TiO₂-reduced graphene oxide nanocomposites for the trace removal of diclofenac

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Abstract

Solar photocatalysis using TiO₂-reduced graphene oxide (T-RGO) nanocomposite as catalyst is explored for the removal of the last traces of diclofenac (DCF) pollutant from water. T-RGO nanocomposites of different compositions were synthesised by a modified process involving solvothermal treatment of titanium isopropoxide and graphene oxide (GO) in isopropanol medium. The prepared catalysts have been characterised by powder X-ray diffraction, infrared spectroscopy, Raman spectroscopy, transmission electron microscopy, photoluminescence emission spectroscopy, UV–Vis diffuse reflectance spectroscopy, X-ray photoelectron spectroscopy and N₂ adsorption–desorption measurements. The degradation of DCF is highly facile under solar irradiation in the presence of T-RGO with more than 98% of the 25 mg/L DCF aqueous solution getting degraded in 60 min followed by complete mineralisation in 100 min. Relevant reaction parameters such as catalyst loading, RGO content in the composite, concentration of DCF and the influence of pH on the degradation of the pollutant were identified and optimised. Reaction intermediates were identified by using LC–MS technique. The degradation followed Langmuir–Hinshelwood mechanism and pseudo first order kinetics. The stability and reusability of the catalyst are established. The efficiency of the catalyst in various real water matrices has also been proved thereby affirming its potential for commercial applications.

Keywords Degradation · Diclofenac · Kinetics · Pharmaceutical degradation · Solar photocatalysis · TiO₂-RGO nanocomposites

1 Introduction

The presence of emerging contaminants such as endocrine disrupting compounds (EDCs), personal care products (PCPs) and pharmaceuticals in water bodies is a matter of serious concern nowadays. The environmental problems created by the pharmaceuticals constitute an area where considerably a little attention is paid into. Extensive use of pharmaceuticals by humans and other living organisms has become a major environmental issue as they end up in water and soil, leading to degradation of their quality. Most of the pharmaceutical products are stable and resistant to biological degradation. The occurrence of more than 80 pharmaceutical

compounds upto ppm level is reported in the water bodies [1]. The presence of these contaminants leads to chronic low level exposure and accumulation with deleterious effects such as endocrine disruption as well as drug resistance of microorganisms. Among the various pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs) are of much environmental concern due to their widespread availability. DCF, [2-(2,6-dichlorophenylamino) phenylacetic acid] is one of the popular NSAIDs in medical treatment as an analgesic, antiarthritic and antirheumatic agent apart from its veterinary use. The annual human consumption of DCF has been estimated globally to be ~ 1500 tons [2]. It has been shown that about 15–30% of the consumed DCF is excreted from

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the human body unmodified and enters the aquatic environment [3]. According to the environmental quality standards, suggested in 2011 by European Commission, threshold level of DCF in water bodies is 100 ng/L [4]. However, the presence of DCF higher than the permissible value is detected in water bodies, the adverse effects of which are reflected in aquatic and other species [5, 6]. Considering its severe side effects, DCF has been added to the list of priority pollutants by the European Union [7], which necessitates the trace removal of the chemical from aquatic environment.

Conventional wastewater treatment methods are ineffective for the total elimination of DCF. Studies on the elimination of DCF from polluted water by means of ozonation [8], Photo-Fenton reaction [9] and sonolysis [10] have already been reported, where challenges still remain to be addressed. Heterogeneous photocatalysis involving highly efficient photocatalysts are also explored to this effect. Though this area is probed in detail using various semi-conducting materials, smarter catalytic systems are always demanded for commercial applications.

TiO₂, a celebrated photocatalyst in UV region is known to serve in visible region also when modified with proper species. Amongst the modified analogues, TiO₂-graphene or more precisely TiO₂-reduced graphene oxide (T-RGO) nanocomposites are widely investigated as potential photocatalysts in recent years [11]. The integration of TiO₂ with graphene promotes enhanced light absorption in the visible region, good adsorptivity and excellent mobility of charge carriers which could improve photodegradation of pollutants. However, the evaluation of photocatalytic performance of TiO₂-graphene nanocomposites has been limited towards certain types of compounds such as dyes [12], volatile organic compounds in gas phase [13] and reduction of Cr(VI) [14]. Only very few studies are reported on the effectiveness of the catalyst for the removal of emerging micro pollutants like pharmaceuticals [15, 16] from water. Therefore, further research is essential to assess the feasibility of application of these nanocomposites for the degradation/mineralisation of pharmaceuticals.

This paper highlights the potential of T-RGO nanocomposites for the removal of DCF from water in presence of sun light. T-RGO systems were prepared, well characterized using various spectroscopic/analytical tools, and employed for the mineralisation of DCF. This is probably one of the first attempts of using T-RGO combination for the photocatalytic removal of DCF from water.

