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Degradation of Ciprofloxacin Antibiotic Waste Using TiO_2 Nanotube with Addition of Anthocyanin Dye-Sensitizer In Photocatalysis Process: Review

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Abstract

Antibiotics Ciprofloxacin (CIP)'s waste from healthcare facilities can contaminate the environment. One of the potential methods for treating CIP waste, that is cheap, effective, and environmentally friendly is the photocatalytic method using TiO_2. The performance of the TiO_2 photocatalyst can be improved by modifying the catalyst morphology into nanotube arrays and coating them with anthocyanin,as natural sensitizers. The morphology of nanotubes can be obtained using the anodization method. Natural dyes that are often used as sensitizers for TiO_2 are anthocyanins. Anthocyanins, purple to red colors, can be extracted from parts of plants such as mangosteen peel (*Garcinia mangostana*), rosella (*Hibiscus sabdariffa*), and blue pea (*Clitoria ternatea*). The maceration, reflux, and soxhletation processes can be used to obtain anthocyanins.The objective of this study is to critically evaluate the potential of anthocyanins as sensitizers in the photodegradation of organic waste. It has been demonstrated that the breakdown of organic waste can increase by 85% to 95% when dye-sensitizers are used. This makes the potential for using anthocyanins from specific plants to accelerate CIP breakdown quite significant. This paper review demonstrates that TiO_2 photocatalysts with anthocyanin dye sensitizer coating have tremendous potential for the remediation of liquid waste, particularly antibiotic waste such as ciprofloxacin.

Keywords: Ciprofloxacin, Photocatalyst, TiO_2, Dye-sensitizer, Anodization

1. Introduction

The number of pharmaceutical industries in Indonesia has increased every year. This is in line with the increasing number of hospitals in Indonesia. Hospital activities produce a large amount of waste. Banten Province has a total of 112 hospitals that produce a total medical solid waste of 24,439 tons and a total medical liquid waste of 5,526 m^3 (Redaksi, 2021). One of the hospital wastes is an antibiotic-containing waste. Ciprofloxacin (CIP) is one antibiotic type that belongs to the fluoroquinolone group and is effective in treating various types of infections such as infections of the skin and urinary tract (Zeng et al., 2019). The CIP waste can pollute aquatic ecosystems, even in low concentrations, and can kill aquatic flora and fauna species (Zeng et al., 2019; Kurniawan and Mariadi, 2019). Therefore, to avoid these environmental negative impacts, the CIP compounds need to be removed from the waters.

Several technologies have been conducted to reduce the contamination of CIP waste in the environments, including the ozonation process (Zuhaela et al., 2020), nanofiltration method (Das et al., 2020), reverse osmosis (Wei et al., 2021), absorption (Samadi et al., 2019), and ultrafiltration membrane (Bhattacharya et al., 2019).

However, these technologies have several disadvantages, including high cost, secondary pollution that can be easily formed, high energy consumption, low efficiency, and suitability only for certain wastes (Du, J et al., 2019). One of the waste treatment methods, that tends to be new and attracts a lot of researcher's attention, is the photocatalytic method. The advantages of the photocatalytic method are environmentally friendly, energy-efficient, and economical because it only uses semiconductor-based catalysts and photon energy (Wildan et al., 2016). The semiconductor most often used for photocatalysis is TiO_2. TiO_2 can degrade organic matter well because it has a higher surface area (Prastiwi et al., 2017). However, the TiO_2 photocatalyst has drawbacks such as having a wide band gap energy and producing easy electron-hole recombination.

