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Degradation of Selected Analgesicsin Aqueous Solutions by TiO_2 Photocatalysis: A Review

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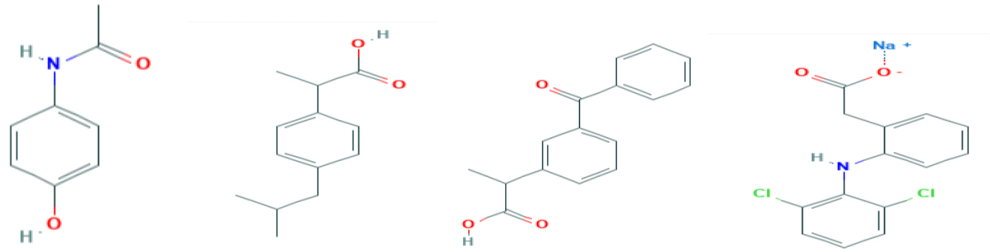
ABSTRACT: This review aims to explain the effect of using TiO_2 as a catalyst in the photodegradation process of analgesic compound waste that can cause water and environmental toxicity. Data sources were collected from Google Scholar, Elsevier, Pubmed, and all available literature from 2000-2020. The results show that TiO_2 can help degradation by increasing the surface-active side so that the number of photons absorbed on the catalyst surface is higher and produces more reactive species such as hydroxyl radicals, which accelerate the degradation process of analgesic compounds.The results of degradation will increase if TiO_2 is combined with metals such as Cu, Sn, Fe, or other atoms such as C and N. The degradation of analgesic compounds is observed by UV-Vis spectrophotometry, HPLC, and TOC.

Keywords: Photodegradation, Photocatalysis, TiO_2, analgesic

I. INTRODUCTION

Analgesic is one of the waste drugs detected in waters, lakes, and groundwater,increasing water toxicity and developing resistance to pathological bacteria and endocrine disorders. [1][2]To overcome this effect, photodegradation can be carried out, namely a process of decomposing compounds (usually organic compounds) with photon energy. This process generally requires a semiconductor material, which will cause charge separation or photoexcitation. TiO_2 is a heterogeneous photocatalyst that is the most common and efficient used to destroy pollutants in aqueous solutions or organic pollutants.This semiconductor catalyst has a bandgap value about 3.2 eV, which can only be activated in higher energies such as ultraviolet irradiation. Besides, TiO_2 is photochemical stable, non-toxic, and low cost.[3][4][5][6]At the absorption of Ultra Violet (UV) light, which corresponds to the bandgap, TiO_2 will form a photogeneration charge carrier (holes and electrons). The resulting holes in the valence band will diffuse to the surface of TiO_2 and react with adsorbed water molecules to form hydroxyl radicals (• OH), which will oxidize the organic molecules nearby.Meanwhile, the conduction band's electrons participate in the reduction process, reacting with oxygen molecules in the air to produce superoxide radical anions (O_2•-). [7][8]TiO_2 surface can minimize electron pair recombination, which will accelerate photocatalysis, [9] where the rate of degradation of drugs by UV/TiO_2 depends on the type and amount of TiO_2 load, pharmaceutical concentration, presence of acceptors, and pH of oxidation.[10][11]

This review focuses on the analgesic compound's photodegradation: paracetamol, ibuprofen, ketoprofen, and diclofenac sodiumusing TiO_2 as a catalyst. The analysis was carried out using UV-Vis Spectrophotometry and High-Performance Liquid Chromatography (HPLC), and complete mineralization to CO_2 and water was analyzed using Total Organic Carbon (TOC).



(a) (b) (c) (d)

Figure 1. The Chemical structure of (a) Paracetamol[12](b) Ibuprofen[13](c) Ketoprofen[14](d) Diclofenac Sodium[15]

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II. DATA COLLECTION

In compiling this review article, the technique used was the literature study method. Also, in making this review article, several keywords, such as "photocatalysis," "titanium dioxide," "photodegradation," "analgesic," were used to conduct online research. Research for the main references used in this review article conducted was through trusted websites such as Google Scholar, Elsevier, Pubmed, and all available literature from 2000-2020.