2 Materials and methods

2.1 Materials

Titanium(IV) isopropoxide used for the preparation of the catalyst was purchased from Sigma Aldrich, India, and diclofenac sodium was obtained from Alfa Aesar, India. Graphite powder, KMnO₄ and other solvents were procured from Merck Pvt. Ltd. India, and were used without further purification.

2.2 Synthesis of T-RGO nanocomposites

Graphene oxide (GO) was synthesized using the modified Hummers method [17]. T-RGO composites with 1, 2, 5, 8 and 10 w/w ratios of GO (T-RGO1, T-RGO2, T-RGO5, T-RGO8 and T-RGO10 respectively) were prepared from titanium isopropoxide precursor by modifying the procedure reported in literature which used TiCl₄ as the precursor [18]. Briefly, GO was ultrasonicated for 30 min in isopropanol to obtain a clear brown dispersion. Then 7 mL of titanium isopropoxide was added to the required amount of the GO solution under vigorous stirring. After stirring for one hour, 10 mL of deionised water was added drop wise to the above mixture followed by sonication for 2 h to obtain a homogeneous grey suspension. TiO₂ coated GO was then heated at 180 °C in a Teflon-lined stainless steel autoclave for 8 h. The resulting product was then washed several times with distilled water and dried in vacuum at 60 °C. The reduction of exfoliated GO and crystallisation of TiO₂ on its surface are concurrently carried out by solvothermal treatment. Parent TiO₂ for comparison purpose was synthesised adopting the same synthetic strategy, without incorporating GO. RGO for control experiment was prepared separately by the following standard procedure. 500 mg of GO was dispersed in 100 mL of water and sonicated for half an hour. The dispersion was then reduced with 200 mL of 0.5 M freshly prepared sodium borohydride (NaBH₄) solution. The black residue formed was washed several times with water and ethanol and dried at 60 °C.

2.3 Characterisation of the synthesised catalysts

X-ray diffraction (XRD) patterns of the prepared catalysts were obtained using Bruker AXS D8 diffractometer using Cu K α radiation (1.5418 Å) with a Ni filter and at a scan rate of 0.5°/min. Thermo NICOLET Fourier Transform Infrared (FTIR) instrument was used for FTIR measurements. Transmission electron microscopy (TEM) images were observed with Jeol/JEM-2100 high resolution transmission electron microscope (HR-TEM). The Raman spectra of the samples

were recorded in WITech alpha 300RA Raman system. Shimadzu model RF-530IPC fluorescence spectrophotometer was used for recording the photoluminescence (PL) spectrum. UV–Visible diffuse reflectance spectra (UV–Vis DRS) were obtained from a Jasco V-570 UV–Vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was made with Axis Supra (XPS) Surface analysis instrument with a monochromatic Al K α radiation. Surface area and porosity of the catalyst samples were measured using Micromeritics Tristar surface area and porosity analyser. LC–MS analysis was carried out with Agilent Tech 6460 Triple Quad LC–MS equipped with an ESI interface. The mass spectra data were obtained by scanning m/z from 50 to 800.

2.4 Photocatalytic study

A specially designed double walled pyrex glass reactor was used to perform the solar photocatalytic experiments. The suspension containing DCF solution and the solid catalyst, after attaining the adsorption–desorption equilibrium was introduced into the inner compartment of the reactor and coolant water ($27 \pm 1^\circ\text{C}$) was circulated through the outer compartment to control the temperature of the reaction system. The experiments were performed during sunny days in March 2019 at Kochi, Kerala, India ($9^\circ 57' 51''\text{N}$, $76^\circ 16' 59''\text{E}$). The suspension was irradiated with sunlight having an average intensity of $1.25 \times 10^5\text{ lx}$ as measured by Digital Lux meter (Lt-Lutron LX-101A). DCF concentration was monitored periodically by measuring the absorbance at 274.6 nm spectrophotometrically.

3 Results and discussion

3.1 Characterisation of the catalysts

The XRD patterns of the synthesised T-RGO and of TiO_2 nanocomposites prepared under identical conditions are given in Fig. 1.

The characteristic peaks observed at 2θ values 25.2° , 37.6° , 48.1° , 54.2° , 62.4° , 69.3° and 75.14° correspond to the (101), (004), (200), (105), (204), (116) and (215) crystallographic planes of anatase TiO_2 respectively (ICDD 00-1-0562). T-RGO nanocomposites also show a diffraction pattern similar to that of pristine TiO_2 . The characteristic diffraction peak of RGO at about 24° is not observed in the composites. It is reasonable to consider that the TiO_2 particles grown on the graphene sheets effectively exfoliated the sheets and prevented their restacking [19]. When compared to the peaks of TiO_2 , that of the composites are broader. This happens due to the distortion of the lattice structure of TiO_2 as a result of the

Fig. 1 XRD patterns of TiO_2 and T-RGO nanocomposites

Fig. 2 FTIR spectra of TiO_2 , RGO and T-RGO5

interaction with RGO. Due to this the crystalline structure of TiO_2 on RGO is less developed. Peak broadening suggests a decrease in particle size. The crystallite sizes calculated for the composites following Scherrer equation based on the (101) peak were in the range of 4–5 nm and smaller than that of TiO_2 ($\sim 11\text{ nm}$).

