Research Article

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Photocatalytic Degradation of Acetaminophen Using Carbon-TiO_2 Nanocatalyst Extracted from Hibiscus Flower under Visible Light

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ABSTRACT

In today's world pharmaceutical waste in the environment has become a worldwide issue. These compounds are used in living beings to cure diseases and prevent them. But the disposal of these types of waste was not disposed of properly. In this study, the pharmaceutical compound acetaminophen was degraded using photocatalytic degradation which is one among the pharmaceutical waste. The compound is much harmful to living beings and causes severe disorders like vomiting and nausea. In this paper, acetaminophen is degraded using the carbon-TiO_2 nanocatalyst. The carbon-TiO_2 nanocatalyst was synthesized and characterized such as particle size, zeta potential, FTIR, surface area analyzer, EDX, and SEM images. The compound was degraded by using photocatalytic degradation under transparent condition. The analysis of disintegration was performed by using the UV-vis spectrophotometer. The results obtained indicated the maximum degradation efficiency of around 87% obtained. Hence, C-TiO_2 can be utilized under visible light to effectively degrade acetaminophen.

Keywords: Pharmaceutical waste; Acetaminophen; Photocatalytic degradation; Nanocatalyst.

1. INTRODUCTION

In today's world, the use of pharmaceuticals has increased tremendously. However, disposal of this pharmaceutical waste requires proper norms and regulations. The presence of pharmaceutical compounds in various sources of water is a great deal of concern. Since the pharmaceuticals, even at a very minimum concentration could pose a severe risk to the ecosystem, their disposal in aquatic environments is alarming (Shaban and Fallata, 2019). Environmental pollution in the marine environment has raised due to the improper disposal of medication and health care products (Fan *et al*. 2018). Water pollution causes a dangerous health problem to human- beings and marine life globally (Haq *et al*. 2020). Emerging contaminants comprise of various active pharmaceutical ingredients (APIs) (Meenakshi Sundaram, 2019). To discharge the wastewater consists of pharmaceutical waste, it should be treated up to the minimum prescribed discharge standards (Behravesh *et al*. 2020). The common contaminants of emerging concern are acetaminophen (ACT), carbamazepine, triclosan, etc., (Meenakshisundaram, 2019). Acetaminophen, a widely used mild analgesic medication, provides pain relief globally. A previous study on the occurrence of ACT in ecology reveals the presence of ACT in urban wastewater effluent and effluent from pharmaceutical manufacturing plants (Reza katal *et al*. 2019). About 58 to 68% of ACT enters the environment through urines and feces (Behravesh *et al*. 2020). In addition to water environment, microorganisms present in the soil also been affected which retards the growth of plants (Fan *et al*. 2018). Acetaminophen in wastewater has become a major problem because of its intricate molecular composition and unrestrained discharge due to which the conventional biological route of wastewater treatment is not able to remove ACT and its metabolites. Due to the inefficiency of conventional wastewater treatment plants in removing APIs, it is imperative to adopt some advanced treatment options. One such option is heterogeneous photocatalysis of advanced oxidation process. Several photocatalysis studies of APIs were carried out using TiO_2 as nanocatalyst under visible light and proved its high efficiency in degrading APIs, less toxicity, cost-effectiveness (Bagheri *et al*. 2017; Meenakshisundaram, 2019). Despite of its several advantages, the wide band gap of TiO_2 affects its photocatalytic performance under solar radiation. Consequently, numerous studies have concentrated on advancing a catalyst based on TiO_2 which can effectively utilize visible light in photosensitization studies (Awofiranye *et al*. 2020). One such method is the doping of TiO_2 with metal oxides. In a study on the comparison of doped and undoped catalyst, the doped catalyst showed improved results in optimizing the photocatalytic degradation of pharmaceutical compounds (Razani *et al*. 2017). Utilizing lignin as the carbonaceous precursor, TiO_2 materials were modified

