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Titanium Dioxide Based Nanoparticles to Decompose Hypertension Drug from Municipal Waste Water

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Abstract

Hypertension drugs usage will be increasing in developing countries in that our India is one. One of the pharmaceutical effluents contain amlodipine is toxic to water bodies to create major ecological issue. This study focus to develop an economical nanophotocatalyst like Fe doped nanoTiO_2 and Copper doped nanoTiO_2. Obtained Cu/Fe doped nanoTiO_2 indicates the rutile –anatase phase transformation improves the surface property of composite. The Fe doped nanoTiO_2 shows 96 % photodegradation of amlodipine compared to the Cu- TiO_2 and it is competitive to literature.

Keywords: *Copper Doped Nano TiO_2 and Fe Doped Nano TiO_2, Metal Oxides, Photo Catalysis, Water Pollution*

1.0 Introduction

Water pollution is increasing and becoming a global problem. The cause of water pollution is the pollution of water bodies such as rivers, lakes, oceans, aquifers, streams and estuaries. Water bodies can be contaminated with a variety of substances, including active pharmaceutical compounds, pathogenic microorganisms, fusible organic waste, fertilizers and phytonutrients, and toxic chemicals, sediment, oil and radioactive materials. Most of chemicals present in wastewater constitutes very toxic, biodegradability causes hazardous impacts on the ecosystem[1-3]. Antihypertensive drugs in India and most of the metropolitan cities in the world uses calcium channel blockers[4,5] to almost 70%. 57% deaths due to stroke and 24% deaths due to coronary heart disease are due to hypertension in India and most other counties. Calcium channel blockers with hydropypyridine type drug Amlodipine (55.6%) was the highly medicated drug in India[4]. Presence of such amlodipine in the aquatic environment and its effect on the aquatic animal is miserable, removal of such a contaminant by processing is challenging limited.

Photocatalysis is major technique for the decomposition of various organic toxins into carbon dioxide and water using very less energy and it is totally environmentally friendly. TiO_2 has been identified as the most promising catalyst for pharmaceutical products for photodegradation[5].

As TiO_2 is a good semiconductor, offers several opportunities to processes large variety of drug or organic waste matter because it is benign, photochemically stable, economical, and available in different forms[6-8]. Limitations of TiO_2 are its large band gap and low photocatalytic efficiency due to ready coalesce of photo-induced electrons and holes. To controle these limitations, TiO_2 has been doped with different suitable system to adjust its energy bandgap and thereby improve photocatalytic efficiency[9]. To improves the photocatalytic activity of TiO_2 by enlarging the visible light sensitivity and impeding the

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electron-hole pair coalesce can be achieved by doping TiO_2 with metals[10] like Ag, Fe, V, Cu, Co, Mo etc., or non-metals (N,S,C). Literature study show few efforts to photodegrade amlodipine by using Montmorillonite[11-13] and Ag doped TiO_2 are effective in photodegrading the amlodipine.

2.0 Problem Formulation

As silver being a non-economical and toxic such elements are replaced by Fe and Co doped TiO_2 will effectively applied in photodegradation. This study will explore the advantage and efforts to photodegrade amlodipine to maximum extent. Fe and Cu doping is done by sol-gel method. And obtained products are photodegraded at different pH, degradation timing and different amount of photocatalyst.

Nanocomposites have been used as a catalyst for the degradation of amlodipine besylate and found it shows efficient photocatalyst due to their band gap (E_g) energies after doping, i.e Fe/TiO_2 2.93eV and Cu/TiO_2. 2.96 eV in crystalline form, solar energy is renewable energy source for the treatment of wastewater from industries.

3.0 Materials and Methods

The materials like ferric nitrate nonohydrate and copper nitrate dihydrate are procured from SD Fine Chemicals methanol, acetic acid are procured from RANKEM and amlodipine besylate, $C_{12}H_{28}O_4Ti$ (titanium isopropoxide) of 98% pure are purchased from Avra Bengaluru**.** All above chemicals are of analytical grade. The nanoparticles were prepared by using sol-gel method. Obtained TiO_2, Cu-TiO_2 and Fe-TiO_2 are characterized by XRD for the phase formation. X-ray diffraction (XRD) analysis was carried out at room temperature for the crystallite size and phase determination using an Advanced Bruker system using CuKα (wavelength = 0.154 nm) and diffracting angle varying from 0–80° at a scan rate of 5°/min. Synthesized nano doped catalysts are used for photodegradation with amlodipine. Using a Shimadzu UV-2600 spectrophotometer, the concentration of amlodipine was determined by the absorbance at the characteristic band and scanning the wavelength range of 200–800 nm. The diffuse reflectance measurements in solid mode with $BaSO_4$ as the reference material.