The FTIR spectra of the synthesized TiO_2 , RGO and T-RGO nanocomposite are shown in Fig. 2. The broad band below 1000 cm^{-1} in the TiO_2 spectrum is attributed to the stretching and bending vibrational modes of Ti–O–Ti network. It also shows a broad peak at around 3400 cm^{-1} , which are due to the O–H stretching vibrations of surface hydroxyl groups. The peak at 1635 cm^{-1} originates from the stretching vibrations of hydroxyl groups of adsorbed molecular water [12]. In the spectrum of RGO, the peak appearing at 1600 cm^{-1} is ascribed to the skeletal vibration of RGO sheet [16]. The FTIR spectrum of RGO also shows absorption bands at 1747 cm^{-1} and 2923 cm^{-1} , which are attributed to the stretching vibrations of C=O and CH_2 groups respectively. The broad absorption band centred at 3420 cm^{-1} is attributed to the residual OH groups of

RGO. These results confirm the partial reduction of GO to RGO which contains residual oxygen containing functional groups, such as –OH and –COOH. These functional groups of RGO can be susceptible to the interactions with TiO_2 in the nanocomposite. All the characteristic peaks of TiO_2 and RGO are present in the T-RGO composite, as shown in the corresponding spectrum. Compared to TiO_2 the peak below 1000 cm^{-1} is much broader in the composite. The broadness can be considered as a combination of Ti–O–Ti and Ti–O–C vibrations indicating chemical bond formation between TiO_2 and RGO [20].

The TEM images of RGO, TiO_2 and T-RGO5 are shown in Fig. 3a–d. RGO is characterised by the sheet like morphology in the TEM image (Fig. 3a). The TEM image of TiO_2 (Fig. 3b) shows well-formed tetragonal crystals with sizes

Fig. 3 TEM micrographs of **a** RGO **b** TiO_2 **c**, **d** T-RGO5

ranging from 6 to 14 nm. Figure 3c, d confirms that in the composite a large number of TiO_2 nanoparticles with sizes between 3 and 5 nm are uniformly dispersed onto the graphene sheet. The images provide evidence for the layered morphology of graphene sheets in the presence of TiO_2 .

Raman spectral details of T-RGO nanocomposites also confirmed the presence of both TiO_2 and graphene in the composite. Typical bands at 140 cm^{-1} (E_g), 395 cm^{-1} (B_{1g}), 515 cm^{-1} (A_{1g}), and 639 cm^{-1} (E_g) (Fig. 4a) corresponds to the Raman active modes of anatase [21]. The peaks representative of the E_g mode (140 cm^{-1}) for the entire composites have broadened and distinctively blue-shifted from 140 cm^{-1} of TiO_2 to 156 cm^{-1} (Fig. 4a inset). This change in the lowest frequency E_g Raman mode is mainly related to the confinement of phonons in the nanocrystals. It is well documented [22] that phonons are confined within the nanocrystallites when their sizes are less than 10 nm and in the present case the nanocrystals are in the size range of 3–5 nm as evident from XRD and TEM analyses. Another reason for this change in line shape is the non-stoichiometric effects which can be reasonably expected to exist in the present nanocrystals as they were prepared by chemical methods via heat treatment [23]. The strain developed on the T-RGO surface as a result of the strong chemical interaction between TiO_2 and RGO sheets in the composite can also be attributed to this behaviour.

Figure 4b shows the D and G bands in the Raman spectra of GO, RGO and T-RGO nanocomposites. The carbon sp^3 defects and disorders seen particularly along the edges of graphene sheets represent the D band. The G band

corresponds to the in-plane vibrations of C sp^2 atoms. The GO shows peaks at 1344 and 1587 cm^{-1} which correspond to the D and G-bands respectively. In the T-RGO nanocomposites, the D-band is found intact and the G-band is changed to 1599 cm^{-1} . The intensity ratio of the D and G band (I_D/I_G) is a metric of defects in graphene. The I_D/I_G of GO is 0.995 which increases to 1.083 in RGO and 1.235 in T-RGO8. During the reduction of GO, fragmentation is likely to occur, resulting in a decrease in the average size of the sp^2 domains. Hence it is rational to assume that a large number of new graphitic crystallite sp^2 domains which are smaller in size than originally found in GO are formed after reduction [24]. This can cause an increase in the I_D/I_G value. The phenomenon indicated that the layers of GO were partially reduced to single and multi-layer graphene during solvothermal process. The changes in Raman band intensity as well as the blue shift of the G band provide a solid proof for the presence of a strong interaction between TiO_2 and graphene.

