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Recent Development and Application of TiO_2 Nanotubes Photocatalytic Activity for Degradation Synthetic Dyes – A Review

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Abstract

Synthetic dyes waste from textile industries, produce of the problematic pollutants in wastewater. TiO_2 based photocatalysis are materials that exhibit excellent absorption behavior for organic compounds in wastewater due it properties including nontoxicity, high photocatalysis degradation ability, and chemical stabilities. However, several challenges exist regarding TiO_2 nanotubes pure applications for dyes degradation such as poor affinity, high band gap energy, and difficulty of recovery and easy to recombination so it would decrease effectiveness of the photocatalysis process. Therefore, more design and optimization testing need to be conducted on the treatment conditions in order to reach higher removal efficiencies with lower costs. The modified physical properties by adding metal dopant, nonmetal, and sensitizer significantly enhanced photocatalysis activity. These parameters, which affect photocatalysis activity on degrade dyes waste pollutants, are discussed in the current review. As a result, the photocatalysis becomes more expected, and encourages to further research development.

Keywords: Degradation, dyes, Photocatalytic, synthetic, TiO_2

1. Introduction

Waste processing is a critical technology for both human life and the environment. Liquid waste is considered a problem, especially waste from the textile industry. The textile industry wastewater contains organic and inorganic materials with a high concentration in every process unit (Kustiningsih et al.,2020). Many textile industries use synthetic dyes because synthetic dyes have advantages such as being more economical, has many variations of colors, and being durable (Wildan et al., 2018). Organic compounds in water will reduce dissolved oxygen levels for aquatic organisms because this oxygen is used as an oxidizer for organic compounds (Widyo et al, 2018).

Synthetic dyes are categorized as azo dyes. It has high toxicity, easily absorbed into the skin, and can be carcinogenic (Da et al., 2015). Various synthetic dyes are available, such as methyl orange, rhodamine B, remadzol red, and methylene blue. About 60%-70% of the dyes used in textile dyeing are synthetic dyes of the azo group (Bethi et al., 2016). Azo dyes are widely used in dyeing fabrics, especially for made of cellulose, rayon, and wool fibers. Azo dyes are difficult to degrade because it will be environmental pollution. And then, dye pollutants have a more serious environmental impact because it were contain mutagenic harmful chemicals and contained more metal components, such as Cu, Ni, Cr, High, and Co (Haryono et al., 2018).

Various conventional wastewater treatment options are proposed, such as biological (Pavithra et al., 2019), chemical oxidation (Hartanto et al., 2019), adsorption methods (Thahir et al., 2019), and membrane filtration (Kiswanto.,2019). However, this method has some weaknesses, such as pollutants that are not always feasible and effective. Table 1 shows a list of weaknesses and strengths of different methods. The biological measures implemented by the bacterial strain are referred to as biodegradation methods (Sari et al., 2019).

Waste treatment using microorganisms is in demand by industrialists and environmental practitioners because it is easy and inexpensive to operate and invest. In additionally, waste treatment using microorganisms has high resistance to various types of pollutants in the waste, but the drawback is that it requires a long adaptation time (Chen et al., 2020). Chemical oxidation processes are used to reduce contaminants from various types of wastewater (Hsu et al., 2013). Chemical oxidation has several disadvantages, such as the consumption of chemicals are high, the pH needs to be controlled, produces much sludge, and it can cause the secondary pollution problem (Sanford et al., 2019).

Membrane filtration is another alternative for the removal of wastewater (Mózo, 2017). The separation mechanism depends on the size of the particle, its solubility, and effective action.

It has the advantages of being simple, efficient, and quick to vanish even in high contaminants (Seifhosseini et al., 2018), but membrane membranes are easily brittle and the operating costs are expensive the process is expensive (Wildan et al., 2018).

Table 1. The limitation and endurance of each specific treatment for wastewater.