3.1 Preparation of Nano TiO_2

Titanium isopropoxide of 5 ml, methanol and acetic acid 10 ml of each added in crystalline dish. Stirred for 60 min using Teflon coated magnetic bead. Gel formed is dried for 24 hours by keeping in hot oven at 70 ^{0}C and then calcined at 450 ˚C for 2 hours.

3.2 Preparation of Iron Doped TiO_2

5 ml titanium isopropoxide, 0.2626 g (5 weight %) of $Fe(NO_3)_3.9H_2O$ as precursor in a crystallizing dish, add 10 ml methanol and 10 ml acetic acid, solution stirred using magnetic stirrer for 90 min. until gel is formed. The gel is dried at 120 ˚C in a hot oven, powder is formed which is grinded and calcined at 600 ˚C, finally brown colour Fe doped TiO_2 is obtained. As we are fixing particular to 5wt.% of Fe and Cu doping into TiO_2 is from literature at low concentration of Fe doping do not have significant photocatalytic activity and above that also have a saturation activity due to more of anatase phase formation[14].

3.3 Preparation of Copper Doped TiO_2

5 ml titanium isopropoxide and 0.3061g (5 weight %) cupric nitrate Cu $(NO_3)_2.6\ H_2O$ as precursor in a crystallizing dish into it, to the above same procedure is used to get greenish Cu doped TiO_2. Fixing of the 5 wt. percentage of the Cu doping also have a saturation weight percentage from the literature[15] lead to anatase phase formation. Rutile phase will be less at this concentration of doping.

4.0 Photodegradation

Amlodipine besylate drug solution is used to study the photocatalytic activity. 0.125g Fe-TiO_2 /Cu-TiO_2 of photocatalyst is added to 125ml of Amlodipine besylate drug solution and kept for stirring in direct sun light. To attain drug adsorption equilibrium, mixture containing amlodipine besylate drug and the nanocatalyst of suitable amount and isolated by covering with aluminium foil to be isolated from light for 30 min before irradiation shown in Figure 1. The solution was stirred by magnetic stirrer for a well-defined contact time t (0, 30, 60, 90, 120 150 and 180 min) and exposed to sunlight from 10 O'clock to 4 O'clock. 10ml of sample was collected at regular intervals of 30 mins. till 180 min. and catalyst is removed by centrifugation and supernatant liquid is subjected for UV analysis.

Solar light exposed samples of doped and pure TiO_2 with amlodipine solution were taken at above said time

interval and analysed by UV–visible spectrophotometer Shimadzu UV-1800 after dilution.

5.0 Results and Analysis

5.1 Powder XRD

XRD patterns were obtained for synthesized TiO_2 and doped TiO_2 to understand the crystallographic phase transformations. XRD patterns for the doped and undoped phtocatalysts are shown in the Figure 2. The main diffraction peak in the Figure 1 indexed to (101) crystal plane observed at 25.5 degree, and 37.5,47,54.5,55.5,64 and 69, 75.5 degree indicates the 004, 200,105, 201, 204, 116, 215 planes respectively. Peaks at different 2θ values indicates the anatase phase, low intense peak near the main peak also indicates small fraction of rutile phase (approximately 1%) along with 70.5, 220. This also well match with the JCPDS card NO. 21-1272 for anatase. Higher loading of Fe dominates the rutile phase.

After doping copper into TiO_2 lattice structure, the peak corresponding to rutile phase completely disappears (Figure 2b) that signifies formation of 100 % anatase phase without any traceable impure phases. In the case of Iron doped TiO_2 the peak corresponding to rutile phase is observed, revealing that incorporation of iron into TiO_2 lattice structure did not lead to single anatase phase. It is also observed from the XRD patterns that the diffraction peaks of the doped samples (Cu-TiO_2 and Fe-TiO_2) are slightly shifted with respect to peaks of the undoped samples i.e TiO_2 indicating that the dopants (Cu and Fe) are fully assimilated into the lattice structure of TiO_2 phase. The peaks in the XRD patterns are considerably broad due to nanocrystalline nature of the particles. The average crystallite sizes of the samples have been calculated using the Scherer's formula and the obtained values are listed in the Table 1. It is observed that the average crystallite sizes of all three samples found to be nearly the same. Decreased average particles sizes of the Fe-TiO_2 nanoparticles should influence high photocatalytic activity[12].

