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Involvement of process parameters and various modes of application of TiO_2 nano particles in heterogeneous photocatalysis of pharmaceutical wastes – A short review

Santanu Sarkar [a], Ranjana Das [a], Heechul Choi [b] and Chiranjib Bhattacharjee*[, a]

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In recent years, occurrence of persistent organic compounds in industrial as well as municipal effluents is becoming a serious threat to the environment. The pharmaceutical compounds present along with those organics have a detrimental effect on our environment. Among various well established wastewater treatment technologies, advanced oxidation processes (AOPs) using TiO_2 nano particle have shown promising results against various organic wastewater pollutants. This study represents an in-depth review on applications of TiO_2 in treatment of various pharmaceutical wastes and the effect of associated process controlling parameters. It also highlights aspects of different techniques of application of TiO_2 nano particle and involvement of reaction kinetics in photocatalytic degradation.

1 Introduction

Increasing human and livestock population, along with industrial developments have raised the concern for environmental protection, waste management and pollution control along with the supply of safe drinking water. It has been estimated that around 4 billion people all over the world are facing little access to clean and sanitized water supply, and millions are dying from waterborne diseases annually[1]. These statistical figures are steadily growing, due to increase in water pollution from micro pollutants and contaminants discharged to the natural water cycle [2, 3]. Studies have shown that, pharmaceutical wastes are directly entering the sewage treatment process[4-6] and adversely affecting the aquatic life[7-9]. In the present context of safe water supply, the developments of advanced, low-cost and high efficiency wastewater treatment technologies are becoming obvious. Techniques related to removal of suspended solids, health-threat coli forms and soluble refractory organic compounds from wastewater are very tedious and expensive[10]. In current scenario, processes like adsorption, coagulation and concentration of the pollutants using phase change methodology does not completely eliminate or destroy the pollutants[11]. Due to high operating cost and generation of secondary pollutants, processes of sedimentation, filtration and chemical wastewater treatments are also not well accepted[12-15]. To overcome the limitations of conventional wastewater treatments and effective utilization of available economic resources, various advanced treatment technologies have been adopted, optimized, and applied[12-14]. Among well adopted technologies, membrane filtration, advanced oxidation processes (AOPs), and UV irradiation have been proven beneficial in removal of a wide range of challenging contaminants.

Advanced oxidation processes (AOPs) are the modern trend of pharmaceutical and municipal waste water treatment. The AOPs can be categorized as: photolysis, ozonization, Fenton's oxidation, heterogeneous photocatalysis, electrochemical oxidation, ultra sound irradiation and wet air oxidation[16]. According to Klavarioti et al.[16] ozonization and heterogeneous photocatalysis are the most accepted water and wastewater treatment methodologies. Several researchers have observed that, ozonization is more suitable for purification of drinking water[17, 18] than pharmaceutical waste water treatment because; the latter requires several downstream processing steps. Hence, heterogeneous photocatalysis using nano particles has become more effective in the treatment of pharmaceutical wastewater. Nano particles offer high surface area, which pretences higher surface reaction rate and they are also commercially available and photo chemically stable. Due to presence of light absorption properties, charge transport characteristics, excited-state lifetimes and favourable combination of electronic structure[19] semiconductors namely TiO_2, MnO_2 is mostly used as photo catalysts in the AOPs.

This review aims to study the application of TiO_2 nano particles in the field of heterogeneous photocatalysis for treatment of pharmaceutical waste as well as several other related parameters that controls the process efficiency. Moreover, it also covers the several ways of utilization of TiO_2 nano particle so that the process becomes more acceptable as well as more economic. The involvement of different reaction kinetics related to photocatalytic degradation of pharmaceutical wastes using TiO_2 has also been studied here.

2 Heterogeneous photocatalysis-a new trend of advanced oxidation process

Developments toward heterogeneous photocatalysis (HPC) in presence of TiO_2 are gradually rising and asserted to the maximum percentage among all AOPs[16, 20, 85]. The most important literatures available on photocatalytic degradation of pharmaceutical components which, has evidenced the effectiveness of photocatalysis as a promising process for pharmaceutical wastewater treatment have been summarized in table 1.

HPC by definition is oxidation of target molecules with the help of active radicals using nano particles as catalyst under UV light illumination. As soon as the UV radiation energy becomes equal or larger than band gap energy, minimum energy is required to move one electron from valance band to conduction band, electrons (e^-) move from the valance band to conduction at the photocatalytic surface and therefore, it results in generation of holes (h^+). Photo hole converts the water (H_2O) molecules to hydroxyl radical ($OH^\bullet$) and hydrogen cation (H^+). The formed $OH^\cdot$ works as highly oxidizing agent and it transforms organic substance, mainly present in pharmaceutical wastewater into carbon dioxide, water and other often less hazardous materials than the original one.

The whole mechanism for the process can be represented using equation (1) to (4).

$$\text{Photo catalytic nano - particle} + h\gamma \rightarrow e^- + h^+ \qquad (1)$$

$$e^- + O_2 \rightarrow O_2^- \qquad (2)$$

$$h^+ + H_2O \rightarrow OH^\bullet + H^+ \qquad (3)$$

$$OH^\bullet + \text{Pharmaceutical waste} \rightarrow CO_2 + H_2O + \text{Others} \qquad (4)$$

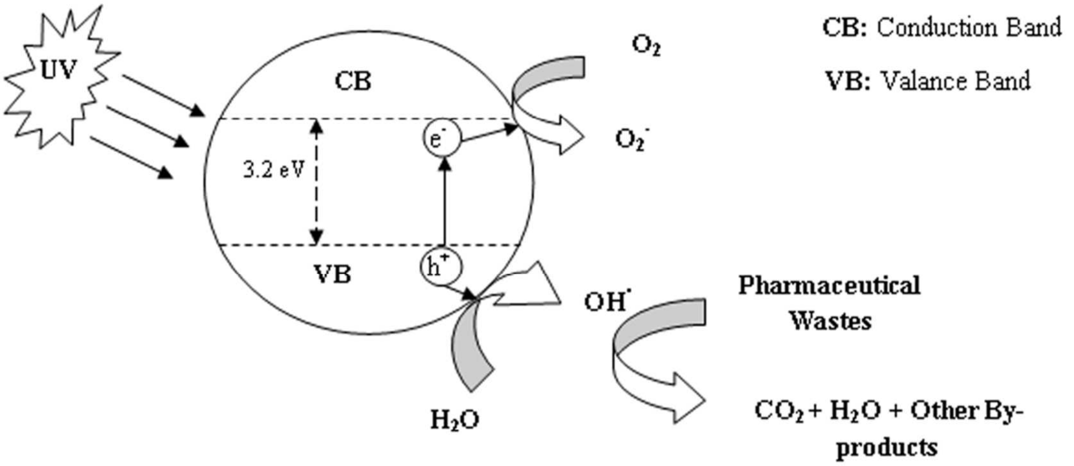

Fig. 1 Schematic representation of photocatalysis of pharmaceutical waste on the surface of TiO_2 nano particle.

In heterogeneous photocatalysis two reactions occur consecutively; first one is the reduction of oxygen and the second one is the oxidation of pharmaceutical waste by hydroxyl radical. During the excitation of TiO_2 nano particle electrons are accumulated in the conduction band, and thus it causes the generation of a hole. Therefore, it is necessary to consume electrons to increase the efficiency of HCP in presence of nano photocatalyst and here it is consumed by the dissolve oxygen. The whole reaction has been schematically represented in the figure 1. Some important parameters which influence the photocatalytic oxidation are light intensity, catalyst concentration, substrate concentration, temperature, pH of the medium, etc.[21-93].