Analysis Method

UV-Vis Spectrophotometry

Table 1. Measurement of the photodegradation of analgesic compounds using UV-Vis Spectrophotometry

No.	Sample	Concentration	λ Max	Result & Discussion	Reference
1.	Paracetamol	25 g. dm^{-3}	246 nm	The degradation efficiency was 35% with Visible light irradiation and 93% with UV light irradiation after 2 hours with the addition of 0.9 g TiO_2 catalyst.	[16]
2.	Paracetamol	4 mg/L	257 nm	Degradation with 20 mg of TiO_2 co-doped CN catalyst increased to 69.31% in UV light and 34.29% in Vis light.	[17]
3.	Ketoprofen	10 mg/L	260 nm	Degradation increased by 51.04% at UV-A and 91.08% for 120 minutes at UV-C with the addition of 15 mg of TiO_2 catalyst	[9]
4.	Ibuprofen	10 mg/L	220 nm	Degradation was achieved at 65% with the addition of 500 mg / L TiO_2 after 120 minutes of UVA irradiation.	[18]
5.	Na. Diclofenac	5 mg/L dan 25 mg/L	276 nm	Degradation reached 94% using a nanotubular TiO_2-PES membrane (polyethersulfone) after 240 minutes of UV irradiation. After 4 days, the degradation increased by 42% for a concentration of 5 mg/L and 28% for a concentration of 25 mg/L.	[19]

The photocatalytic degradation of paracetamol was evaluated through a Shimadzu UV-2600 spectrophotometer at a wavelength of 246 nm, where the paracetamol concentration was 25 g. dm^{-3} with the addition of 0.9 g of TiO_2 catalyst. Irradiation is carried out for a maximum of 6 hours with 1 hour in the dark to achieve the adsorption-desorption equilibrium using UV (368

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nm) and Vis (446 nm) lamps. Irradiation carried out for 2 hours showed that the photodegradation occurred in 35% for Vis light and 93% with UV irradiation.[16]

The efficiency of paracetamol degradation carried out by the photolysis method under UV light (365 nm), visible-light (Philips LED 13 watts 1400 lux) and sunlight, showed that 4 mg /L paracetamol degradation increased 46.2-67.87% with the addition of 10-20 mg of TiO_2 catalyst coded CN. After 120 minutes of UV light irradiation, the degradation increased to 69.31% with the addition of 20 mg of catalyst, while in Vis light irradiation, the degradation increased from 16.96% to 34.29%.Photolysis with direct sunlight for 30-120 minutes without a catalyst only degraded 5.77-12.27%, while with the addition of 20 mg TiO_2 catalyst coded CN with the same conditions, the degradation increased significantly to 70.39%.[17]This shows that the rate of paracetamol degradation increases linearly with increasing catalyst content. The increase in catalyst mass will accelerate the decay of paracetamol and the higher surfaceactive site in photolysis so that the number of photons absorbed on the surface is higher and produces more reactive species such as hydroxyl radicals.[20]

Degradation is influenced by the amount of catalyst, duration of radiation (irradiation), and pH of the solution.[21]Ketoprofen with an optimum concentration of 10 mg/L was conditioned by photolysis of UV-A and UV-C rays, which showed degradation of 22.75% and 61.12%, respectively. With the addition of 15 mg of TiO_2 catalyst, the degradation of ketoprofen on UV-A was 32.99% and 82.49% at UV-C. The highest degradation of pure ketoprofen was 51.04% at UV-A with irradiation for 180 minutes and 91.08% at UV-C for 120 minutes. The results show that photolysis with UV-C light (254 nm) is greater than UV-A light (366 nm) because the UV-C wavelength is shorter than UV-A, which causes the energy is greater, the greater energy will accelerate the degradation process. ketoprofen.[9]

Heterogeneous photocatalysis depends on the initial concentration of the organic substrate [22]. Tests carried out on ibuprofen with initial concentrations of 5, 10, and 20 mg/L after 120 minutes showed decreased conversions of 80%, 70%, and 65%, respectively, with the addition of 250 mg/L TiO_2 catalyst with UV irradiation. The change in concentration was observed using Jasco V-530 UV-Vis spectrophotometry with a wavelength of 220 nm, which shows that catalyst loading affects ibuprofen's degradation.Ibuprofen was observed at an initial concentration of 10 mg/L with TiO_2 as the catalyst, which had been irradiated by UV-A, which showed degradation of 65% after 120 minutes with the addition of TiO_2 catalyst as much as 500 mg/L accompanied by removal of 46% DOC. [18]