Increasing the surface area of TiO_2 can be conducted through modification of its morphology into nanotubes (Slamet et al., 2018; Pelawi et al., 2020), nanorods (Santhi et al., 2020; Shahvaranfard et al., 2020), or nanowires (Al-Hajji et al., 2020; Rahmatet al., 2019). The morphology of TiO_2 nanotubes results in better photocatalytic effectiveness than the others (Kustiningsih, I., et al., 2015). The TiO_2 nanotubes can be produced through some methods which are the hydrothermal method, the template method, and the anodization method (Gunlazuardi et al., 2017; Pelawi et al., 2020). However, the hydrothermal method requires operating conditions of high pressure and temperature. Furthermore, the template method needs a relatively long processing time and it is difficult to obtain a uniform size (Quang et al., 2018). On the other hand, the anodization method has advantages because it results in nanotube scales that can be controlled, it results in nanotubes that are neatly arranged, it is feasible for wide applications, and it produces a photocatalyst surface area with very significant performance (Slamet et al., 2018). The anodization process is influenced by several factors including the anodization potential, the concentration of the electrolyte solution (water content), pH, anodization time, fluorine ion concentration (F^-), type of stirring, and temperature (Gunlazuardi et al., 2017). However, from these factors, the best condition of each factor still needs to be revealed.

In addition through morphology modification, increasing the effectiveness of TiO_2 photocatalysis can be conducted through the dye-sensitizer addition. The dye-sensitizer functions to absorb visible light so that electrons can be excited (Pujiastuti et al., 2021; Hasanah et al., 2021). The TiO_2 semiconductors with the dye-sensitizer have a higher response to the visible light than that without the dye-sensitizer. There are two kinds of dye-sensitizers, namely synthetic dyes and natural dyes. However, synthetic dyes can harm the environment due to their chemical hazard properties. Therefore, the use of natural dyes is the right choice because it has no negative impact on the environment, it is abundant availability, it can be produced through a simpler synthesis process, and it has lower prices. One kind of natural dye is anthocyanin which is obtained from leaves, flowers, and fruit of plants and is in the color range of purple to red color. Anthocyanin has carbonyl and hydroxyl groups that will bind to the TiO_2 semiconductor surfaces, where electrons will be excited from the dye-sensitizer (anthocyanin molecule) to the conduction band in TiO_2 nanotubes (Pujiastuti et al., 2021; Diaz-Angulo et al., 2020). The primary objective of this review paper was to determine how effective anthocyanins are as natural dye sensitizers for increasing the photoactivity of TiO_2 against the degradation of ciprofloxacin antibiotic waste.

2. Ciprofloxacin (CIP)

Ciprofloxacin (CIP) is the most commonly used broad-spectrum fluoroquinolone antibiotic with the mechanism of action of inhibiting DNA gyrase (topoisomerase II) and topoisomerase IV found in bacteria (Zeng et al., 2019). The inhibition of enzymes involved in DNA replication, recombination, and repair results in the inhibition of bacterial cell growth (Bhattacharya et al., 2019).

The CIP is applied in treating the infections caused by gram-negative bacteria such as E. coli, *Proteus mirabilis*, Shigella sp., Klibsiella sp., Enterobacter, Salmonella sp., Chlamydia sp., as well as certain gram-positive bacteria. The mechanism of action of this antibiotic is by inhibiting the formation of DNA supercoils that bind to the enzyme of DNA gyrase subunit A which is an important enzyme in DNA replication and repair. Bacterial resistance to this antibiotic can occur due to mutations in the gene encoding the polypeptide subunit A of the DNA gyrase enzyme (Mondal et al., 2018).

CIP antibiotic compounds that are in the environment for a certain time and continuously can cause some pathogenic microorganisms to become persistent and survive in the environment because they are difficult to decompose naturally. Micropollutants in very small concentrations in drinking water have a detrimental impact on human health because they are chronic (Kurniawan and Mariadi, 2019).

Several treatment methods have been conducted to eliminate contamination of CIP waste from the environment, which are biological, physical, and chemical methods (Table 1). Treatment using ultrafiltration membranes, nanofiltration membranes, and reverse osmosis methods requires high installation, investment, and operating costs. The biological method has drawbacks, namely the long retention time and the difficulties in removing the sludge (Hollman et al., 2020). The photocatalysis method can be an efficient way to remove CIP waste in water because it can degrade CIP into CO_2 and H_2O molecules so that it will not harm the environment and can use visible light energy from the sun (Hu, K et al., 2020).