with carbon, to target ACT as the compound of interest, resulting in an enhanced removal efficiency (Gómez-Avilés *et al*. 2019). The photocatalytic degradation of acetaminophen was performed by synthetically prepared TiO_2 solution under visible light (Dalida *et al*. 2014). The pH plays a vital role in the photocatalytic degradation process in the removal of Acetaminophen (Zyoud *et al*. 2020). In a study reported earlier, the photocatalytic degradation of atenolol and acetaminophen follows a pseudo-first-order kinetic model and also TOC reduction was observed with both the contaminants along with OH radical pathway as a major removal process (Ramasamy *et al*. 2021). Synthesis of nanomaterial with the aid of plant material as a reducing and capping agent is gaining momentum in recent times due to its environment-friendly aspect (Haq *et al*. 2020). *Hibiscus sabdariffa*, a member of the Malvaceae family, is a shrub characterized by its red flowers resembling catalysts. The compounds present in these plants were phenolic compounds. The varying concentrations of biological entities, in combination with organic agents, exert influence over the size and shape of nanoparticles (Hussain *et al*. 2016). In this experimental work, the carbon-TiO_2 was synthesized using the hibiscus flower extract and the characterization was performed to analyze the nano catalyst. The characterization of the catalyst includes particle size, zeta potential, XRD, FT-IR, SEM, EDX and surface area analysis to evaluate their structure, size, shape, and optical properties. The pharmaceutical compound acetaminophen was degraded by photocatalytic degradation under visible light by varying the concentration of the catalyst, pH, and retention time.

2. MATERIALS AND METHODS

Acetaminophen of purity 99.98%, and titanium (IV) butoxide, titanium(II) propoxide were purchased from Sigma-Aldrich. The petals of the hibiscus flowers were collected from the local area and washed thoroughly for the process of green synthesis.

3. SYNTHESIS OF CARBON-TIO_2 NANO CATALYST

The flowers were collected and the petals were separated from the flower and washed in the water to remove the dust particles present in the petals. Then, the petals were allowed to dry in a shadow region place for 2 days to obtain dry petals. About 10 g of air-dried petals were placed in a 500 mL beaker, followed by the addition of 200 mL of Millipore water. The mixture was then boiled continuously for two hours. After allowing the beaker with the extract to cool for a specific duration, the extract was filtered using Whatman filter paper, covered with paraffin and stored for the further synthesis process of nanocatalyst. Titanium(II) propoxide (1.0 N) was dissolved in 100 mL of Millipore water. The filtered extract was added dropwise into the beaker followed by stirring to obtain a pH of 7 and the mixture was continued for 3 hours. The particles were washed and calcinated at temperatures of 200 °C to 300 °C for 4 hours. Titanium(IV) butoxide (TBT) was selected for its dual role as a titanium precursor and a carbon source, as well as its capability to enhance photocatalytic activity. About 10 g of TBT was added to absolute ethanol equivalent and this solution was mixed with the prepared particle and then 5 mL of 0.1 M glycerin solution was added dropwise along with the constant stirring. The solution was centrifuged at 5000 rpm and the settled particles were collected. The collected particles were calcinated at 200 °C to 300 °C which aims to remove the water content trapped in the carbon-doped TiO_2 nanocatalyst. Finally, the C/TiO_2 nanocatalyst was prepared for the further process of characterization and degradation in Fig. 1.