Table 1 The photocatalytic degradation of pharmaceutical wastes using TiO_2 nano particle

Pharmaceutical wastes	Solvent Matrix	AOP parameters			Reaction Kinetics	Major observations
		Nano particle	Sources	pH		
17β-Estradiol 0.05–3 μM	Acetonitrile / water	Immobilized TiO_2	UV-light 300–400 nm	1–12	Langmuir–Hinshelwood (L-H) kinetics	Up to 98% degradation was possible after 3.5-hours irradiation time. The variation of the reaction rate with pH was established, and it reached the maximum at pH 12. Thus photocatalysis had better efficiency than photolysis.[21]
17β- estradiol, estrone, ethinylestradiol 0.1 mg/L	Deionized water,	Immobilized nano structured TiO_2	20 W backlight, 359 nm	NM†	First-order kinetics	Without catalyst 90%, removal was possible in 2 hours of irradiation but same degradation was observed in presence of TiO_2 within 30 minutes.[22]

17β-Estradiol 1 μM	Deionised water	Suspended Degussa TiO_2 (P25)	UV-365 nm	NM	First-order kinetics	The total removal of 17β-Estradiol was possible, and it lost its activity. After 3 hours, the mineralization process completed and all by-products were identified.[23]
17β-Estradiol, estrone 250 μg/L	Deionized water and industrial effluent.	Immobilized TiO_2	UV-black fluorescent lamp	NM	First-order kinetics	Rate of reaction depended on diffusion constant. As rate of diffusion of substrate molecules increased with surface area of catalyst and the temperature, the rate also increased with increase of both parameters.[24]
Buspirone 15 mg/L	Distilled water	Suspended P25	Artificial sunlight	NM	First-order kinetics	Several structures of by-products were identified with different mechanisms. Maximum drug removal was possible during photocatalysis.[27]
Unconjugated and conjugated estrone and estradiol 1 mM	Distilled water	Immobilized TiO_2 on glass beads	UV lamp	NM	First-order kinetics	17-glucuronide and estrone was completely depredated within 4hrs of UV irradiation. Conjugates remain unaltered after 6.5 hours of the oxidation process.[28]
Clofibric acid, carbamazepine, iomeprol and iopromide	Distilled water	Suspended P25 and Hombikat UV100	1000W Xe short-arc lamp < 400 nm	6.5	L-H kinetic model	P25 showed better degradation of clofibric acid and carbamazepine than Hombikat UV100 but in case of iomeprol it was reversed. As higher adsorption of iomeprol by Hombikat UV100 was observed. Possible degradation pathways were established.[29]
17β-Estradiol, estrone, 17α-ethylestradiol, 10 μg/L	Distilled water	Immobilized TiO_2	High-Pressure Mercury UVA lamp	NM	First-order kinetics	The photocatalysis process was much faster than direct photolysis. Immobilized TiO_2 inside the photo reactor helped to reuse catalyst more than single time. Thus efficiency of the process was improved.[30]
17α-Ethinylestradiol, 17β-estradiol, estriol 0.1–3 μM	Acetonitrile/ water	Immobilized P25	UVA & UVB	3 - 4	First-order degradation kinetics	Photocatalysis was more effective than photolysis. The rate of reaction increased with light intensity and initial substrate concentration. Pt and Ag were added a little amount to the system to boost the reaction and only Pt could enhance the performance of the reaction. [31]
Iomeprol, clofibric acid, carbamazepine ~2 mg/L	Deionized water	Suspended P25 or Hombikat TiO_2	254 nm	6.8	Not mentioned	Microfiltration with backwashing enhanced the reusability of TiO_2 and membrane. Hombikat was more active in pilot plant than other type of TiO_2 but batch studies showed reverse results.[32]
Carbamazepine, clofibric acid, iomeprol 0.5–5.2 mg/L	Spiked lake water	Suspended P25 or Hombikat TiO_2	Artificial sunlight	6.5	Pseudo-first-order kinetics	P25 had more activity than other. The rate of degradation decreased and increased with an increase of substrate concentration and TiO_2 loading respectively. The total mineralization was done by photocatalysis.[33, 34]
Lincomycin 10–75 μM	Distilled water	P25/ coupled with nanofiltration	Sunlight	6.3	First-order kinetics	Membrane photo reactor helped to separate nano particles and by-products during degradation of drug. Thus, TiO_2 can be used more than one time.[35]
Sulfamethazine 10–70 mg/L	Distilled water	Suspended P25 or ZnO	350–400 nm	4.8	First-order kinetics	The result showed that ZnO was more effective than TiO_2. In presence of H_2O_2 degradation rate increased and it also increased with catalyst loading.[36]

B-Estradiol 0.5 mg/L	Distilled water	Suspended TiO_2	366 nm	3-11	NM	Both the adsorption and degradation increased considerably with increase of pH as OH radical of reaction mixture increased simultaneously.[37]
Diclofenac, 0.76–15 mg/L	Distilled water	Suspended P25	Artificial sunlight	Ambient pH	L-H kinetic model	Response surface methodology (RSM) was employed to optimize catalyst loading and drug concentration. Finally the toxicity was removed.[38]
Triclosan 15–37 µM	Distilled water and surface river water	Suspended P25 or anatase TiO_2	300–450 nm	5	First order reaction kinetics	P25 was more active than other type TiO_2. Up to certain range, degradation rate increased with catalyst loadings. Detection of intermediates, by-products and pathways were achieved for complete removal of drug after 60 minutes of reaction. Degradation was slower in case of river water than in distilled water.[39]
Triclosan 9 mg/L	Distilled water	Suspended P25	UV- 365 nm	NM	NM	Up to 95% degradation of Triclosan was possible. The mineralization efficiency was increased with addition of H_2O_2. By-products and degradation pathways were identified.[40]
Furosemide, ranitidine, ofloxacin, phenazone, etc. 5–10 mg/L	Distilled water and surface river water	Suspended P25 /MP UV coupled with nanofiltration	125 W medium pressure Hg lamp	2-12	First-order kinetics	The degradation rate increased with pH. Filtration separated catalyst particles for reuse. Characteristics of different type of membrane were studied in both alkali and acid medium.[41]
α-Methyl-phenylglycine, 500 mg/L	Distilled water	Suspended P25	Sunlight	2.7-2.9	NM	Complete drug degradation was possible, and the chemical oxygen demand (COD) value reduced to 504 mg/L after 1500 minutes irradiation time. LCA (Life cycle assessment) measured the environmental impact of degraded by-products.[43]
Tetracycline 40 mg/L	Deionized water	Suspended P25	HPLN (>254 nm), Solarium (300-400 nm), Black light (365 nm)	NM	NM	Photocatalysis was more effective than photolysis. Rate of oxidation was higher under UV and solarium radiation. Partial mineralization was possible. However, the antibacterial activity of the by-products reduced completely after 1 hr irradiation.[44]
Sulfamethoxazole 25–200 mg/L	Distilled water	Suspended P25	Artificial sunlight	2–11	First order kinetic model.	The effects of catalyst loading and pH were studied. After 6 hours of irradiation, there was some amount of aromatic compound due to presence of sulphur and nitrogen-containing aromatics. [45]
Sulfamethhoxazole 5–500 µM	Deionized water with NOM and bicarbonates	Suspended P25 or anatase or rutile TiO_2	UV- (324–400 nm)	3–11	Pseudo-first-order reaction followed by L-H kinetic	The rate of the reaction depended on concentration of drug, TiO_2, pH of the medium. P25 showed more activity as compared to other. It intermediates, and by-products were identified and mechanism pathways were established.[46]
Salbutamol 15 mg/L	Distilled water	Suspended P25	Artificial sunlight	2.5–9.5	L-H kinetics	RSM was implemented to optimize catalyst loading and pH. The by-products and the pathway of the reaction were identified. The toxicity level was gradually decreased. [47]