The degradation test of diclofenac sodium was carried out photo catalytically using a nanotubular TiO2-PES membrane (polyethersulfone). This degradation was observed by spectrometry with initial concentrations of 5 mg/L and 25 mg/L, where 94% of the diclofenac solution (5 mg/L) was degraded after 240 minutes. Continuous degradation (cross-flow) showed that after 4 days, the degradation increased by 42% for a concentration of 5 mg/L and 28% for 25 mg / L. After 18 days of photocatalysis, the diclofenac solution (5 mg/L) was degraded 100%.[19]This indicates that the rate of degradation increases with a lower initial concentration.[23]

HPLC (High-Performance Liquid Chromatography)

Table 2. Measurement of photodegradation of analgesic compounds using HPLC

No.	Sample	Column	Mobile Phase	Detector	Chromatographic conditions	% Degradation	Reference
1.	Ibuprofen (25 $mg.L^{-1}$)	An eclipse XDB-C18 (3 µm particle size, 4.6 x 150 mm)	40% of 1% formic acid solution/60% acetonitrile.	Diode array detector (DAD) Wavelength =230 nm	The flow rate is 1.0 mL.minutes-1 injection volume 20 µL	60%	[24]
2.	Ibuprofen (20 mg/L)	10 cm a column with Mediterranea Sea18 as	Acetonitrile/acetic acid with ratio 70/30	Not listed	wavelength 254 nm and the isocratic retention time for the sample	99%	[25]

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		packing material			was 8.8 min.		
3.	Paracetamol (96 $mg.L^{-1}$)	the column was an Altima HPC18 of 5µ with 4.6 mm ID and 150 mm length	The mobile phase was a 30/70% (v/v) a mixture of methanol/phosphate buffer adjusted to pH 2.6	Detector UV-Vis 116A	At 0.8 x 10^{-3} dm^3min^{-1} flow rate. tRparacetamol (3.2 min). Temperature control LC-22°C.	80%	[26]
4.	Paracetamol (100 $\mu mol.L^{-1}$)	Kromasil 100-5C18 column (4.6 x 250 mm, 5µm)	CH_3OH/ H_2O mixture (30/70) v/v	UV absorbance detection (waters 481 detector)	Injection volume : 20µL wavelength 243 nm	95%	[27]
5.	Paracetamol (100 mg/L)	C-8 Column	0.7 L DI water, 0.3 L methanol, 6.6 g disodium hydrogen phosphate, and 2.8 g sodium dihydrogen phosphate, 1.15 tetrabutylammonium hydroxide (TBAOH).	UV detector	The flow rate of the mobile phase was 1.5 ml/min. The column temperature was 35 °C.	100%	[8]
6.	Paracetamol (50 mg/L)	Agilent column ZOBRAX Eclipse XDB-C18 (4.6 mm x 150 mm, 5 µm)	25% methanol and 75% miniQ water	UV absorbance detection at 245 nm.	flow rate = 1.0 mL / min Injection Volume: 10 µL	100%	[28]

Analysis of ibuprofen using HPLC (1200 series, Agilent Technologies, Santa Clara, USA) equipped with Eclipse XDB-C18 (3 µm particle size, 4.6 x 150 mm column) (Phenomenex, Torrance, USA) with diode array detector (DAD) at a wavelength of 230 nm. The mobile phase consisted of 40% formic acid (1%)/ 60% acetonitrile solution. The flow rate is 1.0 $mL.minute^{-1}$and the injection volume is 20 µL. Testing on ibuprofen showed the peak retention time was 4.1 minutes.The photocatalytic ibuprofen (25 $mg.L^{-1}$) with the addition of TiO_2 powder (0.1 - 0.5 $g.L^{-1}$) showed degradation with a 21.8% decrease in the ibuprofen concentration from the initial concentration after 5 minutes of irradiation, and the concentration reduced to 60 % after 30 minutes followed by the appearance of new peaks. In contrast, complete elimination of ibuprofen was obtained after 270 minutes. The combined results showed that within 80 minutes of simulated solar irradiation, degraded ibuprofen was higher than 87%.[24]

