separately.

The experiment is performed for 100 min at the normal pH of the dye solution. The rates of change of dye degradation with respect to time under various DV 71 concentrations are showed in Fig.-7. Figure elaborates; the amount of DV 51 dye degraded for the optimum catalyst dosage is decreased from 93 to 64 % and 91 to 55% on increasing the concentration of DV 51 from 50 to 250 mg/L under UV and solar lights respectively. The degradation efficiency is found reversed with the DV 51 dye concentration.

Increasing initial dye concentration influences the retardation of light penetration which results in the least photon striking over the surface of the catalyst. Reports also support the discussed description moving from lower to higher dye concentrations.

Fig.-7: Effect of Dye Concentration on Photocatalytic Degradation of DV 51 Dye

Mechanism of Photocatalytic Degradation

The semiconductor-conductor hybrid photocatalyst makes a relaxed photoelectron transfer; throughout the high electrical conducting rGO surface⁴⁹ with exceptional nano layered morphology, emitted from the defective surface semiconductor CeO₂ layer. Similarly, rGO drives the electrons from the semiconductor to the surrounding environment. Super oxide radical ions are produced from the water by these driven electrons and this process also retards the electron-hole recombination,⁵⁰ retentions of pairs ensures the availability of oxidizers and reducers. The OH⁻ ions are oxidized to OH[•] radicals by the holes in a semiconductor. The dye molecules present in the aqueous medium is degraded by the super oxide radical ion and OH[•] radicals⁴⁸. The overall mechanism of photodegradation is presented pictorially in Fig.-8.

Fig.-8: Graphical Representation of the Mechanism of Photodegradation in CeO₂/rGO-HYBD Surface

Kinetics of DV 51 Dye Degradation

For the determination of detailed mechanism and performance of photocatalysis by CeO₂/rGO-HYBD, it is essential to evaluate the kinetics of photocatalysis. Kinetics of heterogeneous system has great importance during the large scale implementation in the industrial sector like photocatalysis.⁵¹ It is most suitable to evaluate the kinetics of photodegradation of DV 51 dye by photocatalyst CeO₂/rGO-HYBD with the help of the Langmuir-Hinshelwood kinetic model,

$$\ln C_t = -k_{app} t + \ln C_0 \quad (1)$$

Where C_0 and C_t are the concentrations of DV 51 (mg/L) at the beginning and after time t (min) in the photocatalytic reaction and k_{app} ($k_r k_e$) is the pseudo-first-order apparent rate constant (min^{-1}). k_{app} is measured from the slope of the curve obtained by plotting time and $\ln C_t$ in x and y-axes respectively as shown in Fig.-9(a) and (b) under UV and solar irradiations respectively. The results derived from the plots are presented in Table-1 under different concentrations of DV 51.

Table-1: Results of Pseudo-First-Order Kinetic for the DV 51 Degradation by $\text{CeO}_2/\text{rGO-HYBD}$ Catalyst

Concentration of DV 51 (mg/L)	Under UV Illumination		Under Solar Light	
	k_{app}	r^2	k_{app}	r^2
50	0.0979	0.9460	0.1177	0.8909
100	0.1027	0.9192	0.1009	0.9354
150	0.0944	0.9180	0.0767	0.9553
200	0.0684	0.9761	0.0544	0.9746
250	0.0502	0.9897	0.0424	0.9797
Average	0.0827	0.9498	0.0784	0.9472

The above data in Table-1 reveals the first order shows minimum deviation, it is obvious that the photocatalytic degradation of DV 51 dye by $\text{CeO}_2/\text{rGO-HYBD}$ follows pseudo-first-order kinetics. First-order kinetics of the photodegradation too infers the gradual retardation in rate constant irrespective of the light used for the photodegradation may be due to the fully engaged catalyst surface, delayed further degradation.

Rearranging the eqn. (1),

$$\frac{1}{r_0} = \frac{1}{k_r} + \frac{1}{k_r K_e C_0} \quad (2)$$

Where k_r and k_e are the rate constant of reaction and adsorption equilibrium constant.