17α-Ethinylestradiol, 17β-estradiol, estriol 0.8 mg/L	Distilled water	Immobilized P25	Artificial sunlight or UV-350 nm	NM	First-order kinetics.	Among all heterogeneous photocatalysis UV-irradiated photocatalysis was more effective than other. TiO_2 immobilization technique was employed to get better performance by recycling of photo catalyst .[48]
Gemfibrozil, tamoxifen 2.5–50 mg/L	Deionized water	Suspended P25 or anatase TiO_2	UV-360 nm	10	Pseudo First-order kinetics followed by L-H model	The impact of photocatalysis on tamoxifen was negligible as it was degraded using photolysis, but it was opposite for gemfibrozil. P25 was more effective than other type of TiO_2. The pathway of reaction was understood and verified.[49]
Estrone, 17β-estradiol 0.1–1 µg/L	Deionized water	Suspended P25	UV-253 nm or UV-238–579 nm	2–10	First-order kinetics	Reaction at 253 nm is three times faster than at 238–579 nm. Degradation increased with catalyst loading and H_2O_2 addition and also depends on pH. Humic substances facilitated degradation due to photosensitization.[50]
Imipramine, 15 mg/L	Deionized water	Suspended P25 / combined with Fenton	Xenon arc lamp, 290 nm	NM	L-H kinetics model	The combined effects of H_2O_2 and Fe^{+2} on photocatalytic degradation were analyzed. The application of artificial neural network (ANN) was introduced for optimization. The by-products were identified though they were as toxic as imipramine and had a resistant to photocatalysis.[51]
Chloramphenicol, 10–80 mg/L	Deionized water	Suspended P25 or anatase TiO_2 or ZnO	320–400 nm	5	L-H kinetics model	The rate of degradation was increased with substrate and catalyst concentration as well the addition of H_2O_2. P25 was more effective than ZnO. The complete pathway the reaction was indentified. Within 90 minutes the target drug was completely removed.[52]
Diclofenac, naproxen, ibuprofen, 25–200 mg/L	Deionized water	Suspended P25	Artificial sunlight	NM	First-order kinetics model	The total organic contains (TOC) was decreased with TiO_2 and O_2 concentration. Temperature affected the degradation of naproxen. By-products were identified but the post biological treatment could be done for by-products of ibuprofen.[53]
Paracetamol 2–10 mM	Deionized water	Suspended P25	UV-254 nm or UV-365	3.5–11	Pseudo First-order kinetics	The rate of degradation was much higher under UVC irradiation than UVA. Up to certain concentration of TiO_2 the value of reaction rate constant was increased, and it also depended on the initial substrate, O_2 concentration and pH of reaction medium. The by-products were identified.[54]
Triclosan	Deionized water	Suspended P25 in Photo Reactor	UVA lamp	6-8	Pseudo First-order followed by L–H kinetic model	The intermediates during photocatalysis were identified. The formation of toxic elements using TiO_2 photocatalysis is less compared to be other. This method could reduce the formation of dioxin with effective mineralization of triclosan. [56]
Mixture of amox-icillin 10 mg/L, carbamazepine 5 mg/L, Diclofenac 2.5 mg/L	Deionized water	Suspended P25	Artificial UV 300-420 nm	4-5.5	Pseudo First-order followed by L–H kinetic model.	Effective mineralization, detoxification and degradation could be possible using heterogeneous photocatalysis. The intricate relationships between process parameters were identified.[57, 59]

Ofloxacin and the β-blocker atenolol initial concentration of 5-20 mg/L	Deionized water	P25 suspension in the range 50–1500 mg/L	UVA lamp 350-400 nm	3-10	L–H kinetic model	The effects of different process parameters were studied, and addition of H_2O_2 enhanced the effect of photocatalytic reaction. It intermediates were more stable and less toxic compare to parent molecule.[61]
Diclofenac initial concentration of 5-20 mg/L	Deionized water	Six types TiO_2 suspension	UVA lamp 350–400 nm	6	NM	The conversion rate for different types of TiO_2 was analyzed, and effective one was identified. H_2O_2 could the photocatalytic reaction.[62]
Sulfachlorpyridazine, sulfapyridine and sulfisoxazole	Deionized water	TiO_2 suspension	High-pressure mercury lamp, 365 nm	3-11	Pseudo First-order followed by L-H kinetic model	Up to 90% removal of sulfa drug was possible less than 60 minutes of illumination time. pH of reaction matrix played a significant role on photocatalytic degradation. However, rate of degradation was increased with catalyst loading.[63]
Oxolinic acid 20 mg/L	Deionized water	P25 suspension	Cylindrical black light lamp as UV source	7.5-11	Pseudo First-order kinetics	The intermediates formation was confirmed. Optimization showed that 1.0 g/L TiO_2 concentration at pH 7.5 is the most favourable condition for photocatalysis.[64]
Amoxicillin, ampicillin and cloxacillin with concentration of 104, 105 and 103 mg/L, respectively	Distilled water	TiO_2 suspension	UVA lamp 365 nm	5-11	Pseudo-first order kinetics	The degradation of drugs was very low at 300 nm irradiation and maximum degradation was achieved at pH 11. The complete degradation was possible at pH 5 in presence of H_2O_2 with TiO_2. Rate of drugs constant for different degradation were calculated.[65]
Carbamazepine, clofibric acid and iomeprol	Deionized water	TiO_2 suspension with activated carbon in a ratio of 1:3	UV Hg lamp, below 300 nm	7.5	Pseudo-first order kinetics	High removal efficiency was observed using TiO_2 suspension. With addition of activated carbon reduced the intermediates, although it enhanced turbidity of the current system. Lower affinity of clofibric acid towards activated carbon provided higher surface area, which led to faster degradation rate.[66]
sulfonamides (sulfathiazole, sulfamethoxazole and sulfadiazine)	Deionized water	P25, $FeCl_3$	UV lamp, maximum irradiation 366 nm.	3-8	First and second order kinetics	Removal of sulphonamides was 15 times higher in presence of $FeCl_3$ and HCl along with TiO_2 than TiO_2 alone.[67]
Chloram phenicol initial concentration 6.6-23.4 mg/L	Deionized water	P25 suspension	Mercury lamp, 365 nm	4-9	NM	The optimization of parameters was made using RSM and optimized parameters were pH 6.4, TiO_2 concentration 0.94 g/L and initial substrate concentration 19.97 mg/L.[68]
Indomethacin, concentration 0.1 to 1.5 mmol/L	Deionized water	P25 with activated carbon	125 W medium pressure mercury lamp,	NM	Pseudo-first order kinetics followed by L–H kinetic model	Langmuir, Freundlich, and Sips isotherm were used to describe adsorption. With the increase of TiO_2 concentration, the rate of adsorption and rate of reaction was increased, and those reached the maximum value with 10% of TiO_2 concentration.[69]
Caffeine, diclofenac, glimepiride and ibuprofen with initial concentration of 100 µg/L and 25 µg/L for methotrexate	Deionized water	TiO_2 modified with SiO_2	Solar bath	NM	Zero order or Pseudo- first order kinetics	TiO_2 was successfully modified with SiO_2. Both wastewater and simulated solution was used for the experimental study. Lower degradation was observed in case of real wastewater. Removal percentage of those drugs was 79-96%.[70]
Atenolol, metoprolol and propranolol with initial concentration of 50-200 µM	Milli-Q water	P25	High-pressure mercury UV lamp, 365 nm	3-11	Pseudo-first order kinetics followed by L–H kinetic model	Complete mineralization of substrates and intermediates was possible by photocatalysis. Adsorption played the major role on photocatalytic degradation. The pathway of the reaction and intermediates