Figure 5 presents the PL spectrum of TiO_2 and T-RGO nanocomposites. PL emission results from the reunion of an electron hole pair which can emit energy in the form of fluorescence and its intensity is directly proportional to the rate of recombination. Here, the peak around 370 nm is due to the de-excitation of photogenerated electrons from the conduction band to valence band. The broad emission band centred at around 485 nm is due to excitonic PL and oxygen vacancies [25]. The PL intensity of T-RGO nanocomposite is much less than that of TiO_2 . The quenching of PL intensity in the composite is attributed to

Fig. 4 **a** Raman spectra of TiO_2 and T-RGO. Inset Raman spectra showing the blue shift of the E_g bands in the composites, **b** Characteristic D and G bands of GO, RGO and T-RGO nanocomposites

Fig. 5 PL Spectra of TiO_2 and T-RGO nanocomposites

the decreased rate of recombination of photogenerated electrons and holes. It can be inferred that RGO acted as an electron acceptor in the composite and might have suppressed the electron–hole recombination of TiO_2 which is a prerequisite for efficient photocatalysts.

The effect of graphene on the optical properties of TiO_2 was measured using UV–Vis DRS (Fig. 6). It can be observed that the spectra exhibit a characteristic absorption band around 400 nm, with a red shift in the absorption edge of T-RGO nanocomposites compared to TiO_2 . This indicates a reduction in the band gap of TiO_2 . In comparison to TiO_2 , the spectrum of T-RGO nanocomposite has relatively higher absorption intensity in the visible region. The Kubelka Munk plot for TiO_2 and T-RGO5 are shown in Fig. 6b. The band gap of T-RGO5 is calculated to be about 2.75 eV which is smaller than the 3.25 eV of TiO_2 . The narrowing of band gap due to the existence of additional

C2p mid energy levels of graphene between O2p and Ti3d states of TiO_2 is already established [12, 26].

The chemical interactions between TiO_2 and RGO in the composites were further verified by XPS taking T-RGO5 as a representative candidate (Fig. 7a–d). The survey spectrum shown in Fig. 7a confirms the presence of Ti, O and C in the composite. In the Ti 2p deconvoluted XPS spectrum (Fig. 7b) two peaks centred at 463.6 nm and 458 nm with the separation of 5.6 eV is typical of Ti^{4+} state. The additional small shoulders at 463.5 and 457.8 eV are ascribed to Ti^{3+} oxidation state. The bands around 465.2 and 459.4 eV are attributed to the existence of the Ti–C bond [27]. In the deconvolution spectra for C1s (Fig. 7c), the peak centred at 284.6 eV is representative of C–C, C=C, and C–H bonds of C sp^2 carbon of RGO. The peaks located at 283.7 eV and 288.7 eV are attributed to Ti–C and Ti–O–C bondings and those at 285.7 and 287.1 eV can be assigned to C–OH and C=O, respectively. The peak at binding energy 529.6 eV in O1s XPS spectra (Fig. 7d) is mainly assigned to the lattice oxygen of TiO_2 crystal. Binding energy at 531.9 eV is closely related to the hydroxyl groups on the surface of RGO [28]. From these findings we can conclude that the occurrence of Ti–C and Ti–O–C bondings significantly demonstrates the intense chemical interaction and successful attachment of TiO_2 particles onto RGO layer.

The nitrogen sorption isotherm and the plot for BJH pore size distribution of T-RGO5 are shown in Fig. 8. The isotherm shows characteristic Type IV curve indicating the mesoporous nature of the composite. The average pore size, BET surface area and pore volume are summarised in Table 1. The BET surface area of synthesised TiO_2 ($82 \text{ m}^2/\text{g}$) is calculated to be larger than that of commercial P25 ($50 \text{ m}^2/\text{g}$). The nanocomposites show an increased surface area with every addition of RGO. The high specific surface area can result in increased surface reactive centres

Fig. 6 a UV–Vis diffuse reflectance spectra b A plot of transformed Kubelka Munk function versus the energy of light for TiO_2 and T-RGO5

Fig. 7 **a** XPS Survey spectrum of T-RGO5 **b** Deconvoluted Ti 2p spectrum **c** Deconvoluted C1s spectrum **d** core level spectrum of O1s

Fig. 8 **a** Nitrogen adsorption–desorption isotherm of T-RGO5. **b** BJH Plot of the pore size distribution of T-RGO5

Table 1 Parameters obtained from N₂ adsorption–desorption isotherm measurements

Catalysts	BET surface area (m ² /g)	BJH desorption cumulative pore volume (cm ³ /g)	BJH desorption pore diameter (nm)
P25	50	0.12	10.67
TiO ₂	82	0.57	21.14
T-RGO2	132	0.28	6.95
T-RGO5	140	0.27	6.41
T-RGO8	149	0.28	6.66

which is beneficial to the photocatalytic performance enhancement.

3.2 Photocatalytic degradation of DCF

The solar photocatalytic activity of the synthesised systems for the degradation of diclofenac is discussed in this section. The decomposition was practically nil in the absence of catalysts. The effect of various photocatalysts of varying RGO/TiO₂ ratios on the degradation of DCF is studied and the results are presented in Fig. 9.