Plot of C_0 versus r_0 using equation (2) describes the linear relationship existing up to the initial dye concentration of 150 mg/l after increase in initial concentrations will not further improve the rate of degradation, shows a saturation over the catalyst surface adsorption sites initially as observed from the Fig.-9(c) and (d). Saturated type Langmuir kinetics⁵² is suggested from the linearized $1/r_0$ vs $1/C_0$ plot as presented in the Fig.-9(e) and (f).

Heterogeneous catalysis process is reported in photodegradation of organic pollutants like PCP and organic dyes using solid semiconductor photocatalysts suitably fit with the Langmuir–Hinshelwood (LH) kinetic model^{53,54} and the following equation (3) is one of the widely used kinetic equation, relates the rate of decrease of concentration with respect to time to its rate and equilibrium constants as,

$$-\frac{dC}{dt} = \frac{k_r K_e C}{1 + K_e C} \quad (3)$$

Where, C is the concentration of DV 51 solution being degraded in terms of mg/l and at the given reaction temperature. k_r and k_e are the rate constant of reaction and adsorption equilibrium constant of DV 51 on $\text{CeO}_2/\text{rGO-HYBD}$. The product of k_r and K_e is generally termed as 'apparent rate constant' (k_{app} ; min^{-1}).⁵⁵ Substituting this in equation (3) results in,

$$-\frac{dC}{dt} = \frac{k_{app} C}{1 + K_e C} \quad (4)$$

In the above equations, the factor $1 + K_e C$ turns to unity or more depends on the $K_e C$ value either $\ll 1$ or $\gg 1$ allows this equation to rearrange. Results in two possible routes, classical first order when the concentration of dye solutions used in the experiment are too low or zero order when the higher concentration of the dye solutions are used due to the wide spread of dye molecules over the active centers of the photocatalyst represented in equations (5) and (6), first-order and zero-order rate equations respectively.⁵⁶

$$-\frac{dC}{dt} = k_{app} C \quad (5)$$

$$-\frac{dC}{dt} = \frac{k_{app}}{K_e} = k_r \quad (6)$$

By integrating the equation (4) yields the equation (7):

$$-\frac{C}{\exp [k_e(C_0-C)]} = C_0 \exp(k_{app} t) \quad (7)$$

Where, C_0 denotes the initial concentration of the dyes in solution to be decomposed. The term C can be evaluated only after getting the values of k_e and k_{app} along with the repeated calculation procedures. To simplify this, for a heterogeneous system⁵⁷ the following equation is widely employed,

$$-\frac{dC}{dt} = k_{app}^* C^n \quad (8)$$

The power factor n varies from 0 to 1, as in equations (6) and (8) at the two extremes. In case of n is greater than one, it may be a significance of either the ununiformed irradiation or photo corrosion that generally observed for ZnO.⁵⁸ This type of photo corrosion is restricted in CeO₂/rGO-HYBD naturally due to the surface oxygen sharing in between Carbon and Cerium metal centres in the catalyst evident from the FT-IR results.

Fig.-9: First Order Plot for Photodegradation of DV 51 dye(a) UV Irradiation and (b) Solar Irradiation, Corresponding C_0 Versus r_0 and $1/C_0$ Versus $1/r_0$ Plots of (c) & (e) for UV and (d) & (f) For Solar Irradiated Lights Respectively.

Equation (8) on integration within the limits of 0 and 1, make possible for the straight determination of the concentration of reactants by the expression,

$$C = [C_0^{(1-n)} - (1-n)k_{app}^* t]^{1/(1-n)} \quad (9)$$

While using the power rate equation (8), to calculate the order, it is found that it deviates from the ideal first-order equations, although, it is maintained in between 0 to 1 with the increase of dye concentration. For the same initial concentration, equation (9) can only be practical to fit the curves⁵⁶.