						were identified.[71]
Lamivudine, concentration 100 µM	Distilled water	P25	Mercury lamp, 365 nm	3-11	First-order model followed by L-H kinetic	Maximum degradation was possible at pH 9, TiO_2 of 1g/L and with initial substrate concentration of 100 µM. The process was optimized using RSM. A tentative reaction mechanism was established.[72]
Trimethoprim, initial concentration 2-50 mg/L	Distilled water	P25	Artificial UV lamp, 352 nm	3-8	First order kinetic	Rate of degradation was decreased with the increase of drug concentration, but it remained constant above the UV intensity 47mW/cm^2 and TiO_2 concentration of 0.5gm/L. A continuous mode of degradation was successfully attempted.[73]
Sulfamethoxazole with initial concentration 2.5–30 mg/L	Ultrapure water	P25, Hombikat, Millennium PC-50/100/105/ 500	UVA lamp, 350–400 nm.	5-6.7	L–H kinetic model	Effectiveness of distinct type of TiO_2 catalyst was analyzed and P25 was the most effective catalyst. At the same type, the influences of different process parameters were investigated. [74]
Amoxicillin and Cloxacillin	Wastewater	TiO_2 suspension	Artificial UV lamp, 365 nm	5	NM	The most desirable conditions were AOP followed by SBR process showed 57% removal efficiency, which was the limitation of the whole process. [75]
Carbamazepine, Concentration of 10 mg/L	Distilled water	TiO_2 slurry form used in MBR	UVA lamp, 360 nm	NM	Pseudo-first order followed by L–H kinetic	Up to 95% carbamazepine removal was possible with 4:1 recycle ratio and below the concentration of 10 mg/L it cannot be biologically degradable.[76]
Norfluoxetine, lincomycin, etc. Initial concentration of 0.1 gm/L	Ultra pure water	TiO_2 nanowire membrane	100 W artificial UV irradiation	6.7	Pseudo-first order kinetic	A successful attempt was made to synthesize TiO_2 nanowire membrane. In presence of UV those were more effective than normal TiO_2 to degrade pharmaceutical materials.[77]
Norfloxacin	Deionized water	C-TiO_2 suspension, 0-2.0 gm/L	Mercury lamp, 420 nm	2.5-11.8	L-H kinetics	The most important observation from the recycling study was that degradation efficiency is nearly same for fresh and used TiO_2. Addition of OH^- enhanced the performance of the system.[78]
Amoxicillin trihydrate	Deionized water	TiO_2 and Sn/TiO_2 nano particle suspension	15W (UVC) mercury lamp, 254nm	7	Pseudo-first-order reaction followed by L-H kinetic model	Sn doping enhanced the adsorption efficiency due to enhancement in generation of hydroxyl radicals, band gap energy, specific surface area, and decrement in the crystal size, etc. Thus the degradation efficiency of photocatalysis was increased.[79]
Levofloxacin, initial concentration 20 mg/L	Deionized water	P25, concentration of 0.05 - 0.5 g/L suspension	UVC lamp, 254 nm	6.5	NM	A comparative study was made between ozonization and heterogeneous photocatalysis. The intermediates were more favorable to oxidation process, and it showed higher mineralization efficiency compared to be other. It intermediates had no antibacterial property.[80]
Venlafaxin, atorvastatin, ibuprofen, naproxen, gemfibrozil, lincomycin, norfluoxetine, etc.	Deionized water	TiO_2 nanowires suspension	Low pressure mercury Lamp, 264 and 365	7.4	Pseudo first order reaction kinetics.	Study indicated that a degradation mechanism of waste was a simultaneous process of surface adsorption and photocatalytic degradation. TiO_2 nano wires showed more effective mineralization compared to normal TiO_2 nano particles.[81]

			nm			
Famotidine, tamsulosin and solifenacin	Distilled water	Tetra(4-carboxyphenyl) porphyrin (TCPP)-TiO_2 composite	500 W halogen lamp and sunlight	NM	NM	Study showed that higher degradation rate of nano composite famotidine was observed compare to unmodified P25. The recycle and reuse of photo catalyst could be possible in case of composite materials. Solar photolysis showed promising result.[82]
Carbamazepine	Deionized water	TiO_2 suspension	UVC	4-11	L–H kinetic model	Complete degradation of Carbamazepine was observed with help of photocatalysis with in 30 min. In addition of O_2 improved the activity of catalyst.[83]
Carbamazepine, initial concentration 1mg/L	Deionized water	N-doped TiO_2 suspension	Hg vapor lamp	2-8	NM	The surface coating of modified N-doped TiO_2 ensured multiple use of same catalyst. The modified catalyst surface did not absorb the substrate. Less removal of carbamazepine was observed during the presence of other organic matters. With increase of alkalinity the performance of AOP reduced. [84]
Ibuprofen with initial concentration 5-60 mg/L	Ultrapure water	P25 suspension	UV–Vis solarium lamps	3-9	NM	Study showed that pH~7 is favourable for the photocatalytic reaction. The activity of catalyst could be enhanced using a proper catalyst to the substrate ratio. It intermediates were identified, and it’s had a great impact on reaction.[86]
Sulfamethoxazole, diclofenac sodium, hydrochlorothiazide,4-acetamidoantipyrine, nicotine and ranitinide hydrochloride with initial concentration of 10mg/L	Milli-Q water	P25 suspension	150 W medium pressure mercury UV lamp, 320 nm	NM	First-order kinetics and for 4-acetamido-antipyrine it was zero order	After 6 hr irradiation time over 90% removal was possible. 20% of total organic carbon was removed but intermediates were not indicated here.[87]
Naproxen and carbamazepine with initial concentration of 60.1 and 125 mg/L respectively	Deionized water	P25 nanobelt suspension	100 W middle pressure mercury UV lamp, 365 nm	4-10	Pseudo first-order kinetics	TiO_2 nano particle was modified to nanobelt photo catalyst. Effect of adsorption on photocatalysis has also been studied. Addition of foreign substances to enhance the activity of nano particle also been experimented. Intermediates were not identified. [88]
Diclofenac	Deionized water	C- and C, N-codoped TiO_2 suspension	Artificial UV		Pseudo first-order kinetics	Up to 60% COD removed using modified nano particle. The anastase had better activity than the rutile phase. Complete mineralization was not possible using modified TiO_2.[89]
Carbamazepine and carbamazepine epoxide, acridine, and acridone with initial concentration of 10 μg/mL	MilliQ water	TiO_2 and ZnO nano particle suspension	Artificial solar illumination, Xenon lamp (1500 W lamp, 300-800 nm)	3-11	Pseudo first-order kinetics	In presence of ZnO nano particle the activity of TiO_2 nano particle was reduced. Lower pH was favourable for degradation when only TiO_2 was introduced but in case of ZnO lower and higher pH (3 and 11) was favourable condition. Higher ionic strength of reaction mixture was favoured the reaction rate in presence of TiO_2 only. Intermediates were detected. [90]

5-fluorouracil, 200 µg /L and Cyclo-phosphamide (27.6 mg/L)	MilliQ water	Aldrich-TiO_2, P25, and ZnO suspension	UV lamp, 8 W/254 nm	3-10	NM	In the comparative study it has been observed that P25 was the best photo catalyst and completely removal of was possible within 2 hr for 5-fluorouracil and for Cyclophosph-amide it was 4hr. Catalyst loading was optimised at 20mg/L. But the effect of initial substrate concentration was unsaid. By-products were identified.[91]
Chlorhexidine digluconate with initial concentration of 500 mg/L - 1500 mg/L	Deionized water	Aldrich-TiO_2, P25 suspension	UVA lamp, 10 W, 365nm	4-11	NM	About 70% chlorhexidine removal was possible. The effect of all parameters had been studied so far and optimization was done using ANFIS and RSM as well. Toxicological test was performed to confirm that by-products had no detrimental effects on the environment.[92, 93, 94]

†NM - Not mentioned.