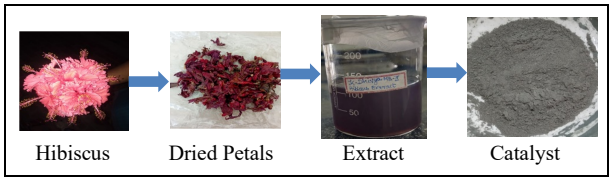


Fig. 1: Synthesized C/TiO_2 nanocatalyst

4. CHARACTERIZATION OF C-TIO_2 NPs

The morphology, crystalline size, and structure of the synthesized carbon-TiO_2 were analyzed. The particle size and zeta potential of the nanocatalyst were analyzed using the Malvern instrument. The functional group and bonding between the nanocatalyst were determined using a Perkin Elmer Two spectrophotometer. The orientation, crystallographic structure, and grain size of the crystalline nanocatalyst were obtained using an X-ray diffractometer. BET surface area analysis was performed to examine adsorption/ desorption data. Field emission scanning electron microscope was analyzed along with EDX. The degradation absorbance was determined using a Perkin Elmer UV-vis spectrophotometer. The vibration stretching of the nanocatalyst was obtained using Raman spectroscopy.

5. PHOTOCATALYTIC DEGRADATION ACTIVITY

The photocatalytic degradation of acetaminophen commenced by preparing a standard stock solution wherein 30 mg of acetaminophen was dissolved in 1000 mL of Millipore water. Various concentrations of acetaminophen, including 15 mg/L, 20 mg/L, 25 mg/L, and 30 mg/L, were then subjected to treatment in the visible photocatalytic reactor. The samples were mixed with carbon-TiO_2 nanocatalyst and stirred magnetically for 10 minutes to ensure complete absorption/desorption process of organic compounds on

the surface. Six sampling tubes were prepared, each containing 100 mL of the sample. Catalyst dosages of 500 ppm, 1000 ppm, and 2000 ppm were added. The pH and reaction conditions were adjusted by varying the concentrations of acetaminophen and reaction times of 30 minutes, 60 minutes, and 120 minutes, respectively. The sampling tubes were irradiated by two fluorescent lamps to ensure the steady-state illumination of the entire surface of the crystalline. The aqueous sample was filtered to eliminate the added nanocatalyst and absorbance of the solution obtained using a UV-vis spectrophotometer at the wavelength of 265 nm before and after degrading the solution. The removal efficiency of the ACT was calculated from the absorbance values.

6. KINETICS

The kinetics of ACT degradation were evaluated using a pseudo-first-order model based on the concentrations C and C_0. Plots of $\log(C/C_0)$ versus time and 1/C versus time were constructed. The resulting plots were non-linear, indicating that the degradation follows pseudo-first-order kinetics.

For first order reaction, equation (1)

$$rc = dC/dt = K \quad \ldots. (1)$$

On integrating equation (1) we get,

$$In(C/C_0) = Kt \quad \ldots. (2),$$

where K is the pseudo-first-order degradation rate constant (min^{-1}).

7. RESULTS AND DISCUSSION

7.1 Morphological Study and Crystalline Structure

7.1.1 XRD Analysis

Fig. 2 shows the XRD pattern of carbon–TiO_2. The major diffraction peaks were observed at 2θ values of 38°, 48°, 68°, and 77°. The corresponding crystallite sizes were calculated as 44 nm, 27 nm, 25 nm, and 24 nm, respectively. These peaks were indexed to the Miller indices (112), (200), (213), and (202). Almost all the sizes are uniform and the structure of the nanocatalyst is tetrahedral. These results correspond to the JCPDS data file No. 84-1285. The deviation in the peaks may be due to the effect and size of the particles in the nanocatalyst. The crystalline size of the prepared nanocatalyst was estimated using the Scherrer equation (3) (Bamba *et al.* 2015)

$$D = 0.9\lambda/ (\beta \cos \theta) \quad \ldots (3),$$

where, D is the crystalline size, λ the wavelength of the incident X-Rays (0.154 nm), θ the diffraction angle of the peak of the cubic phase β is the half-width. Crystalline size of the commercial TiO_2 was determined to be 25 nm and the observed XRD pattern with 2θ as 25.30º and 27.43º with miller indices of (1 0 1) anatase and (1 1 0) rutile (Bamba *et al.* 2015). The peaks at 25º, 38º, 48º, 53º, 55º, and 62º along with the miler indices value (1 0 1) (1 1 2) (2 0 0) (1 0 5) (2 1 1) and (2 1 3) and the average crystalline size is 24.89 nm.