Methods	Weakness	Strength	Ref
Biological treatment	1. The procedure is difficult to control. 2. Unable to remove the high concentration of waste. It has no effect on the quantity of chemical energy demand.	1. Low cost 2. High performance for decoloration dye waste	(Sarayu et al.,2012)
Chemical oxidation	1. Chemical supply is high 2. pH control is required 3. Make a lot of sludge	1. Capable of energy conservation 2. This simple method and compact 3. Connectivity to the material is sensible.	(Devi et al., 2016)
Membrane filtration	1. Requires high maintenance costs 2. Does not apply to wastewaters with a high concentration.	1. Effective and fast handling 2. Environment friendly 3. A fast method of dye removal	(Ghazanfari et al., 2017)
Hydrothermal treatment	1. Requires a high temperature and pressure 2. The operating costs are expensive because it requires much energy	1. The waste decolorization process is incredibly successful 2. It produces no additional pollution.	(Zhang et al.,2016)
Conventional photocatalysis	1. The recovery and renewal of materials are difficult. 2. It is possible for recombination to occur. 1. It is only active in the presence of UV light.	1. Low cost of production, significant energy savings 2. Environmentally critical 3. Adjustment of the catalyst loading would be simple	(Guo et al., 2019)

As mentioned previously, additional treatment of sludge methods is still not economical and unable to treat textile wastewater because dyes used in the textile industry are biopersistent. Each outflow of this inefficient wastewater treatment has serious environmental consequences. The water pollution concerns are caused by a lack of biodegradation. Photocatalysis can be used to change the potential solution in established methods for wastewater processes. To enhance photocatalyst performance, modification uses different doping materials applied to TiO_2 nanoparticles (Kustiningsih et al., 2019). Incorporating the methodology developed into the conventional treatment plan is the best way to improve the treatment process's efficiency. Therefore, the photocatalyst has high performance in the removal of organic compounds.

TiO_2 is a semiconductor material widely used to degrade organic waste (Slamet et al. 2018).TiO_2 material has many advantages such as nontoxic, more economical, non-corrosive, and more stable compared to other materials (Shayegans et al., 2018). Then, extensive studies were conducted to improve the performance of TiO_2 photocatalyst, so it would be effective in degrading synthetic dyestuffs compounds in wastewater.

2. Ti0$_2$ Photocatalyst

Photocatalysis is a combination process of photochemical processes and catalysts, which is a chemical synthesis process involving light as a catalyst and a trigger as an accelerator of the transformation process. Semiconductors can function as photocatalysts due to the existence of an empty energy region called the energy band (Eg), it remains of the conduction band edge and the valence band, then when enabled by photons via higher energy than Eg, it strengthens the valence band to a conduction band (eCB^-) and gives a substantial hole (h^+) inside the valence band (hvB^+) (Ge et al., 2016).

Titanium dioxide (TiO_2) was observed in 1972 through photolysis processes. It has many functions, such as photocatalytic pollution elimination, air separation, sensor systems, inorganic agents, and self-functioning substances (Yoo et al., 2018). TiO_2 photocatalyst has a good ability to interact with the visible region. The TiO_2 photocatalyst attached to the metal will act as a photoanode to prevent corrosion of the metal. This protection system is called photocathode protection or commonly known as cathode protection. In the photocathode system, activation of electrons from the valence band to the TiO_2 conduction band occurs when a metal is coated with TiO_2 and exposed to ultraviolet light (Hu et al., 2016).

Furthermore, the excited electrons will enter the connected metal and cause a shift in the potential of the protected metal to be more negative than in the oxide form. The total electrons on the metal surface cause the metal to be protected and protected from oxidation or anode dissolution events (Kustiningsih et al., 2015). Even so, the prevention of metal corrosion or cathode protection can be achieved (Wahab et al., 2015).

TiO_2 has different categories of crystal structures, such as anatase (tetragonal), brookite (orthohombic), and rutile (tetragonal). Based on these three crystal structures, anatase and rutile have the same structure, namely, tetragonal (Panigrahi et al., 2017). According to thermodynamic review, the crystal structure of anatase is more stable than rutile. The crystal structure of anatase is at low temperatures and it has 3.2 eV bandgap energy (380 nm), whereas rutile crystals are stable at high temperatures and have bandgap energy of 3.0 eV (415 nm), while brookite crystals are difficult to observe because they are unstable (Tian et al., 2018).

The anatase phase of TiO_2 semiconductor shows the highest photocatalytic activity to its energetic separation capability between the conduction and valence bands exposed to UV radiation (Jang et al., 2017). TiO_2 semiconductor receives an absorption spectrum from UV light in the ultraviolet spectrum, enabling light absorption and reactivity at the molecular level (Nasirian et al., 2018). To improve its performance as a photocatalyst, TiO_2 is changing the catalyst's size to a nanosize. To improve the visible light active photocatalyst appearance of TiO_2, chemical treatment must support semiconductor morphology.