3 Process parameters involve in photocatalytic degradation process

HPC is a surface phenomenon where, reaction occurs inside the active site of the catalyst in presence of UV irradiation. Like every chemical reaction, several parameters like catalyst loading, substrate concentration, pH of the medium, presence for other materials etc. affect the reaction rate during the photocatalytic degradation. Several research groups have highlighted those parameters and their influences on photocatalysis. In next subsequent sections, the adverse effects of process parameters on the photocatalytic degradation have been discussed.

3.1 Effect of initial substrate concentration

The initial concentration of target molecule is the primary constraint for photocatalytic reaction and the catalyst loading is dependent on it. In photocatalytic reaction substrate molecule adsorbed on the active surface of the catalyst, therefore degradation rate is significantly depends on the population of target molecule on the active surface. If the substrate concentration is higher, competition between targets molecules for attachment with catalyst surface become more pronounced and thus rate of degradation decreases with increase of initial substrate concentration. Many researchers studied the variation of rate with initial concentration of pharmaceutical wastes. Among them, Coleman et al.[30] reported that the degradation rate of 17β-oestradiol was linearly dependent on its initial substrate concentration. A slightly different observation noted by Hu et al.[46] that initially the rate of the reaction increased with increase of aqueous concentration of sulfonamides up to a certain value. According to them the initial increment was expected because of the substrate adsorption rate at the catalyst surface was higher at initial stage and after that the reaction rate was independent of initial substrate loading. After the initial stage of reaction no such active sites on TiO_2 surface available for further adsorption till completion of earlier reaction. At that time increment in substrate loading does not affect the reaction rate. Although Yang et al.[54] analyzed that the degradation rate of paracetamol was decreased due to the increase of its initial concentration. They explained that at higher concentration large number of substrate molecules occupied maximum number of active sites of the catalyst and thus caused decrement in available protons for oxidation process. After that Mendez-Arriaga et al.[53], Rizzo et al.[57], Hapeshi et al.[61], Achilleos et al.[62], Yanga et al.[63], Yang et al.[71], An et al.[72], Ho et al.[73], Chen and Chu[78], Mohammadi et al.[79], Das et al.[92] and Sarkar et al.[93] reported the same as Yang et al.[54] with their various target materials. Xekoukoulotakis et al.[74] observed that rate of degradation initially increased with increase of initial substrate concentration but up to a certain level, after that it decreased with increase of initial concentration. They gave similar type of explanation that had been already stated by Hu et al.[46]. Therefore, initial substrate concentration plays a crucial role in photocatalytic degradation and with increase of it the rate of degradation along with efficiency of the photocatalysis decreases.

3.2 Effect of catalyst loading

The rate of degradation of pharmaceutical wastes directly depends upon the catalyst loading, as the available active surface area of catalyst increases with its concentration and thus the surface reaction also enhances. In 2006, Calza et al.[38] reported that the efficiency of photocatalytic degradation was increased with TiO_2 concentration up to a certain level and after that, the situation was reversed due to scattering of the incident UV-irradiation occurred on TiO_2 surface. Thereafter, Hu et al.[46] studied that the degradation rate is not directly proportional to the catalyst loading always, and they explained that it happened due to decrease in the number of photon or increase of scattering of UV from the catalyst surface with increase of TiO_2 loading. Sakkas et al.[47] indentified same observation up to 600 mg/L TiO_2 concentration but after that particular value of concentration the rate of reaction was decreased due to shrinkage of active volume of active sites. In the same year, Abellan et al.[45] varied TiO_2 concentrations in a range of 0.0 to 2.0 g/L to degrade sulfamethoxazole, and their observation was as same as Hu et al. [46], but they explained the behaviour as a consequence of uneven competition between nano particles for light absorption at higher concentration of it. Moreover, increment of rate of degradation of paracetamol with the increase of the TiO_2 loading was mentioned by Yang et al.[54] up to 0.8 g/L, and it decreased beyond 5 g/L TiO_2 concentration due to decrease in light penetration through the active sites and Boroski et al.[58] similar type of statement was made from their experimental observation.[58]. The observation of Abellan et al.[45] and Yang et al.[54] on reaction rate behaviour and catalyst loading was alike as previously mentioned above for different target molecules. Though Yang et al.[54] did not mention any decrement in reaction rate at higher concentration of TiO_2, but it was remained constant. Another group of researchers, Mendez-Arriaga et al.[53] and Giraldo et al.[64], supported the statement made by Hu et al.[46]. Sometime screening effect of UV irradiation was responsible for the decrement in rate of photocatalysis for higher catalyst loading than threshold value of it[61, 65]. Though catalyst loading is expected to be directly proportional to substrate concentration, but the excess of catalyst makes an obstacle for light penetration on the active surface. Thus, a proper ratio of initial substrate and catalyst concentration should be maintained[62, 72]. However, Yanga et al.[63] and Ho et al.[73] did not consider the effect of excess catalyst loading as they observed that rate of reaction was increased with increase of TiO_2 loading. Accepting the findings of Hu et al.[46], Elmolla and Chaudhuri[65] explained the decrement of degradation rate at higher concentration of TiO_2 was due to agglomeration and sedimentation of TiO_2. Though rate increased with catalyst loading but Boroski et al.[58], Elmolla and Chaudhuri[65], Xekoukoulotakis et al.[74], Chen and Chu[78], Mohammadi et al.[79] and Nasuhoglu et al.[80] reported lower UV penetration through available active sites at higher concentration of TiO_2 was the vital cause for decrement in reaction rate, which was formerly mentioned by Yang et al.[54]. It refers that with increase of TiO_2 opacity of reaction solution increases and as a result UV irradiation is obstructed by the working solution and certainly some portion of UV irradiation should be absorbed by the working solution. Very recently Lin and Lin[91] reported that at higher concentration of TiO_2 (>20 mg/L) enhanced the scattering of the light meant reduce in light penetration through the active surface of the catalyst. Therefore, catalyst loading should be optimized for every photocatalytic degradation pharmaceutical waste so that, UV can penetrate through TiO_2 suspension and active sites gets necessary energy for activation.

3.3 Influences of various phases of TiO_2 nano particle

In the current scenario, various phases of TiO_2 nano particle are easily available such as Degussa (P25), Hombikat, anatase, rutile, etc. Many researchers have made comparative studies to identify the efficiency of various phase different types of TiO_2 for pharmaceutical wastewater treatment. A large number of studies [46, 33] showed that P25 was more effective than Hombikat TiO_2 as the latter contain only anatase phase and had higher adsorption capacity whereas P25 was a mixture of anatase & rutile phases and had a higher surface area. In the year of 2006, Rafqah et al.[39] made a comparative study during the degradation of triclosan to establish higher effectiveness of P25 than PC50 and PC500. According to them, P25 was the mixture of anatase and rutile where as others were pure anatase phase. Achilleos et al.[62] added new information about P25 and Hombicat UV100, according to them P25 showed higher degradation rate compared to other and they explained that the first one had slower electron-hole recombination rate, and the latter had faster interfacial electron transfer rate. Therefore, availability of electron and hole on P25 helped to increase the degradation rate. Xekoukoulotakis et al.[74] compared the activity of six different types of TiO_2, among them P25 showed the best result as the rate of recombination of hole and electron was slower than others and that explanation had been already indicated by Achilleos et al.[62]. So literatures are indicating that P25 is the best choice of catalyst for the photocatalytic degradation of pharmaceutical wastes and that type of TiO_2 have already been used by a large number of researcher.