The nanocomposite is more active than the parent TiO₂ synthesised via hydrothermal method at all loadings of RGO. The efficient contact of RGO with the TiO₂ nanoparticles in the composite is known to enhance its conducting and transporting properties which could suppress the charge recombination, thereby producing more charge carriers to form reactive oxygen radicals for enhanced degradation. The rate of degradation goes up with an increase in the dosage of RGO which reaches the maximum at 5 wt% RGO and goes down thereafter. The enhancement in

Fig. 9 Effect of RGO concentration in T-RGO nanocomposites on the photocatalytic degradation of DCF

photocatalytic activity with increase in RGO may be due to the increased surface area of the catalyst. Along with this, the enhanced absorption of the catalyst in the visible range may also be contributing to the high efficiency of the composites. The BET surface area (m²/g) determined by nitrogen adsorption desorption isotherm shows that the surface area increases with RGO content as shown in Table 1. However, the degradation is optimum at T-RGO5, indicating that factors other than catalyst surface area also are relevant. Increasing surface area is expected to increase the adsorption of DCF. The adsorption of DCF on the catalysts is determined by standard method and the results show that optimum adsorption is reached in the range of 5–8 weight% of RGO. This is consistent with the degradation efficiency of the composite. At higher content of RGO beyond the optimum some of the surface sites of TiO₂ may be unfavourably occupied by RGO and the shielding of reactive sites negates the effect of enhanced surface area. This limits the ability of the surface of TiO₂ for effective DCF adsorption and generation of reactive free radicals. The two competing factors counteract with each other and hence the optimum RGO in TiO₂ is 5 wt% loading.

The photocatalytic performance of the nanocomposite is compared with that of the synthesised TiO₂, P25 and a mechanical mixture of RGO and TiO₂ (5 wt% RGO), the percentage corresponding to maximum activity, under identical conditions. The results are plotted in Fig. 10.

Prior to photocatalytic experiment, DCF solution with the solid catalyst was kept in the dark to attain the adsorption–desorption equilibrium. Compared to other systems under investigation, T-RGO showed increased adsorption

Fig. 10 Photocatalytic degradation of DCF under sun light over T-RGO5, TiO₂, Mechanical mixture of TiO₂ and RGO & P25. C₀ is the initial concentration of DCF and C, the concentration of DCF at time, t

which can be attributed to the increased surface area of the composite as given in Table 1.

Under solar irradiation without the photocatalyst, the concentration of DCF change is only marginal. In contrast, T-RGO nanocomposite, visibly improved the photocatalytic degradation (> 98% in 60 min) which is ~ 2 times that of commercial P25. All the catalysts including the synthesised TiO_2 are found to have an enhanced activity compared to commercial P25 for the degradation of DCF. The enhanced activity can be due to the surface characteristics including increased surface area, porosity, better solar activation and formation of more reactive free radicals. The mechanical mixture exhibits lower photocatalytic activity than the nanocomposite. This clearly shows that a close interfacial contact and subsequent charge transfer between TiO_2 and RGO are essential factors for enhanced photocatalytic activity.

As optimization of various reaction parameters is essential for commercial applications, an attempt to this effect is made and is presented below. T-RGO5, the efficient candidate among the group is selected for this purpose.

3.3 Effect of catalyst loading

The optimum catalyst loading depends on the concentration of the pollutant(s) present, the reactor geometry, light intensity as well as the properties of the semiconductor. Hence the optimisation has to be made for every system configuration and composite separately. The catalyst loading is tested using T-RGO5 nanocomposites, keeping all other parameters identical. The results in this regard illustrated in Fig. 11 show that the photocatalytic degradation increases with increase in dosage, and gets optimised at

Fig. 11 Effect of catalyst (T-RGO5) loading on the photocatalytic degradation of DCF

the dosage of 0.075 g/L for T-RGO5. Hence, all further studies are carried out using this catalyst dosage.

3.4 Effect of initial DCF concentration

To study the concentration effect, the rate of removal of DCF in the initial concentration range of 10–30 mg/L was investigated, keeping all other parameters identical. The results are summarised in Fig. 12.

The rate of degradation of DCF increases steadily upto 25 mg/L of DCF and thereafter stabilises or slightly decreases. This is consistent with kinetics of heterogeneous photocatalysis which obeys pseudo first order kinetics at lower concentrations. A decrease in the order of reaction is noted with increase in concentration. At still higher concentrations zero order or even negative order kinetics is exhibited.

The kinetics of photocatalytic degradation can be represented by the modified Langmuir–Hinshelwood model. Accordingly, the rate of degradation is,

$$C = C_0 e^{-k_{app}t} \quad (1)$$

or

$$-\ln \frac{C}{C_0} = k_{app}t \quad (2)$$

where C_0 is the initial concentration of the substrate (DCF), C is the concentration remaining after time t , t is the irradiation time and k_{app} is the pseudo first order rate constant.