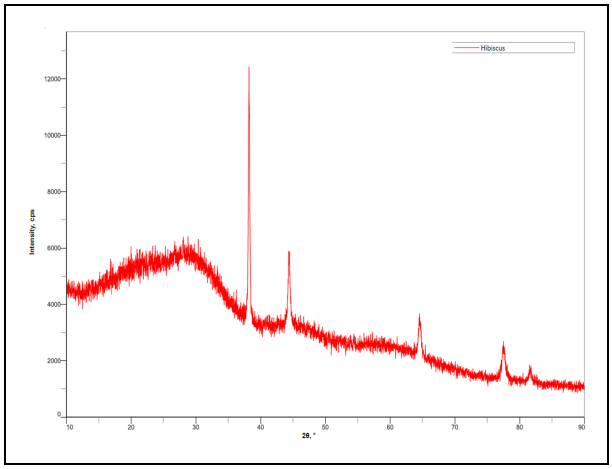


Fig. 2: XRD pattern of C/TiO_2

7.1.2 FTIR Analysis

Fig. 3 presents the FTIR spectrum recorded over the wavenumber range of 400 to 4000 cm^{-1}, revealing characteristic vibrational peaks that confirm the composition of the nanocatalyst. Notably, the peak observed at 407 to 447 cm^{-1} signifies the Ti-O-Ti stretching characteristic of the nanocatalyst's structure. Additionally, the strong peak at 1045 cm^{-1} is attributed to the C-N group of the amine stretching within the particles, while the peak at 1383.34 cm^{-1} indicates C-O carbonyl stretching. Furthermore, the amine bending N-H is observed at 1582.34 cm^{-1}, and a strong O-H stretching is observed at 2918 cm^{-1}. The peak at 2851 cm^{-1} corresponds to alkyl C-H stretching, confirming the presence of carbon-TiO_2 nanocatalyst. Furthermore, the peak at 2900 cm^{-1} exhibits C-H stretching, while the peaks at low frequencies of 600 to 900 cm^{-1} are attributed to Ti-O-TO bridge stretching modes and the Ti-O bond. Additionally, the surface O-H stretching between 3000 to 3500 cm^{-1} is observed, further confirming the composition of the nanocatalyst and the presence of water molecules adsorbed on the catalyst surface. Green synthesized TiO_2, as observed between the peaks at 1631 cm^{-1}, elucidates the stretching of C-O and C=O bonds attributed to the carboxylate group of the flower extract. Peaks at 800 and 450 cm^{-1} signify Ti-O stretching, while O-H stretching is evident at 3342 cm^{-1}, attributed to hydroxyl groups on the TiO_2 surface. Furthermore, the peak at 419 cm^{-1} corresponds to the Ti-O-Ti by the OH group peak at 1628 cm^{-1} vibration characteristic of C-doped TiO_2.