We employ the simplified first order because the fittings are seemingly straight⁵⁹ as shown earlier in Fig.-9(a) and (b), by using the linear form of the integrated equation (1). According to Lima et al.,⁶⁰ the linearization of data is misrepresented in many adsorptions related data analysis. The linearization is followed during the time where the computers and data analysis software's are not available. In the linearized plot there is a possibility of omitting many points that do not coincide with the straight line and it is applicable especially for few numbers of data collected during the experiment. The analysis of a high number of data collected during the experiment using a linear model may lead to erroneous results.⁶¹

The k_{app} and r^2 calculated under different DV 51 concentrations are provided in Table-2. The results of Table 2 substantiated that the degradation of DV 51 by CeO₂/rGO-HYBD follows pseudo-first-order or second-order kinetics.

When the equation (1) is used to test the experimental data through least square method may lead to minimum error in $\ln(C_0/C)$ function (ϵ_{in}) only without reducing the error occurred in C (ϵ_c). For this reason, the equation (9) is fitted to minimize ϵ_c by employing regular algorithms with the aid of "Microsoft Excel-Solve" application. By employing this mathematical application, the curve is fitted at the most possible way with a view to reducing the error occurred in the concentration term (ϵ_c) by tuning the order of the reaction and evaluated the same from the equation (9). The curve fitting method shows a fractional order for the process of photodegradation of dyes using CeO₂/rGO-HYBD. The results substantiated the order reported for the photo degradation reaction of phenol by TiO₂ P25 particles.⁵⁶

Using this nonlinear equation we can calculate the "Model C_t " by applying the corresponding initial concentration (C_0) of DV 51 dye and at the time 't' min. For a particular value of C_0 and 't' values, "Model C_t " values are totally depend on n and k_{app}^* (apparent rate constant for heterogeneous catalysis) and basic algorithm (Levenberg-Marquardt) helps to solve "Model C_t " to fix exactly with the experimental C_t values. Most possible fitting is enabled by changing the n and k_{app}^* suitably with the help of the "Excel-solve" programme resulting in the lowest deviation of $\Sigma(C_t - \text{Model } C_t)^2$. We tabulated the experimental C_t values from the practical observations and calculated $(C_t - \text{Model } C_t)^2$ values.

The curve plotted C_t against t for the 50 to 250 mg/l concentrations of DV 51 under UV as well as solar lights and the most possible fittest curve also reproduced over the curve (figures not shown). The first trial is done by fitting the equation (9) and the resultant n and k_{app}^* are derived for the minimum error, the second trial is done by fitting with fixed k_{app}^* value which is directly taken from the experimental rate constant (k_{expt}) values derived from the slopes of the linear equated (1) in first-order plot of the corresponding concentrations of DV 51 dye degradation and resultant n with its possible errors are derived. The third trial is done by fixing the n value as 0.99 (for 1st order) and curve fitted by synchronizing the only k_{app}^* . Errors $\Sigma (C_t - \text{Model } C_t)^2$ for all the three types of plots are compared in the Table-2.

The data in Table-2 are tabulated for UV and solar light irradiations separately and it is column-wise categorized individually for square deviation of concentration at a time 't', order of the reaction and its reaction rate. Row wise, the above three categories are tabulated for i) curve fitting using equation (9), ii) fixed k_{expt} value and iii) arbitrary n (=1) value. The data also reveals the fractional order is best suited and shows the lowest deviation from the experimental C_t values in all concentrations as well as in both irradiations.

The graphs plotted below in Fig.-10(a) and (b) imparts the sum of the square deviations against the concentration of the dye clearly depicts that the curve fitting option shows minimum deviation (ϵ_c -average error) and shows best for curve fitting using equation (9) when comparing with the other two methods (k_{expt} and $n=1$) in all the concentrations of DV 51 dye. This will eventually put forward the fractional

ordered Langmuir-Hinshelwood heterogeneous catalysis reaction kinetics of DV 51 decomposition under UV as well as solar irradiations.