Based on Eq. (2), the plot of $-\ln(C/C_0)$ against t gives straight line for first order reactions. In the present case, as seen in Fig. 13, for the four concentrations studied in the range of 10–25 mg/L of DCF, the values of the correlation

Fig. 12 Effect of initial concentration of DCF on photocatalytic degradation

Fig. 13 Logarithmic plot for the degradation of DCF with T-RGO5 system

Table 2 Pseudo first order rate constants (k_{app}) for the degradation of DCF in presence of T-RGO

Concentration of DCF (mg L ⁻¹)	$k_{app} \times 10^{-3}$ (min ⁻¹) T-RGO5
10	81.94
15	68.34
20	58.75
25	50.40

coefficient R^2 were above 0.98 establishing very good agreement with first order kinetics. The slopes of the fitted lines will be the values of k_{app} , which are calculated and given in Table 2.

3.5 Effect of initial pH

pH is known to have significant effect on the parameters influencing heterogeneous photocatalytic reaction in aqueous systems. Such parameters include chemistry of the substrate and the surface, extent of adsorption, charge on the surface of the catalyst, type of interactions among the surface, substrate, solvent molecules and the numerous intermediates formed during the progress of the reaction etc. Consequently, the interaction of the substrate as well as the intermediates with the in situ generated reactive oxygen species (ROS) also will be affected. In this study, the effect of variation in initial pH on the degradation of DCF is investigated and the results are shown in Fig. 14. The maximum DCF degradation of 68.4% was obtained in presence of nanocomposite at acidic pH 6.0 after an irradiation time of 20 min.

The point of zero charge (pH_{PZC}) of the composite catalyst T-RGO5 was determined by the procedure reported by Khan et al. [29] and is found to be 4.59. This means that, above this pH the catalyst surface is negatively

Fig. 14 Effect of pH on the photocatalytic degradation of DCF

charged and capable of adsorbing cationic species and below this pH it is positively charged and hence attracts anionic species onto the surface. Thus the ionic state of the substrate species is vital in determining the degree of adsorption and consequently the rate of photodegradation. It has also been observed that operating pH also changes during photocatalytic reaction.

If the pH_{PZC} value of the catalyst which determines the rate of adsorption is considered as the only driving factor for degradation, for an anionic compound like DCF, the degradation should have been maximum below the pH_{PZC} value i.e., pH 4.59 for T-RGO5. However, in the current study, the maximum efficiency was observed at pH 6, indicating that the surface promoted degradation is less in this case. The degradation takes place primarily by the reaction among ROS and the substrate molecules which are present in the bulk of the solution rather than that adsorbed on the surface. Besides, some of the intermediates formed may have positive charges and got adsorbed on the negatively charged surface sites and can enter into increased interaction with surface generated ROS. This leads to faster degradation and eventual mineralisation leaving the surface sites available for fresh adsorption and generation of new ROS. In any case, the pH effect on the process cannot be explained based on any simple premises and in depth study of the effect of pH on all components and factors connected with the catalyst, the medium, various intermediates, ROS and their multitude of interactions are important.

3.6 Mineralisation and degradation pathways

In order to verify the complete mineralisation of DCF by T-RGO5 photocatalyst, total organic carbon (TOC) was determined at regular intervals of time. From the results

plotted in Fig. 15 it can be seen that the composite catalyst mineralises DCF completely in ~ 100 min. While the degradation of DCF is complete within ~ 60 min, it takes about 100 min for the complete mineralisation and TOC removal. This indicates that the degradation is proceeding through intermediates which are more stable and recalcitrant than DCF itself.

Results obtained in this field by other researchers have been compared in Table 3. It is obvious that the system reported herein is commendably efficient when matched with other systems, reported previously.

In order to understand the DCF degradation pathways, LC–MS analyses were carried out at various irradiation times. The structure of the intermediates illustrates that most of the products are formed by attack of hydroxyl radicals. Probable intermediates based on the LC–MS spectrum are shown in Fig. 16.

DCF exhibited a molecular ion peak at m/z 296. During the initial stages of degradation (after 10% degradation), the intermediates with m/z 250 (Int.1) is observed corresponding to the loss of CO_2 . Further oxidation results in Int.2 (m/z 266). Elimination of a molecule of HCl from Int.2 followed by ring closure results in int. 3 m/z 230 m/z value of 312 (Int.4 & 5) observed at this time and at 60% degradation corresponds to the monohydroxylated compound. Intermediates with m/z values 293 (Int.6) and 280 (Int.7) can also be formed from the hydroxylated products. With further hydroxyl radical oxidation, dihydroxylation products (m/z = 328, Int.8) were formed.

Another destruction pathway is arising by the attack at NH-bridge between the aromatic rings. 2,6-dichloroaniline (Int.9, m/z 161) and phenyl acetic acid (Int.10, m/z 137) are formed primarily during this process. Dihydroxylation of phenyl acetic acid and hydroxylation of 2,6-dichloroaniline resulted in intermediates with m/z 170 (Int.11) and 177

(Int.12) respectively. Benzene 1,4-diol with m/z 110 (Int.13) and a simple carboxylic acid, malonic acid (Int.14 m/z 102) were also formed.