Table 1. Treatment of Ciprofloxacin (CIP) waste

Methods		Results	References
Biological	Anaerobic	The anaerobic process in treating the Ciprofloxacin with a concentration of 4.7 mg/L obtains a Ciprofloxacin removal value of 50-76% at optimal conditions of 120 days	Zhou et al., 2021; Do et al., 2019; Carneiro et al., 2019
Physical	Nanofiltration	The nanofiltration membrane method to remove Ciprofloxacin at optimal conditions of a processing time of 60 minutes, a pH range of 6-7.5, and a pressure of 6 bar results in a Ciprofloxacin removal value of 60-76%.	Das et al., 2020; Cristóvão et al., 2020; Sun et al., 2011
	Ultrafiltration	The ultrafiltration membrane method to remove Ciprofloxacin at optimal conditions of a processing time of 60 minutes, a pH of 11, and a pressure of 2 bar can remove 90-99% of Ciprofloxacin with a concentration of 500 μgL^{-1}	Palacio et al., 2020; Bhattacharya et al., 2019
	Reverse osmosis	The reverse osmosis process to remove Ciprofloxacin at optimal conditions of a processing time of 24 hours and a temperature of 26ºC can remove 90-99% of Ciprofloxacin with a concentration of 500 μgL^{-1}	Song et al., 2020; Alonso et al., 2018
	Adsorption	The adsorption process to remove Ciprofloxacin at optimal conditions of a processing time of 24 hours and a pH range of 5-7 can remove 90-99% of Ciprofloxacin with a concentration of 80 mol/L.	Ji et al., 2021; Kumari et al., 2020; Avci et al., 2020
Chemical	Advanced oxidation	The advanced oxidation process to remove Ciprofloxacin at optimal conditions of a processing time of 120 minutes and a pH range of 6-8 can remove 95-99% of Ciprofloxacin.	Milh et al., 2021; Wang and Zhuan., 2020; Mondal et al., 2018
	Photocatalysis	The photocatalytic process to remove Ciprofloxacin using a catalyst at optimal conditions of a processing time of 60 minutes and a pH of 8-11 can remove 90-99% of Ciprofloxacin.	Li et al., 2020; Suwannaruanga et al., 2020; Zeng et al., 2019
	Electrocoagulation	The electrocoagulation process to remove Ciprofloxacin with a concentration of 30 mgL^{-1} using electrodes at optimal conditions of a distance between the electrodes of 1.5 cm, a pH range of 4-7, a processing time of 60 minutes can remove 80-90% of Ciprofloxacin.	Mohammed et al., 2021; Malakootian and Ahmadian., 2019
	Chemical oxidation	The chemical oxidation process to remove Ciprofloxacin at optimal conditions of a processing time of 60 minutes can remove 97-99% of Ciprofloxacin.	Alamgholiloo et al., 2021; Cuprys et al., 2020
	Ion exchange	The ion exchange process to remove Ciprofloxacin at optimal conditions of a processing time of 60 minutes can remove 91% of Ciprofloxacin.	Zhou et al., 2021; Staudt et al., 2020

3. Photocatalysis Mechanism

Photocatalysis can be interpreted as a chemical process involving light and a solid catalyst which will later involve electron-hole pairs (e^- and h^+) (Samadi et al., 2019). The photocatalysis method requires light and a catalyst to speed up chemical changes. With this semiconductor material, when exposed to ultraviolet light having energy greater than the bandgap energy, it will form pairs of electron (e^-) and hole that can reduce and oxidize compounds (Ramchiary, 2020). The photocatalytic mechanism is shown in Figure 1.