5.2 Photodegradation of Fe-TiO_2

Photodegradation of amlodipine besylate in aqueous solution was used to study the photocatalytic activity of Fe/Cu doped TiO_2. In the direct sunlight, the experiments of amlodipine besylate with Fe/Cu doped TiO_2 were carried out. The photocatalytic efficiency of TiO_2 as prepared by Fe doped TiO_2 is 96% in 150 minutes, whereas in the case of Cu doped TiO_2 showed a degradation rate of 58% in 180 minutes.

Table 1. Synthesized nano TiO_2 and doped nano TiO_2 d-spacing values and crystallite size

Compound	d-spacing	Crystallite size (nm)
TiO_2	0.3501	16
Fe- TiO_2	0.3495	16
Cu- TiO_2	0.3607	17

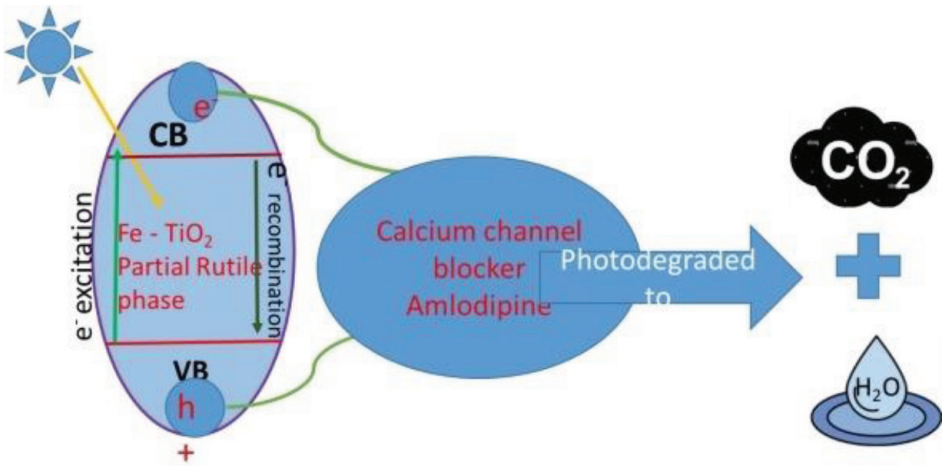


Figure 1. Photodegradation of amlodipine using Fe/Cu doped TiO_2.

The photocatalytic activity of Fe doped TiO_2 has been measured for amlodipine besylate drug solution on direct sun light with stirring rate 380 rpm at different pH. The concentration of the drug solution is 10 ppm and nano catalyst concentration is 0.125 g/l is used. The maximum degradation occurred at the pH -6 at 150 min this will be given in Figure 3 maximum absorbance occur at 270nm.