3.4 Effect of pH of the solution matrix

Variation of pH means alternation in concentration of H^+ and OH^- ions in reaction mixture. The concentration of hydroxyl radical plays a vital role in photocatalytic degradation and that can be explained using equation 4 as $OH^{\bullet}$ is key species for oxidation. Thus, the increase of pH means increase of OH^- and it transforms to $OH^{\bullet}$ radicals as well. Therefore, the rate of oxidation improves further in presence of $OH^{\bullet}$ radicals. That principle is applicable, to some extent, but actual surface chemistry is more relevant to explain the effect of pH. As photocatalytic reaction is a surface phenomenon, the rate of degradation of any compound depends on the attachment rate of the substrate on the active surface of the catalyst. That attachment rate totally depends on the pH of the medium and can be explained with help of point of zero charges (pzc) of TiO_2 at pH 6.25. Thus, the TiO_2 surface is positively charged in acidic media, on the other hand; it is negatively charged under alkaline medium. If the substrate is negatively charged, acidic matrix is favourable for absorption where as for positively charged substrate shows better absorption in alkaline medium. The above explanation can also be described with the help of logarithmic acid dissociation constant (pK_a) of substrate. The acidic medium is favourable lower pK_a value, and it is opposite for higher pK_a of substrate. Therefore, the pH of the reaction medium is greatly influences the efficiency of photocatalysis. The chemical nature of the substrate also affects the reaction behaviour. Coleman et al.[21] observed the variation of rate of reaction within pH range of 1 to 12. They explained that with the increase of pH the formation of hydroxyl radical was increased and thus oxidation process was also enhanced up to pH 7, which quite was obvious. After that the rate decreased up to pH 10 due to huge formation of phenoxide ion from oestradiol made a competition with hydroxyl ion for absorption. But subsequently in the range of pH 10 to pH 12 the phenoxide ion was neutralized by unprotonated hydroxyl radical and formed neutral phenoxy radical which could react at TiO_2 surface. Due to neutralization of phenoxide ion reaction rate increased after pH 10. Moreover, Hu et al.[46], Sakkas et al.[47], Yang et al.[54], Chen and Chu[78] and Avisar et al.[84] cited that rate of photocatalytic reaction increased in the alkaline range of pH as at higher pH (> 7) the formation of OH^- was also enhanced, that caused the reduction of photo holes. Sakkas et al.[47] reported that at lower pH, the active surface area of photocatalyst was reduced due to agglomeration of TiO_2. However, Hu et al.[46] observed the degradation of sulfamethoxazole was not affected with variation of pH of the medium though removal of total organic content (TOC) was enhanced with the increase of pH. On the contrary, Rizzo et al.[57] did not observe any improvement in degradation kinetics of triclosan with an increase of pH since pKa value of substrate varied from 7.9 to 8.1 but rate decreased at acidic medium due to inhibition of hydroxyl radical. At the same time, a different observation was made by Giraldo et al.[64], where they stated that degradation of oxolinic acid was favored at pH>

7.5 but less than 11 as, at pH>11 the repulsion between oxolinic acid and catalyst surface increased. Moreover, Hapeshi et al.[61] stated that pH of the solution less than pK_a value of the substrates was the favourable but medium should be alkaline in nature. Beyond the pK_a value of pH caused the lower attraction between substrate and catalyst surface and as a result rate of reaction decreased. Recently, Yanga et al.[63], An et al.[72], Xekoukoulotakis et al.[74] and Chen and Chu[78] generalized the influence of pH on reaction rate that medium pH depended on pK_a value of substrate. According to their suggestion, acidic medium was favourable for lower pKa value of those substrates and alkaline medium was encouraging for reverse cases. During the degradation of amoxicillin, Elmolla and Chaudhuri[65] mentioned that at acidic pH both the substrate and catalyst surface positively charged, and hence surface repulsion was enhanced, on the other hand, in the alkaline mediums both surfaces carried negative charge and thus repulsive force was generated. Therefore, they reported that neutral pH was favourable than acidic pH but alkaline pH was accepted as the availability of OH radical was more which favoured the reaction as well as the target material was instable in higher pH. Moreover, Boroski et al.[58] found better degradation of pharmaceutical waste at acidic medium as negatively charged pollutants showed better absorption on TiO_2 surface at that particular condition. Therefore, acidic mediums favoured the above reaction. In general, the degradation depends on the pK_a value of reactants or the surface charge of the pollutants and pH of the media should be adjusted accordingly.

3.5 Effect of energy source

Like all other parameters, light intensity plays an important role on photocatalytic reaction. The band gap energy of 3.2 eV for TiO_2 nano particle is supplied from light energy of UV-irradiation or sunlight. Sometime, visible light fails to provide such amount of energy for photocatalysis. At the earlier stage in the field photocatalytic degradation of pharmaceutical waste Augugliaro et al.[35] achieved the degradation of lincomycin in solar photoreactor in presence of TiO_2 nano particle. Next year Munõz et al.[43] had tried same type of experiment and achieved successful removal of pharmaceutical wastes. Thereafter, as per available literature only another group of researcher[70] had tried to carry out photocatalysis experiment under sunlight. Though earlier researches[35, 43, 70] reached their target successfully using solar illumination but due to the uncertainty of solar radiation most of the researcher opted UV irradiation. In the year of 2005, Coleman et al.[31] studied the dependency of reaction rate on the light intensity. They found that the rate of degradation of 17β-oestradiol was proportional to the square root of UV intensity. Moreover, Abellan et al.[45] carried out the experiment under UV wavelength range of 240-310 nm to differentiate the effect of photocatalysis and photolysis. They found that photolysis had an impact upon the photocatalysis process. In the next subsequent year Yang et al.[54] performed photolysis of paracetamol in presence of UVC (254nm) irradiation but not UVA (365nm) as, paracetamol showed negligible absorbance above the wavelength of 350 nm and for the same reason; the rate of photocatalytic degradation was higher under UVC source. They also proposed that rate was approximately proportional to the square of light intensity. In the year of 2010 Elmolla and Chaudhuri[65] made a general comment that if the substrate absorbed certain wavelength of UV irradiation, it could not be degraded at that particular wave length, but it would be degraded at a higher range of UV irradiation. The effect of light intensity on the degradation process was studied by Ho et al.[73], and they mentioned that rate increased with light intensity up to a certain range. Consequently, light intensity and wavelength can be varied for different substrate, and it should be chosen properly to get effective degradation. Very recently, the current research group[92] have also analysed the dependency of photocatalytic degradation of chlorhexidine on UV intensity and it was observed that with increasing intensity the rate also increased up to 80μW/cm^2 but it decreased after that intensity. They[92] reported that it was happened due to the hole-electron recombination rate also increased at higher intensity therefore availability hole-electron for photo oxidation was reduced after certain range UV intensity. Therefore, the wave length and intensity of irradiation is target specific and those should be adjusted very rationally.

3.6 Effect of temperature variation

Heterogeneous photocatalysis in presence of TiO_2 nano particle is a combination of diffusion and reaction phenomenon. First the substrate molecules are adsorbed by means of surface diffusion on catalyst surface then it degraded inside the active pores of TiO_2. The change of temperature does not affect the reaction rate; it affects the rate of diffusion of substrate molecule on catalyst surface. Very few literatures are available where the dependency of photocatalytic reaction rate on temperature has been studied. This is because heterogeneous photocatalysis is less sensitive to the temperature throughout the system. Among them, Nakashima et al.[24], considering the rate of the reaction was dependent of substrate diffusion constant on TiO_2 surface, showed that reaction rate constant value increased with temperature as the substrate diffusion constant increased with temperature. Chatzitakis et al.[52] studied the temperature effect on photocatalytic degradation of chloramphenicol in a temperature range of 3 to 57°C. They observed that degradation rate increases up to 45°C and after that it decreased. They expected that it happened because after 45°C, dissolved O_2, which is one of the major parameters, was disappeared from the system. However, temperature is regarded as a minor parameter for photocatalytic reaction. Liang et al.[88] found that in the range of 4-60^{0}C the rate of reaction increased with increase of temperature and they tried to give their explanation with the help of activation energy though, they found that in that particular range of temperature the activation energy was constant. Therefore, they[88] told that with increase of temperature the rate of diffusion of substrate molecule on the catalyst surface increased and hence rate of photocatalysis. From the above discussion it may be written as ambient temperature is favourable condition for photocatalysis.