From the Figure 1, the electrons move from the valence band to the conduction band in the photocatalyst when subjected to photon energy. When photocatalyst is irradiated with photons, electrons will be activated and jump from the valence band to the conduction band, causing the formation of hole (positive charge) in the valence band interacting with H_2O to form OH radicals which are strong oxidizing agents so that they will degrade organic compounds, while electron in the conduction band (negative charge) is useful for reducing inorganic compounds (Fujishima dan honda., 1972).

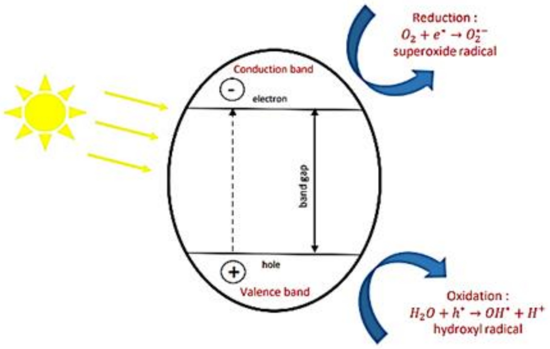

Figure 1. Photocatalysis Mechanism

$$\text{Semiconductor} + \text{hv} \rightarrow e_{CB}^- + h_{vb}^+ \qquad (1)$$

Several reactions that can take place in the electron-hole pairs (Afrozi., 2010) are:

1. Recombination of some pairs in particles (*volume recombination*).
2. Recombination of electron-hole pairs on the surface (surface recombination) or in bulk particles within a few nanoseconds (energy is lost as heat). The reaction of recombination of electron-hole pairs can be written below:

$$\text{Semiconductor}\left(e_{CB}^- + h_{vb}^+\right) \rightarrow \text{Semiconductor} + \text{heat}$$
(2)

3. The holes in the valence band will oxidize the substrate (D) resulting in hydroxyl radicals of D^+. Meanwhile, the electrons in the conduction band will reduce the substrate (A) or solvent on the particle surface once they reach the surface, resulting in radical ions of A^-. Those reactions are written in the following equations:

$$\text{hv} + \text{semiconductor} \rightarrow e^- + h^+ \qquad (3)$$
$$\text{A}\left(\text{ads}\right) + e^- \rightarrow A^-(\text{ads}) \qquad (4)$$
$$\text{D}\left(\text{ads}\right) + h^+ \rightarrow D^+(\text{ads}) \qquad (5)$$

The following are some reactions involving the radical ions (A^- and D^+) that may occur:

a. Radical ions of A^- and D^+ react with other radical ions or adsorbates which are that species adsorbed on the surface).
b. Radical ions of A^- and D^+ recombine via reverse electron transfer to result in an excited state of one of the reactants or release heat (Afrozi., 2010).

4. Titanium dioxide (TiO_2)

TiO_2 is a semiconductor that is widely used as a photocatalyst. TiO_2 is a white, rust-resistant, and non-toxic compound. TiO_2 has several advantages compared to other metal oxides, namely photoreactivity, chemical and biological inert, non-toxic, anti-corrosion, and the ability to be used repeatedly without losing catalytic activity (Muflikhun et al., 2019). Microscopically, TiO_2 has two main forms, namely crystalline and amorphous TiO_2.

Like other amorphous compounds, amorphous TiO_2 does not have a regular atomic arrangement so the material does not have regularity in conduction and valence bands, but amorphous TiO_2 is known to have the ability to degrade pollutants in a short time. Meanwhile, the crystalline TiO_2 structure strongly influences the surface chemistry and photo activity (Macyk, et al., 2010).

TiO_2 has three phases including rutile, brookite, and anatase. By comparing the anatase phase of TiO_2 with the rutile and brookite phases, Halme (2002) found that the anatase phase can offer a greater photon flux. This can be caused by that the anatase phase has a large capacity for photoactivity.

The anatase structure has a greater surface so it has a greater capacity for reduction. In addition, the surface of the anatase structure can absorb a lot of water to react with holes compared to rutile (Liu et al., 2009).