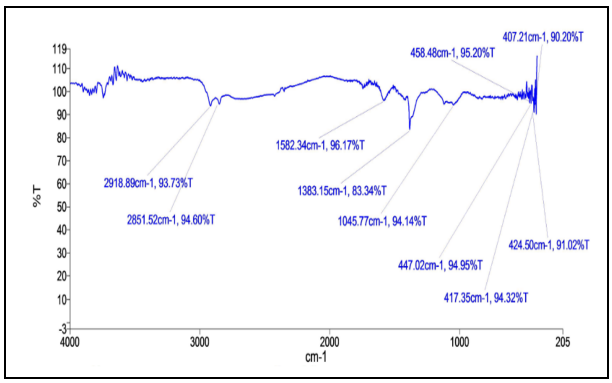


Fig. 3: FTIR analysis of carbon doped TiO_2

7.1.3 Energy-dispersive x-ray Analysis

Energy-dispersive X-ray analysis was performed to confirm the existence of titanium, oxygen, and carbon in the synthesized C/TiO_2 nanocatalyst. The analysis was obtained in 15 kV and amplitude time 3.84 microseconds with a resolution of 127.4 eV. The weight percentage of the elements was obtained. The presence of Ti, O, and C was confirmed by the use EDX spectrum (Fig. 4). The composition of Ti, O, and C are 42.3%. 39.61% and 9.27% respectively. In a literature study, the calcined-TiO_2 at 300°C had an atomic composition of 31.6% titanium, 50.3% oxygen, 18.2% of carbon (Mark Daniel *et al*. 2016). In another work, the elemental composition of Ti, C, and O were observed at 18.72%, 13.42%, and 67.86%, respectively (Lavand *et al*. 2015).

7.1.4 Scanning Electron Microscope Analysis

The SEM analysis (Fig. 5) clearly shows the morphology of the nanocatalyst. The catalyst has a spherical structure and with a nano-size. It also indicates the presence of carbon trapped in the TiO_2 nanocatalyst corresponding to the elemental composition of EDX analysis. In a previous study, the C-TiO_2 and TiO_2 were examined using SEM in which C-TiO_2 showed smaller crystals compared to TiO_2 (Shaban *et al*. 2019). Photocatalyst of the particles has a high surface area which helps in achieving the visible photocatalytic degradation (Dalida *et al*. 2014). The particles exhibited a spherical morphology with varying edges, maintaining individuality without aggregation, thereby ensuring stable dispersibility. The prevention of aggregation is facilitated by the hibiscus flower extract, which forms a coating on the surface of TiO_2 particles (Pasakalis *et al*. 2014).

7.1.5 Surface Area Characteristics

Surface area and the total pore volume play a major role in photocatalytic activity. The adsorption-desorption isotherm (Fig. 6) exhibits the Type IV isotherm. The mean pore diameter of the carbon-doped TiO_2 nanocatalyst obtained was 8.2859 nm due to their uniform structure and the pore volume as 0.1015 cm^3/g. The BET surface area was found to be 25.501 m^2/g with the pressure and temperature of 97.586 kPa and 77 K, respectively. As per the earlier study, Type IV isotherms were recorded for the TiO_2 nanoparticles due to the hysterias loop representing the predominant mesopores structures. The pore size distribution was 7.5 nm (Bamba *et al*. 2015). The BET surface area of the carbon self-doped TiO_2 was from 259 to 114 m^2/g due to the increase in calcination temperature from 200 to 600 °C, which decreased the surface area of the particles (Mark Daniel *et al*. 2016).

7.1.6 Photocatalytic Degradation Studies on Act

Photocatalytic degradation of ACT was performed and the findings are shown in Fig. 7. The optimum degradation values are provided in Table 1. Photocatalytic studies were conducted by varying the contaminant concentration from 15 to 30 mg/L, the pH from 3 to 12, and the catalyst concentration at 0.5, 1, and 2 mg/L. After performing the photocatalytic degradation under the visible light reactor, the aqueous solution was filtered and proceeded with the UV-vis absorbance spectroscopy analysis to determine the degradation efficiency. The degradation efficiency of ACT was maximum at pH 7 with a removal efficiency of 87.07% with 60 min of reaction time.

7.1.7 Effect on Catalyst Concentration

The concentration of catalyst is an important factor to consider. Fig. 8 shows the effect of catalyst concentration on degradation efficiency. The catalyst dosage added to the solution varied from 0.5 to 2 g/L. It indicates that the maximum results were obtained at a contaminant concentration of 15 mg/L with a catalyst concentration of 1g/L and the rate constant value of 0.0080 min^{-1}. By increasing the concentration of the nanocatalyst, the decrease in removal efficiency occurs in the degradation also with the rate constant. The photocatalytic activity increased with the increase of nanocatalyst concentration due to the hydroxyl radicals from the catalyst dosage. At low catalyst dosage, reduced availability of active sites leads to lower degradation efficiency. Additionally, decreased suspension transparency and increased light scattering limit photon penetration, resulting in reduced activation of the nanocatalyst. The photocatalytic degradation rate increased when the concentration of C/TiO_2 was elevated from 0.5 to 2 g/L. Further increase in dosage decrease the degradation rate (Shaban *et al*. 2019). As the catalyst concentration increased, a decrease in the observed rate constant was noted (Chaoqun Tan *et al*. 2014).