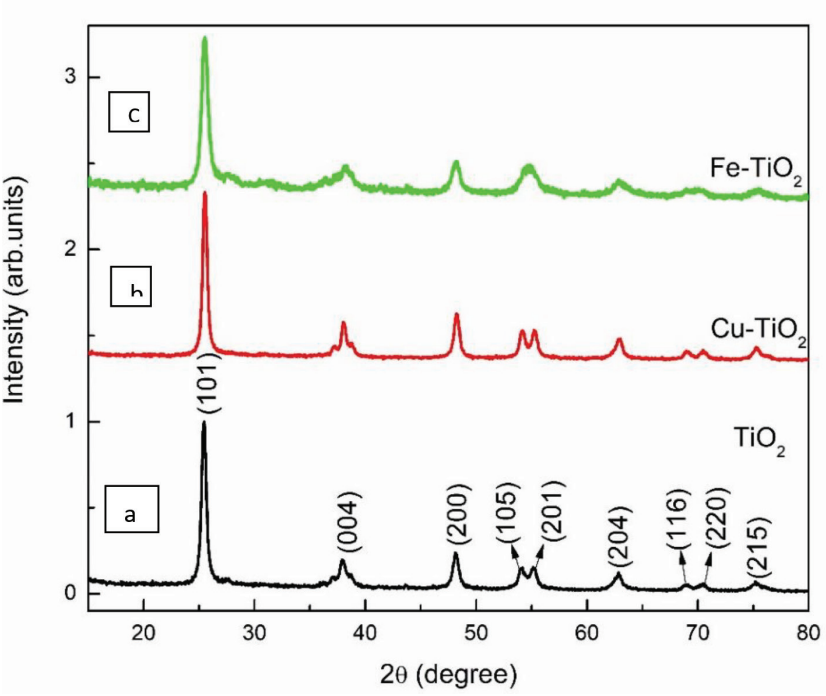


Figure 2. XRD of a) TiO_2, b) Cu-TiO_2 and c) Fe-TiO_2 photocatalyst after calcination at 600 ˚C.

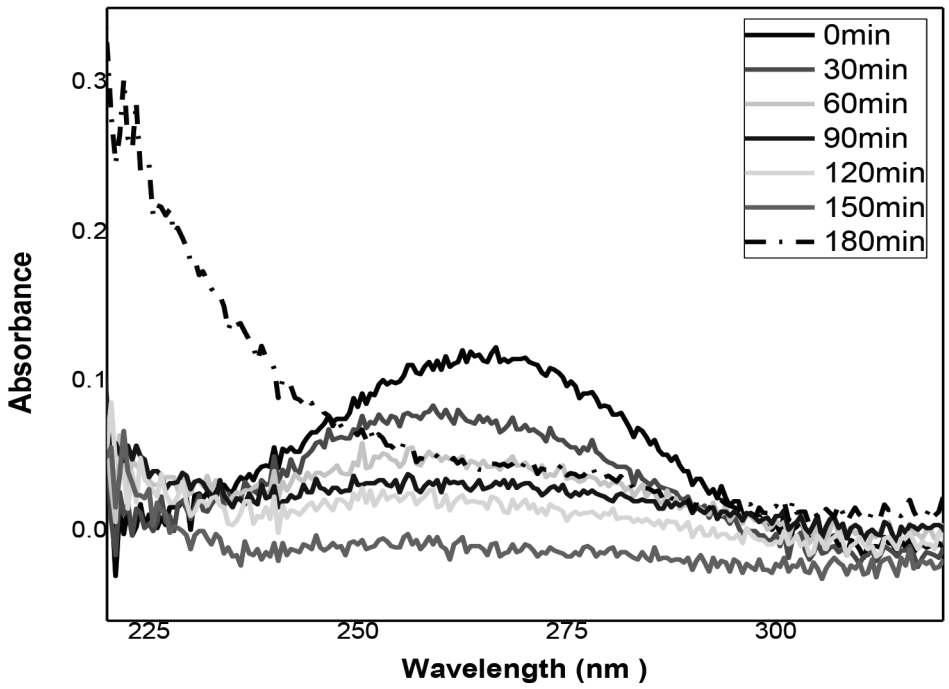


Figure 3. UV spectra of amlodipine photodegradation using Fe-TiO_2.

Black line in the absorption curve indicates the zeroth min for phtotocatalyst and Drug. Other lines indicate the degradation curve for 30, 60, 90, 120, 150 and 180 min. Pink colour absorption curve shows maximum degradation at 150 min.

From Figure 4 shows different pH of Fe doped TiO_2 at pH 6 maximum degradation. At different pH amlodipine besylate is not undergo degradation effectively. Improved photoactivity for Fe doped TiO_2 is possible in comparison with the undoped and copper doped TiO_2 material. Fe^{3+} can influence hole and electron traps to enhance lifetimes of electrons and holes according to the reactions proposed and it is in line with literature[13].