Table 2. Type of Morphology of Titanium Dioxide (TiO_2)

Type	Methods	References
Nanowires	TiO_2 nanowires are flat and well shaped with high crystallinity and a large surface area. TiO_2 nanowires are synthesized by sonication for 1 hour followed by hydrothermal treatment for 12 hours. It has 500 nm in length and 50 nm in diameter.	Al-Hajji et al., 2020; Rahmat et al., 2019
Nanorods	TiO_2 nanorods are synthesized by hydrothermal method to form TiO_2 anatase. The average crystal size increases with increasing the pH. It has a diameter structure of 70-100 nm.	Shahvaranfard et al., 2020; Kang et al., 2008
Nanotubes	It is synthesized through the anodization method. Using SEM analysis, on the TiO_2 surface, there are pores in the form of a tube structure with a tube diameter of 10-40 nm and an average diameter of 166 nm. The template method produces TiO_2 pore sizes between 4 and 250 nm and film thicknesses between 0.1 and 300 µm. The hydrothermal technique uses a single-step reaction in an aqueous medium at high pressure (P > 100 kPa) and low temperature to synthesize materials.	Pelawi et al., 2020; Slamet et al., 2018; Montakhab et al., 2020
Nanoparticles	The hydrothermal method is used to form TiO_2 nanoparticles. The surface of the materials can be formed depending on the length of processing time during the calcination process. For a calcination time of 2 hours, it results in the size of the particle diameter ranging from 25-65 nm, which is dominated by 26 nm nanoparticles.	Mamaghani et al., 2020; Astuti and Ningsi, 2017

4.1. Morphology of TiO_2

TiO_2 is one of the effective photocatalysts for the treatment of organic or inorganic polluted water. When exposed to ultraviolet radiation, organic matter will be degraded and mineralized into CO_2 and water (Abdullah et al., 2017). To increase the performance of TiO_2 as a photocatalyst, a lot of things have been done, namely morphological modification into the form of nanotubes (Slamet et al., 2018; Pelawi et al., 2020), nanorods (Shahvaranfard et al., 2020; Kang et al., 2008), and nanowires (Kustiningsih, I., et al., 2014, Al-Hajji et al., 2020; Rahmat et al., 2019). Type of morphology of Titanium dioxide can be seen at Table 2. Nanotubes are the best morphology because of the larger surface area than the other morphologies thus have better photocatalyst effectiveness (Kustiningsih, I., et. Al., 2019).

Generally, the three main processes used to synthesize TiO_2 nanotubes are anodization, template, and hydrothermal methods. The hydrothermal method and the template method have drawbacks because operating conditions of pressure and temperature are not uniform and the synthesis time is relatively long. Meanwhile, the anodization process has the advantage because the scale of the resulting nanotubes can be controlled, it produces nanotubes that are neatly arranged and feasible for wide applications, and it produces a photocatalyst surface area with very significant performance (Mor et al., 2006). The electrochemical anodization in forming the titanium dioxide (TiO_2) nanotubes from titanium plates can be affected by various parameters i.e. anodization time, voltages, and electrolyte concentrations. Anode and cathode in the electrochemical anodization process are Pt plates and titanium plates, respectively. Ammonium fluoride (NH_4F), water, and glycerol or ethylene glycol are used as electrolyte solutions. The process can result in nanotubes with a wider size when using thick electrolyte solutions compared to that when using aqueous solutions. However, agitation is necessary to speed up mass transfer across the nanotube surface and achieve the speed of nanotube formation (Macak et al., 2006).