The degradation rate analysis of ibuprofen was carried out using a Shimadzu Prominence LC-20A HPLC equipped with a 10 cm column with the Mediterranean Sea 18 axles packing material with a mobile phase of acetonitrile/acetic acid (70/30) at a wavelength of 254 nm and the isocratic retention time for the sample was 8.8 minutes with the optimum TiO_2 (1.5 g/L) which shows about 90% degradation of ibuprofen occurred within 15 minutes under pure UV/ TiO_2 conditions.Irradiation using UV light and the addition of a catalyst for 15 minutes causes ibuprofen to degrade up to 99%. This is better than irradiation using Solar (Quartz) and Solar (Borosilicate) with the addition of TiO_2, which only degrades 44% and 37%, respectively,because TiO_2 is less active under visible light than pure UV light.[25]

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Tests were observed on paracetamol (96 $mg.L^{-1}$) with TiO_2 made with modified Carbon Vitreous Reticulated electrodes using HPLC CC5, Solvent Delivery System PM80 equipped with the column was an Altima HPC18 of 5 µ with 4.6 mm ID and 150 mm length with UV-VIS detector 116A and temperature control LC-22C. The mobile phase is a 30/70% (v/v) mixture of methanol/phosphate buffer adjusted to pH 2.6 at 0.8 x $10^{-3}dm^{-3}.min^{-1}$ flow rate with the concentration of phosphate buffer was $1x10^{-3}$ M. The results of degradation showed that the photocatalytic degradation of paracetamol (96 mg L^{-1}) with TiO_2/UV at pH 5 reached 80%, the concentration dropped to 19.2 $mg.L^{-1}$ after 6 hours.Using a $CuO/TiO_2/Al_2O_3$/UV catalyst, the concentration became 38.6 $mg.L^{-1,}$ which indicated that the degradation occurred at 60%. In contrast with the photolysis method only using UV light, the concentration decreased only <20% to 76.8 $mg.L^{-1}$ after 6 hours.[26]

According to Zhang Xu, the degradation of paracetamol will increase with the increase in TiO_2 catalyst. Paracetamol was degraded 36% using $0.25g.L^{-1}TiO_2$, whereas increasing the amount of catalyst to 1 $g.L^{-1}$, about 95% of paracetamol was degraded after 100 minutes of irradiation using 250 W metal halide lamps (λ ≥365nm).[27]The same thing has also been obtained in DesaleAmolkumar's research with variations in the addition of Degussa P-25 TiO_2 from 1-4 g/L. After 180 minutes, 2 g/L TiO_2 loading was better than the other catalyst concentrations. Paracetamol with a concentration of 50 mg/L, 100 mg/L, and 200 mg/L with the addition of a catalyst was observed to show that paracetamol (50 mg/L) was degraded entirely at 90 minutes, and degradation was 100%, 80%, and 50% at 90 minutes. Concentrations of 100, 200, and 500 mg/L after 240 minutes of irradiation of the batch process with an annular cylindrical reactor using 80 W UV light (λ max = 365nm).[8]

Paracetamol degradation (50 mg/L) was observed using the photolysis method using a modified Cu-doped TiO_2 sphere (Cu-TS) catalyst using a Rayonet RPR-100 photoreactor equipped with 16 Visible-light lamps. Concentration analysis was performed using HPLC (Agilent, ZOBRAX Eclipse XBD-C18 column 4.6 mm × 150 mm, 5 µm) with a flow rate of 1.0 mL/minute with a 245 nm absorbance UV detector and a mobile phase of 25% methanol and 75% miniQ water with an injection volume of 10 µL. The results showed that about 100% paracetamol was degraded by 0.1 Cu-TS after 3 hours of visible light irradiation. This is influenced by Cu doping activity on the photocatalytic Cu-TS. Activity increased with increasing Cu doping to 0.1%.[28]

Total Organic Carbon (TOC)