Table-2: Square Deviation, Order and k_{app}^* collated data for DV 51 Dye Photodegradation under UV and Solar Irradiations

Irradiation Source: UV Light															
Category	Sum of the $(C_t - \text{Model } C_t)^2$					Order (n)					k_{app}^*				
	Concentrations of DV 51					Concentrations of DV 51					Concentrations of DV 51				
	50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
i	1.1	3.5	6.1	57.8	157	0.47	0.49	0.499	0.506	0.558	0.184	0.214	0.222	0.210	0.155
ii	6.3	47	139	321	547	0.66	0.68	0.69	0.745	0.786	0.098	0.103	0.094	0.068	0.050
iii	32	225	648	1134	1386	1.00	1.00	1.00	1.00	1.00	0.033	0.029	0.026	0.022	0.018

Irradiation Source: Solar Light															
Category	Sum of the $(C_t - \text{Model } C_t)^2$					Order (n)					k_{app}^*				
	Concentrations of DV 51					Concentrations of DV 51					Concentrations of DV 51				
	50	100	150	200	250	50	100	150	200	250	50	100	150	200	250
i	1.5	14.9	109	107	424	0.342	0.429	0.418	0.429	0.463	0.275	0.254	0.265	0.258	0.211
ii	17	49.6	167	506	1300	0.598	0.659	0.708	0.759	0.783	0.118	0.101	0.077	0.054	0.042
iii	81	264	720	1267	2264	1.00	1.00	1.00	1.00	1.00	0.032	0.027	0.022	0.018	0.015

The fractional-order varies from 0.47 to 0.56 and 0.34 to 0.46 for the UV and solar light used photocatalytic degradations of DV 51 dye by the $\text{CeO}_2/\text{rGO-HYBD}$ respectively obtained by curve fitting equation (9) as shown in Fig.-10(c). This fractional-order is greatly influenced by the by-products formed from the degradation of dye molecules during photocatalysis and may compete with the dye molecules during the photodegradation process. Naturally, further degradation of the fragmented molecules may also in consequence with the on-going primary degradation of the dye stuff, resulted in variable functional adsorption processes over the photocatalyst of the photocatalytic process. So, it makes this adsorption cum photodegradation process more complex.

According to “Chemical Kinetics and Dynamics” by Steinfeld et al., (1999) a fractional reaction order indicates that the mechanism for the reaction is more complicated⁶². The mechanism probably entails several elementary reactions. It is evident to analyze that the complexity of the photocatalytic process results with the fractional order with respect to dye molecule degradation. The proposed degraded products of a direct dye such as Congo Red and Direct Yellow 12 are also evident by research investigations carried out by Jo and Tayade⁶³; El Nemr et al.⁶⁴. Correspondingly the rate constant (k_{app}^*) of the reaction varies from 0.22 to 0.15 and 0.27 to 0.21 for the UV and solar light-driven photocatalytic degradation of DV 51 dye respectively by the $\text{CeO}_2/\text{rGO-HYBD}$ obtained by curve fitting equation (9) as presented in the Fig.-10 (d).

CONCLUSION

Synthesis of hybrid photocatalyst by choosing rGO carbon and inner transition metal oxide is performed successfully. The role of electron transfer and photo electron excitation by the respective components of the hybrid catalyst is explicated in detail. *Carica papaya* leaf extract is applied efficiently for making the rGO from GO in the green process. $\text{CeO}_2/\text{rGO-HYBD}$ is proficiently made by chemical co-doping of nano CeO_2 over the green rGO. $\text{CeO}_2/\text{rGO-HYBD}$ catalyst is found high surface area $95 \text{ m}^2/\text{g}$ and lowest band gap of 2.91 eV. Langmuir-Hinshelwood pseudo-first-order kinetics is found suitable for DV 51 degradation under UV and solar lights. However, curve fitting exercise renovates the photocatalytic process follows fractional order with respect to dye molecule degradation. The influences of pH, catalyst dosage and concentration of the dye over dye degradation are conferred. The photocatalytic degradation mechanism is also elaborated in detail aided by graphical abstract.

Fig.-10: Plots of Sum of the Square Deviations under (a) UV and (b) Solar Lights; corresponding (c) Order and (d) Apparent Rate Constant Observed by Curve Fit Operation Using Equation (9) For the LH Isotherm Vs. DV 51 Initial Concentrations.

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