The formation of these intermediates suggests that dehalogenation, decarboxylation and hydroxylation are the initial reactions followed by cleavage of the NH bridge and stepwise aromatic ring opening.

3.7 Reusability of T-RGO photocatalyst

The application of any catalytic process depends on the economy and hence the reuse of the catalyst is important. In this context, the reusability of the T-RGO5 catalyst was investigated (Fig. 17). For the first 3 trials, the nanocomposite performed without any loss in activity. However, marginal activity loss was observed thereafter. In any case, the activity of the catalyst decreases only very slowly, which indicates that it can be recycled multiple times.

3.8 Effect of water matrix on the photocatalytic degradation of DCF

All the studies on the photocatalytic degradation of DCF reported in this paper were conducted with ultrapure water as the medium. However the actual industrial waste water contains contaminants like salts, humus acid, metal ions etc. apart from several unknown materials. These foreign contaminants can adversely affect the efficiency of photocatalytic degradation of target pollutants. In order to scale up for commercialisation the efficiency of the system has to be tested in various real water media. With this view in mind we have conducted the studies by selecting three different water matrices viz. dug well water, river water and the effluent from a pharmaceutical manufacturing company collected from the final point of discharge into the environment. As the effluent was slightly turbid and loaded with considerable amount of suspended particles, the studies in effluent medium were conducted under two categories namely the effluent as such and the filtered effluent after the removal of suspended solids and turbidity. The characteristics of these water samples are given in Table 4.

From the results plotted in Fig. 18 it is seen that T-RGO based solar photocatalysis can effectively degrade the studied pollutant in all the water matrices including the complex industrial effluent though an additional time was needed for the complete degradation. The comparative efficiency in terms of the time taken for the degradation decreases in the order ultrapure water > river water > dug well water > filtered effluent > unfiltered effluent, showing a significant dependence on the water media used. When the photocatalytic degradation in ultrapure water was complete in 60 min it took 90 and 120 min respectively

Fig. 15 Decrease in TOC during the photocatalytic degradation of DCF with T-RGO

Table 3 Comparison of efficiency of various systems for photocatalytic degradation of DCF

Photocatalytic system	Reaction conditions	Parameters	Measured values	Irradiation time, min	References
Degussa P25/UV-A	[DCF]: 10 mg/L [catalyst]: 250 mg/L	DCF removal, %	85	240	[30]
Anatase TiO ₂ /UV	[DCF]: 8 mg/L [catalyst]: 0.5 g/L (pO ₂)(v/v): 50%	Pseudo first order rate constant, k	0.9 min ⁻¹		[1]
TiO ₂ /UVA + US	[DCF]: 10 mg/L [catalyst]: 500 mg/L pH inherent	DCF removal, % Pseudo first order rate constant, k	96 40 × 10 ⁻³ min ⁻¹	120	[31]
US + UV + TiO ₂	[DCF]: 0.07 mM [catalyst]: 1 g/L	Rate TOC removal, %	64.4 × 10 ⁻⁷ M min ⁻¹ 73	60	[32]
1%Ag-TiO ₂ /UV 1%PdTiO ₂ /UV	[DCF]: 50 mg/L [catalyst]: 1 g/L pH: 5, 0.20 L UV 9 mW	TOC removal, %	75 72	120	[33]
Activated C-TiO ₂ -silica xerogel(CTS)/	[catalyst]: 5 g/L Superficial air velocity: 0.007 m/s	DCF removal, %	90	360	[34]
C-N-S tridoped anatase TiO ₂ /solar	[DCF]: 25 mg/L [catalyst]: 0.05 mg/L pH: 7	COD % Pseudo first order rate constant, k	100 0.0632 min ⁻¹	180 90	[35]
N,S,C doped ZnO/UV	[DCF]: 20 mg/L [catalyst]: 0.44 g/L pH: 6.0 [H ₂ O ₂]: 1 mM	DCF removal, %	98.2	240	[36]
FeCeOx/US	[DCF]: 20 mg/L [FeCeOx]: 0.5 g/L pH: 6.5 US: 20 kHz, 3.0 W/cm ³	DCF removal, %	80	30	[37]
TiO ₂ -FeZ/H ₂ O ₂ /Solar	pH: 4 [H ₂ O ₂]: 3.88 mM 4 layers of thin films of immobilized composite	Residual DCF, %	~ 10	60	[38]
Fenton/solar	[DCF]: 50 mg/L pH: 7 Different iron conc (0.05, 0.075, 0.2, 0.75 mM)	DCF degradation, %	100	100–110 (for best system)	[39]
SiO ₂ -TiO ₂ -MWCNT/365 nm & 550 nm light source	[DCF]: 10 mg/L [catalyst]: 0.5 g/L	DCF removal, % Pseudo first order rate constant, k	100 13.6590 × 10 ⁻² min ⁻¹	60	[40]
H ₂ O ₂ /UV	[DCF]: 1.0 × 10 ⁻³ M pH: 7 [H ₂ O ₂]: 5.0 × 10 ⁻³ M	TOC removal, %	39	90	[41]
Graphene-hemin integrated electroenzymatic system	[DCF]: 20 mg/L 0.1 M Na ₂ SO ₄ solution using graphene-hemin coated graphite electrode at a bias potential of -0.4v(vs SCE)	DCF removal, %	96	660	[42]
TiO ₂ -RGO/solar	[DCF]: 25 mg/L [catalyst]: 0.075 g/L pH natural	DCF removal, %	~ 100	60	Present work
		Pseudo first order rate constant, k	50.40 × 10 ⁻³ min ⁻¹	40	
		TOC removal, %	~ 100	100