2.1. The Synthesis of Photocatalyst Methods

Many studies have been optimized TiO_2 performance as a photocatalyst by changing the catalyst to nanostructures. Nanoparticles TiO_2 have been used in photocatalysis for many years (Sun et al., 2018). In the development of photocatalyst technology, researchers have developed many semiconductor morphologies for TiO_2 nanomaterials such as nanowires (Kustiningsih I et al., 2018), nanotubes (Tian et al., 2018), and nanofibers (Yin & Jia, 2015).

TiO_2 nanowires have been synthesized in significant quantities recently. The formation of TiO_2 nanowires from layered titanate particles involves three steps, such as the removal of the layer $Na_2Ti_3O_7$, formation of nanosheets, and the formation of nanowires. Electrophoretic deposition of TiO_2 colloidal suspensions with a template followed by template removal can be used to fabricate highly ordered TiO_2 nanowires. Additionally, solvothermal, physical vapor deposition and electrodeposition methods for preparing TiO_2 nanowires have been reported (Safajou et al., 2017).

The effect of the relative nanowire ratio on the efficiency of the photocatalyst was discussed elaborately. While nanowires counted for less than 20% of the composites, the internal surface of the composite is equivalent to that of a pure nanoparticle film (Wu et al.,2012). The composite cells containing 5% and 20% nanowires showed higher activity than pure nanoparticle cells (Maheswari et al.,2015). Those other results indicated that carefully evaluating the nanowire composites has benefit from the particle size of nanoparticles combined and the extended electron light absorption of nanowires. A nanowire is a nanostructure with a diameter of approximately between 9 and 10 nm (Sun et al., 2018). The relatively homogenous hydrolysis of metal alkoxide and the subsequent oxidation with sodium hydroxide made an interesting method for preparing TiO_2 nanofibers.

Nanofibers are a type of nanoscale material in nanotechnology. Nanofibers TiO_2 can form using hydrothermal (Wu et al., 2018) and electrospinning processes (Ismaya et al., 2017). Electrospinning is a process of producing TiO_2 nanofibers. The parameter process such as calcination temperature, applied voltage, and syringes collector distance. The final phase of TiO_2 was identified by calcination at a temperature of 500 °C (Kim et al.,2019). Their dimensions range between 1 and 200 nm. It is constructed using metals or semiconductors materials. Aspect ratios (width divided by length) are common in both 3-5 nm (Khan et al.,2017). Direct chemical synthesis is needed to produce nanofibers. Integration of binding acts as a structure control agent and forms strong bonds with various aspects of nanofibers.

TiO_2 nanotubes are attracted interest and intensive studies due to their activity of the high specific surface area, ion-changeable, and photocatalytic ability. TiO_2 nanotubes are achieving popularity, resulting in high photoactivity for different kinds of dyes removal. According to the particular geometry, nanotubes have an organized structure and surface volume ratio, show special features, and the specific surface area. TiO_2 nanotubes have tube diameters ranging from 10 to 500 nm, thickness of layers ranging from a few hundred nanometers to 1000 µm (Fu et al.,2018).

Nanotubes were produced using the Ti and Pt sheet as substrates on process electrochemical containing an electrolyte solution. TiO_2 can be used in the application as a powder or as a film. TiO_2 powder has many disadvantages, such as being dispersible, quickly emulsions are too complex to handle, has a low illumination reaction, and causes pollution when used incorrectly (Mo et al., 2018). TiO_2 film has high stability and a larger surface area to further increase the photocatalyst activity compared to TiO_2 powder (Chun Chen et al.,2017).

Nanofibers and nanowires are two quasi-one-dimensional (Q1D) structures with a specific growth and a diameter of less than 250 nm direction. In contrast, nanowires and nanofibers have a similar structure shorter in length. Nanotubes have a hollow internal system similar to that of nanowires, even with excellently structured surfaces.
In table 2 summarized, nanotubes have the largest surface area of any TiO_2 structure based on BET examination for enabling light and reaction conditions to diffuse across the tube length. Holes, ions, and electrons formed by photocatalysis are being transferred to the boundary layer's wide area.