Table 3. Measurement of Total Carbon (TOC) Levels

No.	Sample	Concentration	% Mineralization	Reference
1.	Paracetamol	50 ppm	72%	[29]
2.	Paracetamol	4,0 mM	60%	[211
3.	Paracetamol	50 mg/L	66%	[30]
4.	Ibuprofen	5 mg/L	50%	[31]
5.	Na. Diclofenac	20 mg/L	90%	[32]

TOC analysis of the paracetamol solution was performed using a Shimadzu carbon analyzer model 5000A. Paracetamol solution (50 ppm) irradiated with near UV light (λ max = 365 nm) with a bubble of oxygen obtained 16.0 ± 4% paracetamol was oxidized after 5 hours. However, after 5 hours, the conversion increased to 96% if the air-saturated paracetamol solution was irradiated with UV light with the addition of TiO_2 catalyst without the presence of an oxygen bubble.As the amount of oxygen available to capture electrons decreases, the rate of oxidation decreases over time, so that only 59% of the original reactants are mineralized. 72% mineralization will be achieved during 4 hours of reaction when paracetamol oxidation is carried out in the presence of UV light, TiO_2 catalyst (2 g/L), and a stable oxygen flow (100 mL/min).[29]

During photolysis and photocatalytic oxidation of paracetamol 4.0 mM, observations of the level of mineralization were made under 3 conditions, namely UVC photooxidation (254 nm) without TiO_2 (initial pH = 5.3), UVA photooxidation (365 nm) with TiO_2 = 0.4 g/L (initial pH 5,8), and UVC photocatalytic oxidation with TiO_2 (initial pH = 5.6, TiO2 catalyst = 0.4 g / L). The results showed that in the presence of TiO_2 and UVC catalysts, paracetamol mineralized about 60% in 300 minutes (up to 85% in 450 minutes) compared to other conditions, using only UV-C light showed low and negligible mineralization

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while under UV-A conditions only showed slight changes after 300 minutes.[21]

Total Carbon (TOC) analysis was measured using an NDIR detector, by predefining the calibration curve in the range 0-200 mg/L using a standard solution of potassium hydrogen phthalate. Paracetamol (50 mg/L) with a TiO_2 catalyst (0.1 g/L) and an oxygen flow rate of 100 mL/minute by first filtering using a 0.2 µm cellulose acetate membrane filter to remove the photocatalyst.After 60 minutes of light irradiation, the rate of mineralization increased with increasing TiO_2 in the TiO_2/ Fe_2O_3 core-shell, consistent with the rate of paracetamol photodegradation. However, the rate of paracetamol degradation occurs much faster than mineralization. Meanwhile, about 99% of paracetamol degraded after 60 minutes of irradiation. When 50% TiO_2 / Fe_2O_3 was used as a photocatalyst, the TOC removal was 66%.[30]

The elimination test for ibuprofen with a concentration of 5 mg/L was carried out using TOC equipment from analytic Jena, Multi N/C 2100S. The results showed that with the addition of 20 mg/L of TiO_2 catalyst, the TOC value decreased by 50% after 30 minutes of irradiation of a 125 W Hg vapor lamp and maintained until 60 minutes. However, complete mineralization was not achieved even though the ibuprofen was completely degraded.[31]

The total organic carbon test for diclofenac sodium was carried out using the TOC-VCSH-Shimadzu TOC analyzer with a photocatalytic mixture of TiO_2 -SnO_2 catalyst with a certain ratio made by the hydrothermal method. The results showed that the addition of a small amount of Sn could increase the catalytic activity of TiO_2.The TiO_2 -SnO_2 catalyst (20: 1) ratio is the most effective compared to pure TiO_2. This is indicated by the TOC value, which reaches 90% with an initial concentration of 20 mg/L and a catalyst loading of 0.8 g/L with a pH of 5 after UV irradiation for 5 hours.[32]

III. CONCLUSION

Overall, TiO_2, which is used as a catalyst can accelerate the degradation process of drug compounds by increasing the higher surfaceactive sites so that the number of photons absorbed on the catalyst surface is higher and produces more reactive species such as hydroxyl radicals. TiO_2 will work better on UV rays. The degradation and mineralization results will be higher if TiO_2 is combined with metals such as Cu, Sn, Fe, or C and N atoms, with degradation values reaching 100%.

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