$Fe(III) + e_{ed}^{-} \rightarrow Fe(II)$ + electron trap

$Fe(II) + Ti(IV) \rightarrow Fe(III) + Ti(III)$ electron migration

$Fe(III) + h_{vb}^{+} \rightarrow Fe(IV)$ + hole trap

$Fe(IV)) + OH^{-} + - \rightarrow Fe(III) + OH^{\circ}$ electron migration

h_{vb}^{+} and OH• are the major active species in photocatalytic process. As Fe^{3+} sits into the TiO_2 lattice composite nanoparticle, the role of the iron ions was distinct from Copper ion; Doped Fe^{3+} was isolated in TiO_2 lattice phase and far from the surface, as a result significantly lower chance of shifting of trapped charge carriers to the juncture. Iron act as conjugate centre for the electron–hole pair than as trap sites in due course of charge transfer at the juncture. Such electron transfer step helps to efficiently degrade the amlodipine. From the Figure 5 shows the effect of pH on the photodegradation efficiency. At lower pH i.e high acidic condition degradation is high but it is not suitable, at pH = 6 is more suitable that is weakly acidic condition. Under basic condition photocatalytic reaction rate constant is (min^{-1}) is follow Lagergren first-order reaction but above process is not successful. Fe doped TiO_2 show high 96% photodegradation at 150 min. Figure 4 show absorption initially maximum when the exposer times increases leading to decrease in absorption indicating 96% degradation of the amlodipine.

5.3 Photodegradation Effect of Cu-TiO_2

The process is carried out with Cu-TiO_2 nanoparticles. The concentration of the drug solution is 10 ppm and nano catalyst Cu doped TiO_2 concentration is 0.125 g/l is used. The maximum degradation at 180 min occurred at the pH 9 at wavelength 272 nm shown in Figure 6. Black line in the absorption curve indicates the zeroth min for photocatalyst and drug. Other lines indicate the degradation curve for 30, 60, 90, 120, 150 and 180

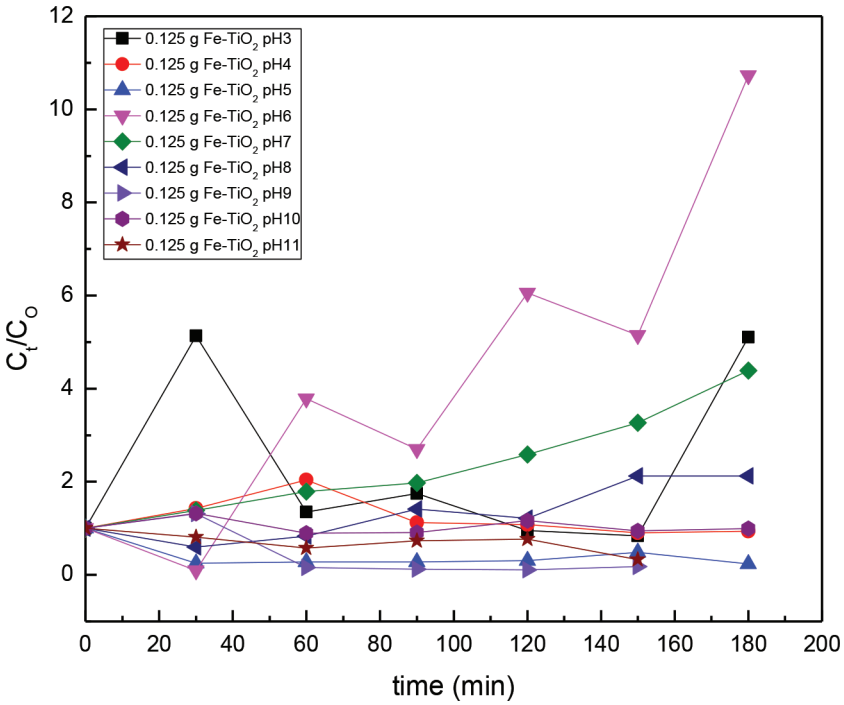


Figure 4. C/C_0 vs time graph at different pH for Fe doped TiO_2 samples.

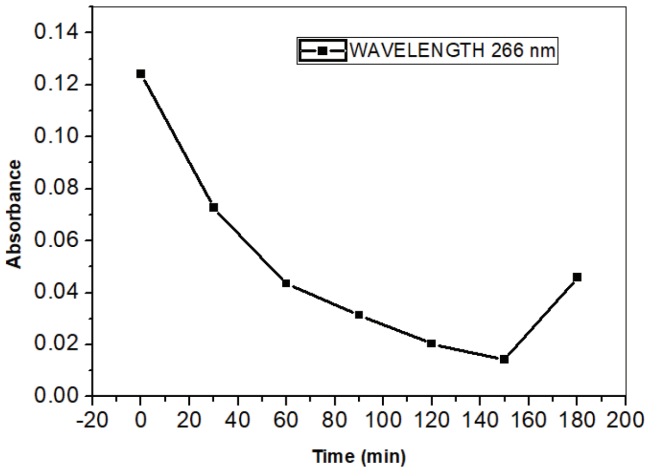


Figure 5. Photodegradation of amlodipine besylate solution with catalyst Fe-TiO_2 at pH -6 at maximum absorption at different time from UV spectra.