Table 2. Examination of BET specific surface areas and bandgap&value systems for TiO_2, nanotubes, nanowires, nanofibers, and nanoparticles

Nanostructure	Average Pore Size (Å)	Surface Area (m^2/g)	Bandgap (Eg)	Ref
Nanotubes	45	354	3,00	(Pelawi et al., 2020)
Nanowires	60	189	3,09	(Cho et al., 2015)
Nanofibers	67	219	3,10	(Truppi et al., 2017)
Nanoparticles	44	228	3,18	(Xiao et al., 2020)

The review of TiO_2 nanotubes synthesis the would be discussed shortly here. The disadvantages of TiO_2 nanotubes have bandgap of 3.0 eV, low in terms of light energy, and recombination is relatively easy. TiO_2 nanotubes can be formed by three methods such as hydrothermal, template, and anodization. The hydrothermal method uses a liquid material's chemical reactivity at a high temperature in an insulated pressure vessel (Ranjitha et al., 2015). The nanotube surface morphology is controlled by the hydrothermal method, such as the type of alkaline, the concentration of alkaline, reaction temperature, and time (Kustiningsih et al., 2020). And then, the most commonly used technique for preparing nanotube systems is the template method.

The precursor nanotubes are formed within tubular structures. The nanotubes physical dimensions will be identical to those of the template (Sun et al.,2020). The nanotubes physical size would also match those of the template accurately. The template has controllable pore sizes of up to 250 nm, and a film thickness ranges from 0,1 to 100 µm (He et al.,2019). The electrochemical anodization ensured be the most valuable processes to receive the titania nanotubes as reasonably easy techniques and it could be automated effectively. Moreover, anodization is a cheap method and can also be acceptable for other transition metals. The anodic oxidation of titanium substrates in a fluoride solution containing electrolytes in the formation of TiO_2 nanotubes and highlighting the critical element of fluoride ions. Titanium film anodizing is a common technique for producing high surface area TiO_2 nanotubes (Elysabeth et al., 2020).

However, all of the Ti plates are used in application areas. In an electrochemical anodization TiO_2 nanotube synthesis process, a titanium substrate is anodized containing fluoride in the electrolyte solution at a constant anodic voltage. A good composition of fluoride is contained in the electrolyte (0.5 wt%). Too much fluoride in the electrolyte composition (more than 1 wt%) will damage the formation of TiO_2 nanotube layers (Yanyuefeng et al.,2020).

Table 3. The method of forming TiO_2 nanotubes

Methode	Advantages	Disadvantages	Ref
Anodizing	1. Easy to apply 2. Can form smooth nanotubes 3. High aspect ratio.	Difficult to make suitable nanotubes if produced in large quantities	(Elysabeth et al., 2019)
Template	1. Cheap 2. Easy to modify	1. Unstable 2. Need more time for the operation	(Hsu et al.,2019)
Hydrothermal	1. Does not require several chemicals 2. The equipment is easy to use	1. Operates at high temperatures and pressures 2. unstable	(Kustiningsih et al., 2015)

According to the explanation from table 3 of the three different methods, anodization is considered the best method because anodization is the best method for produce TiO_2 nanotubes because it is more efficient and effective than other methods. For decades, the anodization of titanium to form oxide layers has been studied. It is necessary to determine the efficiency for controlling anodizing processes such as potential, electrolyte, fluorine concentration, and time. When the optimum anodization is in suitable condition, it would be produced a large diameter and length of the tube. Usually, the anodizing process will occur in 30 minutes to 2 hours to allow the structure to modify and enhance itself.

Almost all electrolyte conditions (salt solutions, organic solvents, and most acids) form a compact oxide layer with a uniformly increasing thickness with a potential range (Pasikhani et al., 2016). The other variation is when determining the solubility of Ti_4^+ (perchloric acid, electrolytes with a high fluoride concentration). The anodization process enables a wide variety of tube structures and morphologies to be formed. A few approaches have been explained to form more complex nanotube structures and morphologies. , these approaches are based on modifying the electrochemical conditions during the anodization.

The first step of the anodization process is dissolving the TiO_2 film layer in an electrolyte solution containing many F^- ions, and then small holes can be formed in the pore formation process. After that, a pore appears on the surface of the TiO_2 layer, and a high level of acidity at the bottom of the tube can scratch the pore into a tube structure (Pelawi et al., 2020). The reaction mechanism for the formation of TiO_2 nanotubes is shown in equations 1 through 5 (Slamet et al., 2018).

$$Ti \longrightarrow Ti^{4+} + 4e^- \quad (1)$$
$$2H_2O \longrightarrow 2\,[O] + 4e^- + 4\,H^+ \quad (2)$$
$$Ti + 2\,[O] \longrightarrow TiO_2 \quad (3)$$
$$Ti + 2H_2O \longrightarrow TiO_2 + 4H^+ + 4e- \quad (4)$$
$$4H^+ + 4e^- \longrightarrow 2H_2 \quad (5)$$