3.7 Factors influencing the performance of nano particle

The presence of foreign substances may enhance the activity of nano particle. Some works have already been published where different foreign materials were added to the process to enhance the performance of heterogeneous photocatalysis. In 2005, Coleman et al.[31] tried to enhance the performance of TiO_2 in presence of Pt and Ag. They reported that no such effect was observed during the degradation of the low concentrated organic pollutants in presence of Pt or Ag where as in presence of Pt, the degradation rate of high concentrated bisphenol A and resorcinol was increased, and thus they concluded that incorporation of metal ion was a substrate specific. Sometime the presence of peroxide could enhance the activity of nano particle, which had been investigated by Yu et al.[40]. According to them, an addition of a very small amount of H_2O_2 enhanced the rate of degradation of triclosan as a result less time was required for its removal. They explained that this happened as H_2O_2 was a better electron acceptor than O_2 in the present system. Although, Calza et al.[51] explained the effect of H_2O_2 in a manner that rate of formation of hydroxyl ion was enhanced thereby leading to the improvement of reaction rate using the following equations.

$$H_2O_2 + h\gamma \rightarrow 2OH^{\bullet} \quad (5)$$

$$H_2O_2 + O_2^{-} \rightarrow OH^{\bullet} + OH^{-} + O_2 \quad (6)$$

They also studied the additional effect of a small amount of ferrous (Fe^{2+}) ion along with a lower amount H_2O_2. As per their suggestion, it helped to produce hydroxyl radicals, although, the excess amount of Fe^{2+} reduced the performance of reaction due to formation of ferret (Fe^{3+}) ions. Chatzitakis et al.[52] mentioned the influence of H_2O_2 is quite similar to the reason described by Calza et al.[51]. They also illustrated that hydroxyl radical enhanced the formation of peroxy compound with TiO_2, which enhanced the reaction performance. Though increasing rate of reaction limited up to certain concentration of H_2O_2. Study of Hapeshi et al.[61], Achilleos et al.[62], Elmolla and Chaudhuri[65, 75] also supported the observation by Calza et al.[51] but higher concentration of peroxide reduced mineralization rate as it absorbed oxidizing agent and acted as electron and radical scavenger. Sometime KIO_3 enhanced the performance of photocatalysis[78] as it worked as a recombinant between hole and electron which, resulted in higher rate of $OH^{\bullet}$ generation. Very recently, Mohammadi et al.[79] tested the doping effect of Sn in TiO_2 matrix. They observed modifications in surface area, band gap energy and crystal structure. Higher surface area, uniform particle size distribution and lower band gap energy ensured higher rate of waste degradation. Sometime, 2-propanol and KI may work as $OH^{\bullet}$ radical scavenger. As $OH^{\bullet}$ radical works as main oxidising agent therefore, with introduction of 2-propanol in photocatalytic system the rate of reaction increases[71, 88, 91]. Therefore, it may be concluded that the introduction material which enhances $OH^{\bullet}$ radical concentration and Sn doping improve the performance of photocatalysis.

3.8 Influence of dissolved oxygen

Oxygen works as oxidizing agent, therefore, it plays a significant role in AOP. In 2007, Abellan et al.[45] made a successful attempt to identify the necessity of dissolved oxygen in photocatalytic reaction. They told that a sufficient amount of oxygen was required for oxidation process to produce hydroxyl radicals. In next year, Yang et al.[54] tested the effect of O_2 concentration, and their finding was quite similar to Abellan et al.[45]. They explained that H_2O_2 was generated during reaction with help of O_2. H_2O_2 played the major role in formation of hydroxyl radical and subsequently reduced the effective wavelength for photocatalysis. To ensure the effectiveness of dissolve O_2, Mendez-Arriaga et al.[53] observed the degradation behaviour of ibuprofen in excess supply of O_2 and ascertained a quite high degradation rate with reduced irradiation time. According to Xekoukoulotakis et al.[74], Nasuhoglu et al.[80] and Im et al.[83] presence of O_2 could reduce the possibility of recombination between generated electrons and holes, and the excess of hole could solely degrade waste molecule, it led to formation of hydroxyl radical, which enhanced the rate of degradation process. Thus, it is necessary to maintain desired O_2 concentration level in the photocatalytic system.

3.9 Influence of flow rate over continuous system

The maximum researchers worked at the degradation rate of pharmaceutical wastes in batch mode. Though batch study shows several disadvantages, i.e. a constant amount of liquid can be handled at a time, time consuming process, processes parameter cannot be altered during reaction, and in some cases it is not commercially viable. To alleviate that issues continuous mode can be a better alternative for downstream treatment. The flowing stream can be easily handled by continuous reacting system. The most important parameter of such a type of the system is retention time; need to be optimized depending on desired conversion. The retention time is a measure of how long a reactant particle retained inside a reactor. It is directly depended upon the flow rate through the system. Lower flow rate means higher retention time and higher rate of mineralization of pharmaceutical wastes. Ho et al.[73] was first implemented for degradation of trimethoprim, an antibiotic in such a mode of operation and adjusted the flow rate of the stream to achieve the maximum degradation of target drug for the continuous system.

4 Mode of application of nano particles

During the photocatalytic degradation, different modes of applications were observed by several groups of researchers, although it was observed that in most cases nano particle suspension was used during photocatalysis for pharmaceutical wastes degradation [22, 27, 32-47, 49-57, 59-76, 78-81, 83, 84, 86-94]. In suspension mode both nano particle and pharmaceutical compound are put together into the reactor and stirring is provided to keep the suspension stable under UV irradiation. It is very hard to recover nano particle from the suspension therefore TiO_2 is lost after reaction and which is the major limitation of that technique. Thus immobilization techniques have been adopted by several group of researcher to enhance the reusability of nano particle as well as to make the process more economic[21, 22, 24, 28, 26, 30, 31, 48, 77, 82]. Mainly two types of immobilization have been observed so far first one is the coating of nano particle on a substrate material and another one is entrapment of nano particle inside a porous structure. All modes of applications of nano particle have been show in the figure 2. To overcome limitations of suspension mode Coleman et al.[21] implemented the immobilization of TiO_2 on Ti-6Al-4V alloy and they got 98% removal of 17-β-oestradiol within 3.5 hr. In 2002, Tanizaki et al.[22] implemented the concept of photo bioreactor of high sensitivity where nano particle, TiO_2 was immobilized in porous quartz structure to increase the available surface area. Sometime, TiO_2 was used in immobilized condition inside the polytetrafluoroethylene mesh sheet[24]. Coleman et al.[53] used another type of photocatalytic reactor in batch mode where TiO_2 coated reactor surface was used. Doll and Frimmel[32] and Ziegmann and Frimmel[66] designed a pilot-scale setup of microfiltration unit to separate TiO_2 from the treated solution to enhance the reusability of nano particles. To fulfil the same purpose, Augugliaro et al.[35] used solar membrane photo reactor. In the next subsequent year of 2006, Molinari et al.[41] induced membrane technology to separate by products and TiO_2 after the photocatalytic reaction in a batch system to make the process cost effective. In 2007, Abellan et al.[45] applied tubular quartz reactor to carry out photocatalytic reaction and two parabolic mirrors were used to concentrate irradiated UV towards target solution but TiO_2 suspension was used during the degradation reaction. For the same purpose, Coleman et al.[48] developed '*sol-gel spiral reactor*' under both solar and UV irradiation where, immobilized as well as suspension of TiO_2 was used. Though UV radiated system showed the best performance. To enhance the performance of the system Mendez-Arriaga et al.[53] incorporated stirred tank reactor with integrated O_2 supply, temperature and pH indicator, thermostatic control bath, etc. All sorts of area exposed to the catalyst were covered with Teflon or made of glass to enhance the effectiveness of TiO_2. To treat wastewater from the pharmaceutical industries directly Ziemiańska et al.[67] followed conditioning, microfiltration and coagulation method before photocatalytic degradation to reduce the waste load from the solution matrix. Ziemiańska et al.[67] and Laera et al.[76] introduced membrane bioreactor (MBR) along with photocatalysis for wastewater treatment where they maintained a certain recycle ratio to achieve a sufficient amount of drug removal.