Table 2. Nanophotocatalyst absorbance from the UV spectra and calculated Band gap values in eV

Materials	Absorbance	Band gap(eV)
TiO_2	293	2.99
Fe- TiO_2	272	2.93
Cu- TiO_2	272	2.96

min. yellow colour absorption curve shows maximum degradation at 180 min.

Photodegradation efficiency of the 0.05 Cu-TiO_2 at 180 min shows highest degradation from the Figure 6. As revealed by the XRD analysis, photocatalysts contain Cu^{2+} ionic size (0.73 Å) is larger due to electron hole recombination as we studied in Fe-TiO_2 and becomes Cu^{+}, so Cu^{+}(0.74Å) oxidized to Cu^{+2} during the photocatalytic degradation and reduces the amlodipine besylate at the atmospheric reaction conditions. As the time duration increases degradation increases and it is maximum at 180 min. The band gap energies of the prepared TiO_2 based composites are obtained by cut-off wavelengths by drawing a tangent to the absorption curves. The Band gap energy calculated from

$\mathbf{E_{bg} = 1240/\lambda}$ Obtained Band gap values are given in the Table 2

Kinetics of photolysis of amlodipine besylate drug using the Cu doped TiO_2 has been performed by measured by exposing solution to direct sun light with stirring rate 380 rpm. Photocatalytic activity of Cu contributes in

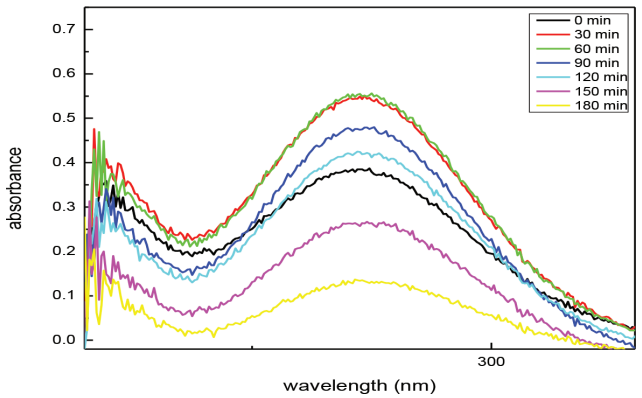


Figure 6. UV spectra of amlodipine degradation using Cu-TiO_2.

several ways. Dopant may be in the form of Cu, Cu^{+} and Cu^{2+}. As Cu^{+} ion is unstable to an ionic radius of Cu^{2+} is higher than that of Ti^{4+}. As atmospheric and photocatalytic reaction conditions Cu^{+} and Cu are less stable. Cu^{2+} ions occupy interstitial positions in the Ti^{+4}. In photocatalysis Cu^{+} would probably oxidize to Cu^{2+}. The possible active species in Cu doped TiO_2 are Cu, Cu_2O, and CuO. Copper oxides can arrange heterojunction structure with TiO_2. Cu_2O and CuO are p-type semiconductors with band gap energies. Heterostructures of the Cu_2O/TiO_2 system would be probably type II, where photo excited electrons of heterostructures are transferred from Conduction Band (CB) of Cu_2O to the CB of TiO_2 and light induced holes shifts simultaneously from the VB of TiO_2 to VB of Cu_2O. Subsequently, light induced electrons and holes are isolated and decreasing the coalesce and increasing the lifetimes of the charge carriers. Increasing the concentration of CuO could promote the light induced electron-hole pair coalesces resulting in a decrease in available holes for redox reactions with amlodipine. Cu doped TiO_2 show low photocatalytic activity due to the less possible coalesce of photogenerated electron hole pairs. Lowest photocatalytic activity with higher Cu doped TiO_2 because Cu_2O is present as the TiO_2 is shielded proper charge migration and isolation at the heterojunction. This possibility can be seen from the Figure 7 at different pH.