Zhang et al (2017), argued that the use of TiO_2 nanotubes prevents charge recombination when randomly packed TiO_2 nanoparticles and TiO_2 nanotubes have the same electron diffusion coefficient. TiO_2 nanotubes with a greater diffusion layer and a bigger electron would show superior electron transport. Consequently, TiO_2 nanotubes demonstrate a greater light absorption impact, which improves the light-harvesting properties. Special features of the internal and external surface area are available for the adsorption and chemical reactions of organic pollutant molecules. (Yoo et al., 2018). TiO_2 nanotubes can increase efficiency due to the fast electron transport and 1D structure with minimum charge recombination sites (Wahab et al., 2015). This step would also lead to an adverse increase in the total density. Combined oxidation and dissolution increase the length of nanosized holes and establish a morphology, decreasing the current of this method here again. The width and length of nanotubes can continue to grow as long because their rate of increase affects the separation value and will continue to grow until the dissolution value equals the growth rate. A pretreatment, both chemical or physical, must raise the oxide film on the Ti foil to increase nanotube growth.
However, nanotubes show a great potential as heterogeneous catalysts for accelerating the degradation of azo dyes in a water solution via photocatalysis. So that, the following sections discuss the advancement of research on TiO_2 nanotube enhancement using various synthesis techniques.

2.2. Modification of TiO_2 Nanotubes as Photocatalyst

The major limitation of TiO_2 is the widest bandgap, which causes a series of factors, most significantly, by reducing the amount of solar energy modified to UV light., which also reports only for 4% of solar irradiance (Yoo et al., 2018). Consequently, electrons and holes obtained by photons quickly recombine due to low effectiveness. Several methods were applied to enhance the photocatalytic quality of TiO_2 nanotubes for further effectiveness for waste degradation. The processes can be defined in three ways: a surface-active area for optimum catalytic performance, band structure for charge exchange, and effective absorption across the total visible spectrum (Sa et al., 2019).

It is important to understand about photocatalytic operation of TiO_2. Enhanced TiO_2 nanotubes have been developed for electron separation and catalytic performance. TiO_2 nanotubes can customize in various ways, such as the relation of a sensitizer and the deposition of metal nanoparticles. The TiO_2 nanotube rearrangement has been discussed using various methods.

Doping Metal and Non-Metal TiO_2 Nanotubes

Doping is a widely used technique for modifying the electrical and optical properties of substances where certain one or even more components or molecules are doped into the substrate to form required electrical and optical properties. Recent studies have reported that doping TiO_2 with carbon, nitrogen, fluorine, iron, and iodine results in the required narrow bandgap leading to a more significant reaction to visible light while also increasing the overall photocatalytic activity (Wang et al., 2019). Conversely, Metal ion doping has been researched to optimize photocatalytic performance. Metal doping would get a more significant effect on the TiO_2 conduction band. because Ti contributes to the conduction band while adding value even a small amount to the valence band.

Specified metals, for example, Cu and Fe can take titanium molecule area, resulting in new energy sizes in TiO_2 conduction and valence bands. (Hejazi et al., 2019). It is discovered that while reducing the bandgap, energy is procured through various metal groups. The study mainly contains different metals to doping TiO_2, such as a noble metal, a rare earth metal, and a transition metal. Transition metals including Fe, Zn, Mn, Cr, and Co have been analyzed as dopants for TiO_2 to increase its photocatalytic activity and change the spectrum of TiO_2 absorption spectra into a visible range (Zhang et al.,2019). Finally, transition metals act as photogenerated charge carriers and enhance photocatalytic activity by lowering the energy required to generate photons.

As demonstrated recently, researchers have shown the ability of TiO_2 photocatalyst with nonmetals doping. Several other nonmetal doping agents such as C, N, S, F, and Cl are mainly used to improve the photocatalysis of TiO_2 (Basavarajappa et al.,2020). Under ultraviolet irradiation, the quantum supply of nonmetal doping with TiO_2 would be greater than visible irradiation. (Joseph et al., 2018). nonmetal nitrogen doping of TiO_2 photocatalysts has attracted attention based on their electrical structures, these included good sensitivity, low ionization, and an atomic width similar to that of oxygen compared to conventional TiO_2 (Bjelajaj et al.,2017), It is commonly integrated as interstitials and replace in nanocomposite structures. Moh Hasmizam et al (2017), discussed based on the fact that nonmetal fluorine does not only change the TiO_2 bandgap,&but also it can increase the surface acidity and lead to the formation of&reduced Ti^{3+}ions. Additionally, the charge separation would be enhanced and promoted in photogenerated methods.