4.2. Ciprofloxacin Degradation Photocatalytic Method

Many researchers have studied the degradation of ciprofloxacin waste through the photocatalytic method using TiO_2 photocatalyst, which can be observed in Table 3. A titanium dioxide (TiO_2) was chosen as a photocatalyst for CIP waste treatment because of its ability to generate electron-hole pairs on its surface which will react with hydroxyl and oxide ions in pollutant compounds and convert them into O_2 and H_2 (Slamet et al., 2012). In the photocatalytic process, the TiO_2 semiconductor functions as a photocatalyst because there is an empty energy region called the energy band gap, which is located between the conduction band and valence band boundaries. When a TiO_2 semiconductor is irradiated by a photon with an energy equal to or greater than its band gap energy, electrons in the valence band will be excited to the conduction band (e_{CB}-) and cause holes in the valence band (h_{vB}+) (Huang, et al. 2013). This method is effective because of the less time required to degrade pollutants, the low risk of new toxicants being produced, and the availability of abundant materials (Kustiningsih et al., 2020).

5. Dye Sensitizer

Synthetic and natural dyes are the two categories of dye sensitizers. Rhodamine B, erythrosine, eosin, and cyanin are examples of synthetic dyes (Chowdhury et al., 2011; Ghosh et al., 2020). Natural dyes including chlorophyll, anthocyanin, nasunin, and carotenoids, which are derived from plant fruits, seeds, flowers, stems, leaves, and roots, are used to create natural colors (Zyoud et al., 2018; Ghosh et al., 2020; Pujiastuti et al., 2020).

The absorption of visible light in electrons that are attracted from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) of the dye causes the mechanism from dye photosensitization to pollutant degradation.

Table 3. Ciprofloxacin (CIP) Waste Degradation Photocatalytic Method Using TiO_2 Photocatalyst

Catalyst	Characteristics	Results	Ref.
TiO_2 nanotube arrays (TiO_2 NTAs) with Ag_3PO_4 nanoparticles	Composition: anatase Surface of BET: 4.7 m^2g^{-1} Band gap: < 3.25 eV	Concentration of CIP: 0.01 gL^{-1} Source of light: 300 W Xenon lamp, visible light, 200 $mWcm^{-2}$ Photodegradation: 85.3% Processing time: 60 minutes	Du, J et al., 2019
TiO_2/Graphene oxide	Composition: anatase Size of crystalline: 12.5 nm (XRD) Surface of BET: 91.25 m^2g^{-1} Band gap: 2.47 eV	Concentration of CIP: 0.005 gL^{-1} Source of light: visible light Photodegradation: 96.73% Processing time: 60 minutes	Khan et al., 2019
TiO_2 nanorod/g-C_3N_4 nanosheet (TiO_2 nanorod-CN)	Composition: anatase Band gap: 2.95 eV	Concentration of CIP: 15 $molL^{-1}$ pH: 6.3 Source of light: simulated sunlight irradiation, 500 W Xenon lamp Photodegradation: 93.4% Processing time: 60 minutes	Hu, K et al., 2020
Black $Ti^{3+}/N^{-}TiO_2$ P25 (b-N-TiO_2)	Particle sizes: < 100 nm (FE-SEM) Composition: anatase Surface of BET: 100 m^2g^{-1} Band gap: 2.0 eV	Concentration of CIP: 0.5 mgL^{-1} pH: 6.7 Source of light: 5 W visible LED lamp, 550 nm Photodegradation: 100% Processing time: 70 minutes	Sarafraz et al., 2020
3D tripyramid TiO_2 architectures	Particle size: 10 nm (TEM) Composition: anatase Surface of BET: 84 m^2g^{-1} Band gap: 3.2 eV	Concentration of CIP: 32.6 M Source of light: UV-vis light Photodegradation: 90% Processing time: 60 minutes	Li, Y et al., 2020
N–TiO_2	Particle size: length of 180 nm and width of 50 nm (FIB/FESEM) Composition: anatase Surface of BET: 42.70 m^2g^{-1} Band gap: 3.17 eV	Concentration of CIP: 20 ppm pH: 5.5 Source of light: three 20 W UV-A lamps 365 nm, 0.493 $mWcm^{-2}$ Photodegradation: 94.29% Processing time: 420 minutes	Suwannaruang et al., 2019
Cu-TiO_2	Particle size: 10 nm Cu (TEM), 200–400 nm Cu (SEM) Composition: anatase Surface of BET: 170.15 m^2g^{-1} Band gap: 3.0 eV	Concentration of CIP: 0.08 gL^{-1} Source of light: 500W Xenon lamp (Simulation of sunlight) Photodegradation: 97% Processing time: 4 hours	Gan, Y et al., 2019
$TiOF_2$/TiO_2 nanosheets	Composition: anatase Size of crystalline: 26.2 nm (XRD) Surface of BET: 119 m^2g^{-1} Band gap: 3.285 eV	Concentration of CIP: 0.02 gL^{-1} Source of light: 300W Xenon lamp (UV+visible) Photodegradation: 95.3% Processing time: 90 minutes	Liu, Z et al., 2019