In 2011, a new technology was adopted by Hu et al.[77] to use nano particle for pharmaceutical wastewater treatment. They synthesized TiO_2 nanowaire membrane on titanium foil. This type of membrane showed more effective degradation than normal P25 and enhanced the reusability of TiO_2. The possible explanation was made by Hu et al.[77, 81] that the energy distribution over the nano wire membrane surface was better than others. Thus it pretended effective photocatalytic effect. Murphy et al.[82] compared the effectiveness of TiO_2 when it was employed as a suspension as well as in composite form, and they found higher degradation rate for a later case due to availability of high surface area. Moreover, composite could be reused as its activity was considerably available. Very recently, Avisar et al.[84] used "*sol-gel N-doped TiO_2*" which was deposited over microscope glass slides. They found it was more advantageous than powdered TiO_2 considering the fact of homogeneous mixing and scattering of light during reaction and the present technique enhanced the reusability of nano particles as well as made that process more economic. Therefore, reuse and enhancement of active surface area of TiO_2 are the important area of research and developments. Then only the photocatalysis can be implemented in wastewater treatment for commercial purpose.

Fig. 2 Different modes of application of TiO_2 nano particle: (a) Suspension mode; (b) Surface immobilization; (c) Entrapped in porous structure.

5 Kinetics involve in photocatalytic reaction

The photocatalytic degradation process is basically classified as heterogeneous catalytic reaction. It has been already discussed in the earlier sections that reaction rate varies significantly with different process parameters such as initial substrate concentration, catalyst loading, pH, dissolve oxygen, etc. The effects of those parameters on photocatalysis can be well described in terms of reaction rate constant. Therefore, it is very important to understand the reaction kinetics of photo catalytic degradation.

Some group of researchers [22-24, 27, 28, 30, 31, 36, 39, 41, 45, 48, 50, 53, 67, 73, 87] described the degradation kinetics described as first- order type, which was presented as,

$$-r_{photo} = \frac{dC_p}{dt} = k_{photo} C_p \qquad (7)$$

r_{photo} and k_{photo} represent first-order reaction rate and rate constant respectively and C_p indicates the concentration of pharmaceutical waste at any time 't'. TiO_2 being a catalyst in the reaction mixture, its concentration assumed constant. Thus, rate of photocatalytic reaction can be considered as pseudo-first order reaction. That can be expressed using following rate equation 8 and equation 9. Several authors [33, 34, 54, 64- 66, 70, 77, 81, 88-90] found good agreement between theoretical pseudo first order kinetic model and experimental observation and had well described the degradation kinetics with help of it.

$$-r'_{photo} = \frac{dC_p}{dt} = k'_{photo}\ C_p \qquad (8)$$

Where, r'_{photo} , and k'_{photo} were pseudo fist order reaction rate and rate constant respectively. The above equation can be written as

$$\ln\left(C_p^0 \big/ C_p \right) = k'_{phot}\, t \qquad (9)$$

Initial concentration of pharmaceutical waste was represented as C^0_p. The rate constant values were calculated from the slope of the plot of $\ln\left(C_p^0 \big/ C_p \right)$ vs. time. However, in recent years, heterogeneous catalytic reaction kinetics has been interpreted using Langmuir–Hinshelwood (L-H) kinetics[55], and since photocatalysis belongs to the similar reaction category, hence in many cases, the photocatalytic degradations were described by the L-H kinetics' model[29, 38, 46, 49, 51, 52, 56, 59, 63, 69, 71, 72, 74, 78, 79, 83]. According to L-H model, the reaction took place inside the catalyst pore surface where the substrate material was adsorbed through the catalyst pores. The rate represented as,

$$-r''_{photo} = \frac{dC_p}{dt} = \frac{k''_{photo} kC_p}{1 + kC_p} \qquad (10)$$

where, k''_{photo}, r''_{photo} and k were L-H kinetic rate constant, rate of the reaction and adsorption co-efficient respectively. Mentioned researchers found that the experimental result had a good agreement with the L-H kinetic model. If the substrate concentration is very low (kC_p<<1), equation 10 turned into the pseudo first order kinetic rate law, and it could be represented through equation 11.

$$-r''_{photo} = \frac{dC_p}{dt} = k''_{photo} kC_p \qquad (11)$$

where, k''_{photo} represented into pseudo first order kinetic rate constant and that could be calculated using the plot of $\ln\left(C_p^0 \big/ C_p \right)$ vs. time.

Therefore, three different types of kinetic model can be adopted during the photocatalytic degradation of pharmaceutical wastewater under UV-irradiation depending on the experimental observation.

6 Conclusions

Considering the impacts of pharmaceutical wastes on aquatic environment, it is high time to take necessary attention against the alarming threat involved in discharged pharmaceutical waste. The present study has tried to make a portrait on the importance of photocatalytic degradation process and consequences of the process variables. Some of the major observations are likely to be mentioned here. Among all other treatment methodology, heterogeneous photocatalysis has already been established as a future trend for treatment of pharmaceutical waste and by this process maximum removal of drug components can be achieved with production of no secondary pollutants. Several process parameters are involved in AOP using nano particle, which are needed to be optimized. To make the process more economic as well as more acceptable to researchers and industries, recycle and reuse nano particle should be investigated. Moreover, optimization of the process parameters and kinetic study are required for better understanding of the degradation process. In most of the cases, researchers have used batch process and very few literatures are available regarding the continuous oxidation process though later one can enhance the performance of the system. Therefore, the continuous process makes the process more acceptable for large scale wastewater treatment.

In most of the reviewed literature, though the immense potential of the photocatalytic degradation approach is well accepted but still needs further improvements for better exploitation in pharmaceutical industries. Above all, recycle and reuse of photo catalyst in a continuous wastewater treatment process is the main area which is needed to be developed in future for large scale implementation of heterogeneous photocatalysis. Moreover, the impact of photo catalyst on environment has not been studied yet according to the available literatures and that will be another area of exploration. The present article has highlighted advantages as well as limitation of heterogeneous photocatalysis of pharmaceutical wastes and thus, this study may be a value addition in further development in photocatalysis. As a consequence, heterogeneous photocatalysis with some necessary modification can be used as potential alternative than the traditional tedious process for municipal as well as industrial pharmaceutical wastewater treatment.

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[a] *Department of Chemical Engineering, Jadavpur University, Kolkata, India. Fax: 9133 2414 6203; Tel: 91 98364 02118; E-mail: c.bhatta@gmail.com, cbhattacharyya@chemical.jdvu.ac.in*
[b] *School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Korea.*

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