From the above Figure 8 shows different absorbance at 272 nm wavelength with reference to zeroth min of Cu-TiO_2 at different time interval. At 180min lowest absorbance indicate the maximum degradation of the drug amlodipine. In case of Fe doped TiO_2 absorbance is still lower so

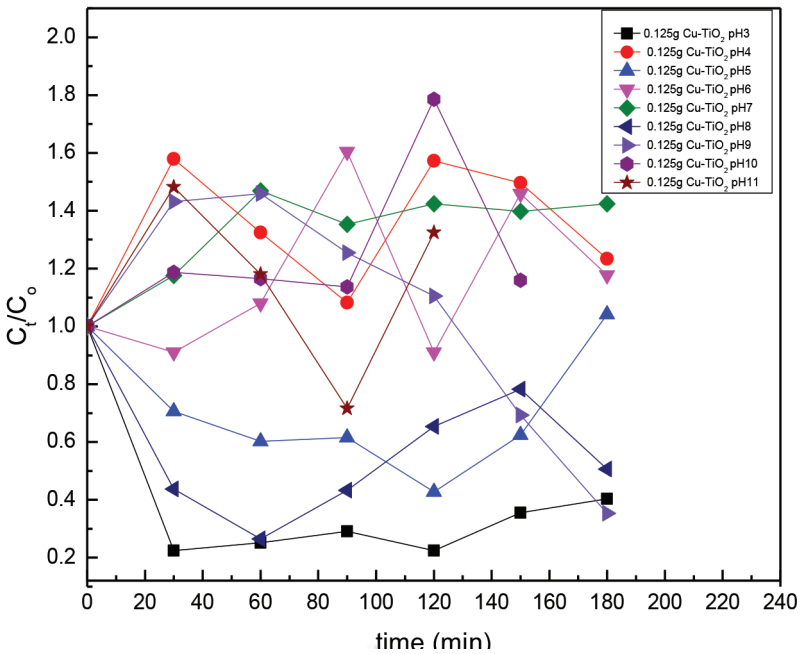


Figure 7. C_t/C_0 vs time graph at different pH for Cu-TiO_2 the samples.

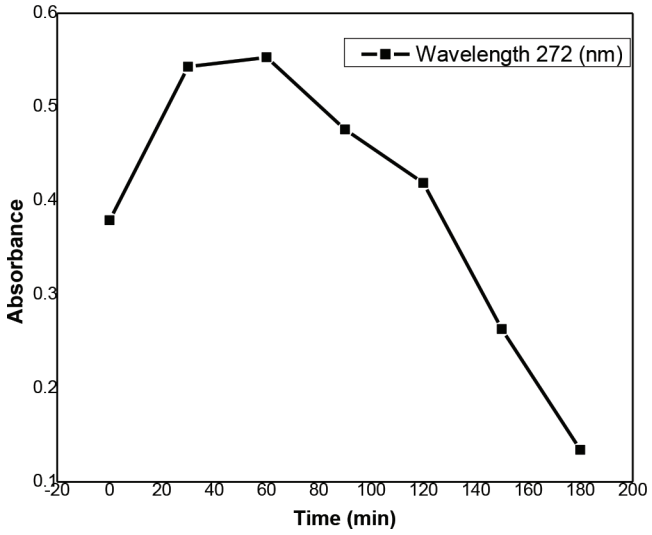


Figure 8. Photodegradation rate obtained from UV spectra of amlodipine using Cu-TiO_2 for pH-9.

degradation of drug is much larger extent. So Fe doped TiO_2 is competitive photocatalyst than literature catalysts.

6.0 Conclusion

The Iron and Copper doping with TiO_2 nanoparticles were successfully prepared by sol-gel method. From XRD spectra, doping of TiO_2 with Fe^{3+} and Cu^{2+} is confirmed by slight shifting of characteristic peak positions towards a lower angle. Lattice parameters and phase transformations of the doped nanomaterials are different from the pure TiO_2. UV spectra of the photodegraded solution of drug amlodipine clearly explains the mechanism. Fe^{3+} have successfully doped into the lattice of TiO_2 resulting in mixture of anatase and partial rutile phases responsible for efficient photodegradation. As Copper doped TiO_2 forms more of anatase phase less suitable for phtodegrdation of drug. UV-Visible spectroscopy results, the maximum degradation is achieved at pH 9 for Cu and pH 6 for Fe doped TiO_2. The Fe doped nanoTiO_2 shows 96 % degradation compared to the Cu-TiO_2 it is competitive to literature photo catalyst. Photocatalytic degradation of Fe-TiO_2 is efficient due to the Fe^{+3} size and Ti^{+4} ionic radii suitable for the photodegradation. Fe^{3+} enhance lifetimes of electrons and holes thereby increasing the phtodegradation of amlodipine basylate.

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