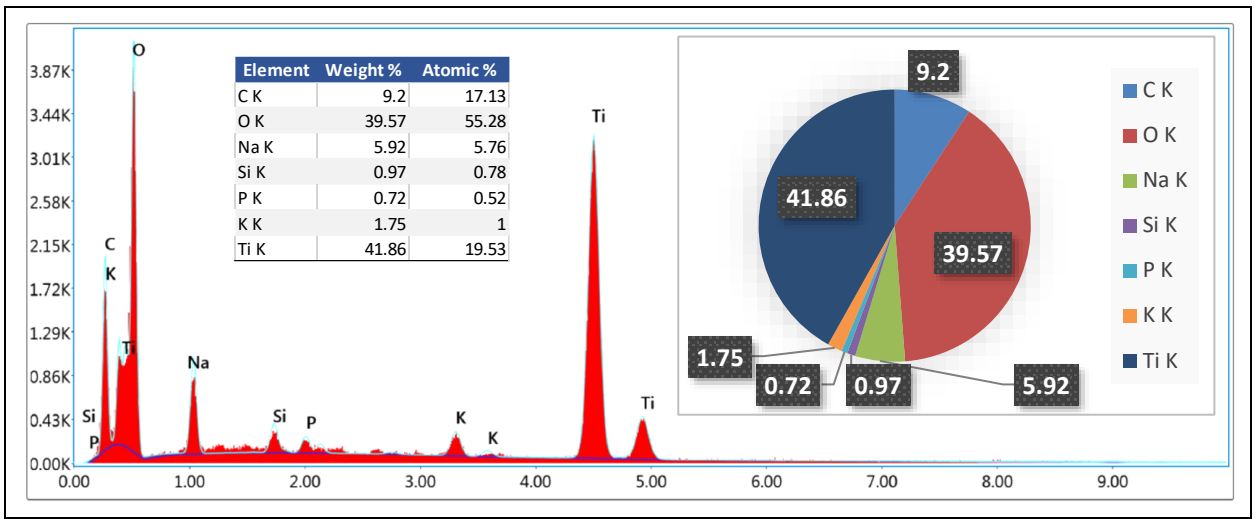


Fig. 4 Optical property of carbon doped TiO_2

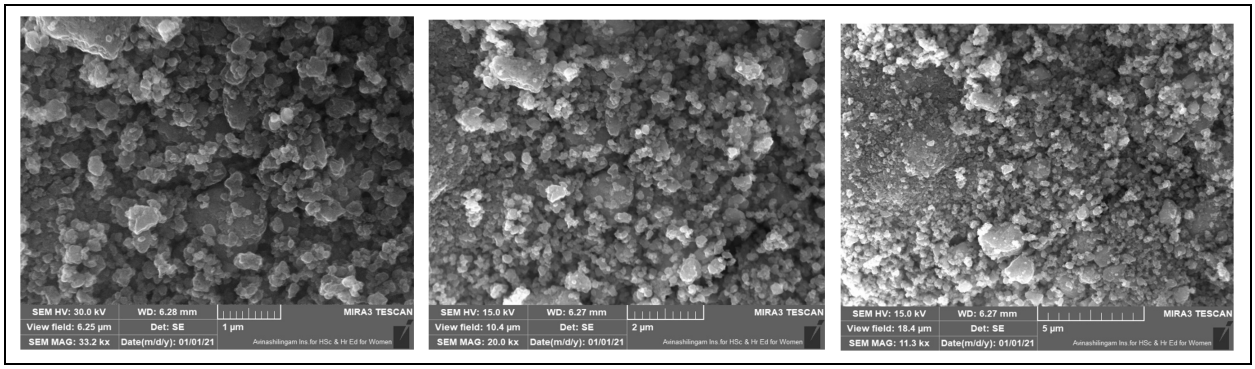


Fig. 5: SEM images of C/TiO_2 nano- catalyst

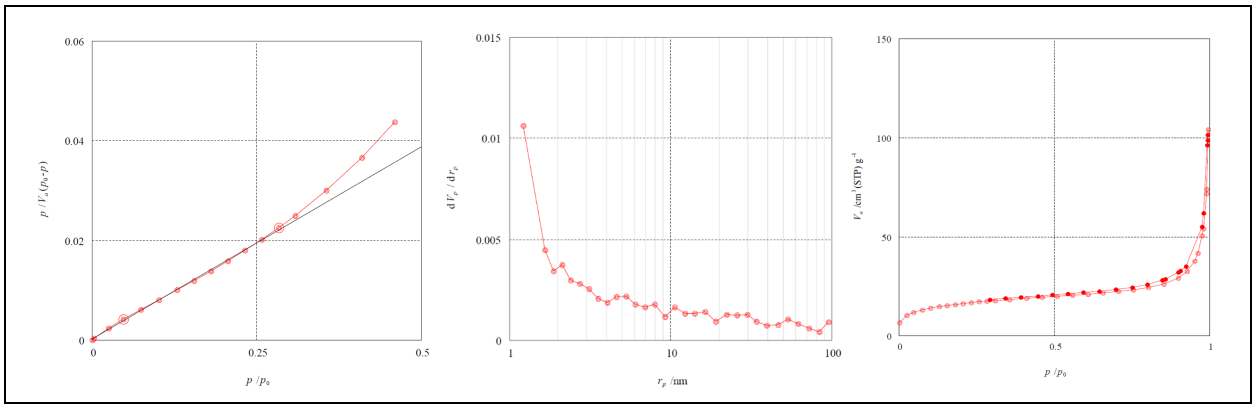


Fig. 6: Adsorption- desorption of carbon doped TiO_2

Table 1. Comparison of contaminant concentration on other parameters

Contaminant Concentration (mg/L)	pH	Reaction Time (min)	Rate Constant K (min^{-1})	Removal Efficiency (%)	Catalyst Concentration (g/L)
15	7	60	0.0080	87.07	1
20	12	30	0.0007	62.13	0.5
25	7	60	0.0064	56.34	1
30	7	60	0.0031	61.18	1