The excited dye molecule becomes cationic radicals when the excited dye molecule donates electrons to the TiO_2 conduction band. The valence band of TiO_2 is unaffected, and the surface of TiO_2 solely serves as an electron acceptor to transfer electrons from the dye-sensitizer to the substrate.

The LUMO of the dye molecule must be more negative than the TiO_2 conduction band in this process. When the electrons are injected, they go straight to the surface of titania, where they are captured by molecules of oxygen, producing superoxide radicals (•O_2) and hydrogen peroxide radicals (•OH). These reactive species can also generate disproportionate amounts of hydroxyl radicals. Visible light is absorbed by the dye-sensitizer substance, which causes electrons to be activated. When compared to the photocatalytic process without dye-sensitizer addition, the process with dye-sensitizer addition results in a higher amount of pollutant degradation (Pelaez et al., 2012; Watanabe., 2017; Diaz-Angulo et al., 2020).

To optimize the performance of TiO_2 as a semiconductor in the photocatalysis process, it is possible to use a dye-sensitizer that affects the light spectrum and can be absorbed on the semiconductor surface. The ability of the dye-sensitizer to adhere to the semiconductor surface can reduce the band gap, which leads to the utilization of visible and infrared radiation more efficiently (Diaz-Angulo et al., 2020).

6. Anthocyanins

Anthocyanins are pigments that can be collected from natural sources through extraction. It belongs to the group of flavonoid compounds. It causes the color red to blue in leaves, fruits, and flowers (Ghosh et al., 2020). The other plant components, such as stems, tubers, and roots, can also be extracted to collect the anthocyanins (Patrocinio et al., 2009; Rajan et al., 2019). In addition to a flavylium cation core structure, anthocyanins contain methoxyl, hydroxyl, and carboxyl groups. Natural anthocyanins always contain one or more sugar components, such as β-D-Glucose, β-D-Galactose, and α-L-Rhamnose (Calogero et al., 2008; Pinto, 2015).

Anthocyanins, that absorps light in wavenumber range 400 – 700 nm, are potentially used as natural dye-sensitizers, due to their abundance, low cost, and non-harmful to the environment. The carbonyl hydroxyl group contained in anthocyanins can be attached to the TiO_2 semiconductor surface. The electrons are excited in the dye-sensitizer (anthocyanins), furthermore move to the conduction band in the TiO_2 semiconductor (Hao et al., 2020; Zyoud et al., 2018; Atli et al., 2019).

The hydroxyl group (OH) contained in anthocyanins can maintain a hydrophilic catalyst surface. As a result, the organic waste molecules in the water are brought closer to the catalyst surface. Simultaneously, it can decrease the surface tension between the organic waste and the catalyst surface (Zyoud et al., 2018). The kinds of anthocyanins contained in mangosteen peel are cyanidin-3-sophoroside and cyanidin-3-glucoside which contribute to coloring the peels of the mangosteen. (Qosim et al., 2007; Chaovanalikit et al., 2012). The conduction band in the semiconductor (for example for TiO_2, -4 to -4.3 eV) has to be lower than the LUMO level of the sensitizer. Meanwhile, the HOMO level of the sensitizer has to be lower than the semiconductor redox potential (for example, TiO_2 has a redox potential range of -4.6 to -5 eV). E (LUMO) and E (HOMO) levels of the anthocyanin dye from mangosteen peel are -2.27 eV and -4.81 eV, respectively. Both levels meet the criteria of being able to efficiently transfer electrons to the conduction band in the TiO_2 semiconductor when illuminated by visible light. (Ismail et al., 2018; Ghosh et al., 2020).