Fig. 16 Identified Intermediates of DCF during photocatalytic treatment

Fig. 17 Effect of recycling of the catalyst on the efficiency of DCF degradation

for river and well water. The degradation efficiency in the effluent medium is considerably reduced and it required 4 h for more than 90% degradation.

An analysis of the water media used showed that river and well water were having the advantage of appreciable amounts of dissolved oxygen and lesser amounts of foreign bodies compared to the effluent which contained significant extent of dissolved solids, COD and considerable quantity of Cl^- , SO_4^{2-} and PO_4^{3-} . On correlating these results with that of the degradation studies it can be inferred that the dissolved as well as the suspended contaminants can inhibit the degradation. Turbidity of the medium can also affect the catalyst activation and subsequent generation of ROS by blocking the amount of sunlight entering in and passing through the solution. Studies using filtered and unfiltered effluents gave more or less the same results showing that rather than the suspended particles, the dissolved salts along with organics were the major detrimental factors towards inhibition. It can also be inferred that mild turbidity does not cause much

Table 4 Physico chemical characteristics of selected water matrices

Parameters	Well water	River water	Pharmaceutical effluent as such	Filtered pharmaceutical effluent
pH	6.028	7.34	6.57	6.50
Turbidity (NTU)	0	1.2	6.10	0.80
Total dissolved solids (TDS) (mg/L)	38	36	636	636
Total suspended solids (mg/L)	0	0.8	23	Nil
DO (mg/L)	4.02	5.32	3.2	3.2
BOD5 (mg/L)	0.6	0.4	8.8	6.4
COD (mg/L)	4	3.2	92	85
Cl ⁻ (mg/L)	30	2.63	80	80
NO ₃ ⁻ (mg/L)	5	2.29	40	40
SO ₄ ²⁻ (mg/L)	Not detected	1.42	250	250
PO ₄ ³⁻ (mg/L)	Not detected	ND	1.5	1.5

Fig. 18 Photocatalytic degradation of DCF under sun light over T-RGO in various water matrices

inhibition of solar photocatalytic process. The inhibitory effect of the dissolved ions on the photocatalytic efficiency can be attributed to two major factors. Firstly, these ions can competitively adsorb on the catalyst surface blocking the reactive sites for the target pollutants. Secondly, these ions can scavenge holes and $\text{OH}^\bullet$ radicals producing less powerful oxidants like NO_3^- , Cl^- , PO_4^{2-} and CO_3^{2-} .

In the case of most of the industrial effluents the chances of contamination by different ions from the processed water and other sources cannot be overruled. The effect of each contaminant has to be worked out before the optimisation of the process for commercial application. Therefore for successful field application of the solar photocatalysis technology, inhibiting factors such as dissolved ions and turbidity should be removed from the secondary effluent before it is subjected to fine tertiary

treatments meant for the trace removal of even microcontaminants like pharmaceuticals.

4 Conclusions

T-RGO nanocomposite is identified as a highly efficient solar photocatalyst for the degradation and mineralisation of DCF in water. The TEM images clearly prove that RGO acts as a two-dimensional (2D) surface onto which TiO_2 particles are embedded. RGO also serves as an electron acceptor thereby preventing the charge recombination which could in effect produce more ROS needed for degradation of pollutants. By compositing graphene with TiO_2 the band gap of TiO_2 is noticeably decreased from 3.25 to 2.75 eV, which can be attributed to the enhanced chemical bonding between TiO_2 and graphene making the system effective in visible region. With this supremely fabricated composite almost total elimination (> 98%) of the 25 mg/L of DCF was accomplished in 60 min and complete mineralisation in 100 min of irradiation. The degradation of DCF follows Langmuir–Hinshelwood pseudo-first-order model. Identification of DCF intermediates demonstrates that dehalogenation, decarboxylation and hydroxylation are the primary reactions followed by the breaking of the NH bridge bond and stepwise ring opening of the aromatic rings to form carboxylates. The stability and reusability of the photocatalyst have been verified and established. The efficiency of the photocatalyst in various real water matrices has also been confirmed making it highly suitable for industrial applications.

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Compliance with ethical standards

Conflict of interest There is no conflict of interest to declare.

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