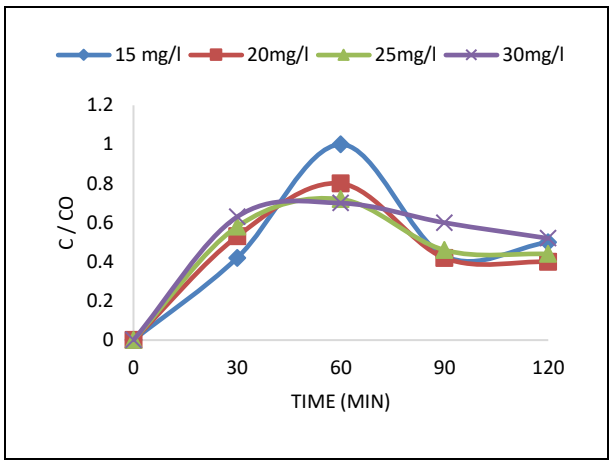


Fig. 7: Effect of photocatalytic degradation on acetaminophen

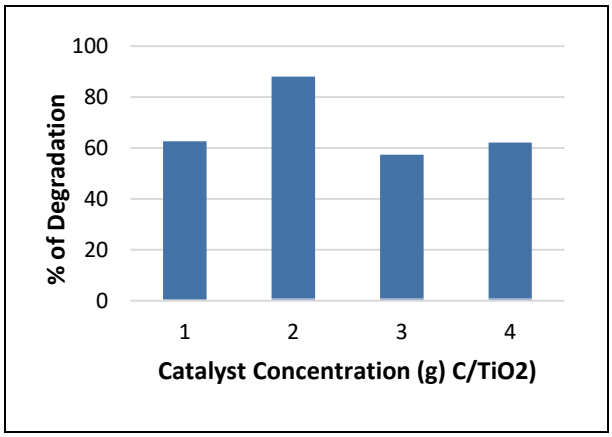


Fig. 8: Effect of catalyst concentration on degradation efficiency

7.1.8 Effect of pH

The pH plays a major in the degradation of ACT. In this study, the pH was varied between 4 to 12. The optimum pH value obtained is shown in Fig. 9. The optimum degradation efficiency was obtained at a neutral medium for various concentrations of acetaminophen. The degradation efficiency was 87.07%, 62.13%, 56.34% and 61.18% with the rate constant of 0.008, 0.0072, 0.0064, 0.0031 min^{-1}.

The decrease in efficiency and rate constant was observed while increasing the pH value. At neutral pH the degradation of acetaminophen was maximum due to the adsorption of ACT on the surface of the catalyst is maximum. Beyond pH 9, there was a decrease in degradation efficiency due to the surface ionization value of the nanocatalyst. The pH significantly influences the photocatalytic degradation of the nanocatalyst by modulating the surface charge and oxidation potential. Optimal loading of C-TiO_2 at 2.0 g/L demonstrated enhanced photocatalytic activity across a pH range of 3 to 9, with activity peaking at pH 7 (Shaban *et al*. 2019). Variations in pH can impact the solid catalyst and alter the equilibrium structure of contaminating molecules. (Zyoud *et al*. 2020).

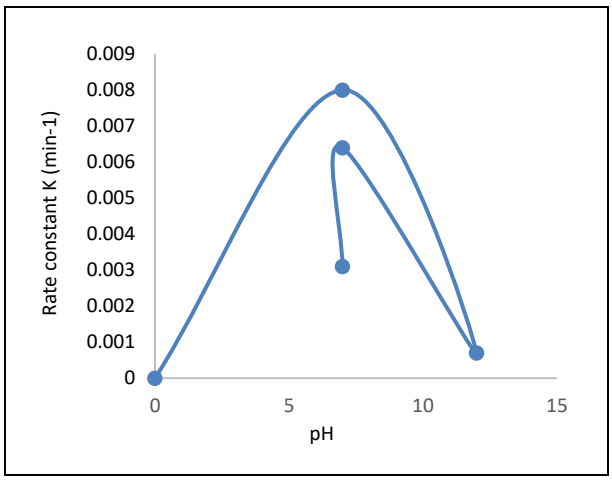


Fig. 9: Effect of pH on degradation efficiency (experiment conditions ACT = 15 mg/l and C-TiO_2 = 1g)

8. CONCLUSION

The C–TiO_2 nanocatalyst was synthesized *via* a green route and applied for the degradation of the pharmaceutical compound acetaminophen (ACT), which was prepared synthetically. The synthesized nanocatalyst was characterized using particle size analysis, zeta potential, FTIR, XRD, SEM, and EDX, confirming its nanoscale catalytic nature. Photocatalytic degradation of ACT was performed under visible light irradiation. Maximum removal efficiency was achieved at pH 7 with a reaction time of 60 minutes. Further degradation studies showed removal efficiencies of 87.07%, 62.13%, 56.34%, and 61.10% at different initial ACT concentrations. By increasing the pH and contaminant concentration, there is decrease in the rate constant from 0.008 to 0.0031 min^{-1} and a decrease in the removal efficiency up to 61.18%. Hence, from these results, it was concluded that carbon-doped titanium dioxide nanocatalyst is efficient in degrading the pharmaceutical compound acetaminophen under visible light and practically used for the degradation process.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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