Reflux, maceration, and soxhletation are some extraction techniques to extract important compounds from dry plant tissue powder using a solvent with a certain level of polarity (Jalali et al., 2021; Patni et al., 2020). The maceration technique is conducted by immersing the samples in the solvent with occasional agitation.

Table 4. Types of Plant Anthocyanin Pigments

Type of plants	Pigment	Methods	References
Mangosteen peel (Garcinia Mangostana)	Anthocyanin	Maceration	Pujiastuti et al., 2021; Ghosh et al., 2020; Jalaludin et al., 2020.
Colombian Caribbean Species (Syzygium Cumini)	Anthocyanin	Reflux	Surana et al., 2020; Diaz et al., 2018
Red Cabbage, Onion	Anthocyanin	Maceration	Jalali et al., 2021; Arafa et al., 2021; Mejica et al., 2020
Rosella (Hibiscus Sabdariffa), blue beans (Clitoria Ternatea)	Anthocyanin	Soxhletation	Patni et al., 2020; Fatimah et al., 2020

Commonly, the immersion process is complete after 24 hours. After that, the new solvent is added to replace the old solvent. The maceration technique can be also operated with continuous agitation, which is called the kinetic maceration process.

The superiorities of the maceration technique are that (1) it works well for heat-resistant compounds (which can be damaged by heat), and (2) it uses equipment that is easy to use, affordable, and accessible. On the other hand, this technique has several disadvantages which are that it needs long processing times, it needs a large solvent volume, and it is suitable for compounds with high solubility at room temperature only (Sarker et al., 2006). Furthermore, the reflux technique is conducted under a temperature of the boiling point of the solvent used, for a certain amount of time and solvent using a reverse cooler (condenser). Commonly, three to five repetitions of the process are carried out in the first raffinate. This technique can be utilized for samples having coarse textures and being resistant to direct heating. However, this technique has a disadvantage which is that it requires a large solvent volume (Irawan 2010). Moreover, the soxhletation technique is conducted under continuous high-temperature operation. Comprehensively, the reflux technique needs a shorter processing time than the maceration technique and it needs a less solvent volume than soxhletation technique (Surana et al., 2020).

Photocatalysis is an efficient, economical, and environmentally beneficial method for Ciprofloxacin degradation. As a result of morphological engineering into nanotubes and the addition of pigment sensitizers, TiO_2 photocatalysis can be made more effective and sensitive to visible light. Anthocyanins, one of the natural dye sensitizers that have the potential to be used, can be extracted from fruits peel .

7. Conclusion

In this review, the basic principles of dye-sensitization to TiO_2 have been discussed and CIP waste can be treated using a variety of biological, physical, and chemical waste treatment techniques. The photocatalysis approach is the one with the greatest potential for processing CIP. The photocatalysis has the advantages of being low cost, highly effective, and environmentally friendly. To improve the performance of the TiO_2 photocatalyst, morphological engineering is used to create nanotubes, which are then coated with an anthocyanin natural sanitizer. The anodization process allows for the morphological engineering of TiO_2. A dye-sensitizer can increase the effectiveness of TiO_2 photocatalyst. Anthocyanin as one of natural sensitizers is more preferable than synthetic dyes. The addition of dye sensitizer causes the photocatalyst of TiO_2 more responsive to visible light. Therefore, by employing an anodization method to change the TiO_2 photocatalyst's shape into nanotubes and coating them with organic anthocyanin sensitizers, it is possible to minimize the energy band gap so that it can degradation CIP waste more effectively.

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