Sensitizer

A further critical method for reducing the recombination rate is implementing a heterojunction band structure. The primary purpose of optimizing the adsorption electron transport of TiO_2 nanotubes with various materials create pairs of electrons that can be effectively divided and streamed into various directions. Nanostructured TiO_2 nanotubes can generate many photons during a phase transition and have higher efficiency in the visible light spectrum. This element would be measured to use various materials, including chalcogenides (binary and ternary), carbon nitride, and metal oxides).TiO_2 photocatalytic activity under visible light can be further increased by combining sensitizer with the TiO_2 surface. Sensitized TiO_2 has been successfully used to reduce various contaminants (Daghnir et al., 2013). This method involves several electron transfer stages. The adsorption mechanism of the sensitizer occurs due to the molecule's contact with the TiO_2 surface.

Tiwari et al (2018), discussed many methods that have been developed to increase the photocatalytic activity under visible light, and using a sensitizer with a semiconductor material that has a small band gap. Several researchers have researched to increase the absorption of visible light in TiO_2 nanotubes by adding a sensitizer using chalcogenide material. Chalcogenide material has a small band gap and is suitable because it has good absorption capacity from ultraviolet to infrared wavelength regions and has good stability (Torimoto et al., 2014).

Several chalcogenide materials can be used as sensitizers such as, Cu_2ZnSnS_4, FeS_2, Cu_3SbS_4, $CuInS_2$, SnS, CuS_2, and $AgInS_2$ (Malankowska et al., 2020). $AgInS_2$ is the best chalcogenide material (Cui et al., 2015). Recently, the $AgInS_2$-TiO_2 nanocomposite configuration has been applied to various solar-based energy, photocatalytic (Liu et al., 2015). Combining $AgInS_2$ and TiO_2 nanotubes improve the photoelectrochemical performance of TiO_2 nanotubes in visible light (Kobosko et al.,2017). $AgInS_2$ has high absorption in the visible area, has low bandgap energy, and close to the infrared area due to the absorption coefficient and bandgap energy between 1.87 and 2.03 eV is an excellent approach for photocatalytic applications.

The other techniques are available for combining sensitizer and TiO_2 nanotubes are chemical bath deposition. (Wang et al., 2011), hydrothermal (Liu et al., 2016), and SILAR (Successive ionic layer adsorption and reaction) (Zhang et al., 2017). SILAR method is an effective method in combined the manufacture of sensitizer and TiO_2 nanotubes. The advantages of the SILAR method are easy application, more economical in terms of costs, and the equipment required is easy to apply (Kalarivalappil et.al., 2018). Synthesis of sensitizer and TiO_2 nanotubes using the SILAR method is more efficient at transferring electrons in the photocatalytic process (Z. Liu et al., 2014). Compared to other techniques, the successive ionic layer adsorption and reaction (SILAR) are simple, inexpensive, and having a faster method. Additionally, it can also use to develop sizeable thin films (Shameem et al.,2017).

The SILAR technique involves immersing the substrate in two precursor solutions sequentially and then washing it with water to remove any loosely attached species. Thus, a SILAR cycle consists of the following steps: adsorption of the cation precursor, washing with water, the adsorption of the anion precursor, reaction, and further rinse. The growth rates of thin films using the SILAR technique have been shown to range between a quarter and half of a monolayer, depending on the experimental circumstances. Additionally, the process reports that aqua receptors accept at least some of their structure after adsorption, reducing the concentration of cations and anions in a single layer. Therefore, the thin film development can be perfectly arranged in one SILAR round (Tian et al., 2019).

2.3. Application of TiO_2 Nanotubes Modification as a Photocatalyst For Dyes Wastewater Treatment

There is two processes for reducing of dyes wastewater using the photocatalysis method. First, an intermediate process the dye initiates excitation is an effect of the energy provided by visible light. The transformed into a semi-oxidized radical by electron injection into the TiO_2 conduction band (Cai et al., 2020). The second mechanism dyes was photodegraded process, where the dye compounds connect with the hydrogen peroxide agents formed, and with the electron-hole pairs created because of band-edge excitation, resulting in dye oxidation and reduction directly (Wazir et al., 2020).

Titanium dioxide nanotubes have been identified to become a strongly efficient agent when used on activated approval, with catalysts indicated high removal patterns of more azo dyes (Chen et al ., 2020). Yang et al (2019) reported TiO_2 nanotubes have shown incredible performance in eliminating methyl orange. The formulation via a hydrothermal process utilizing the solvent NaOH achieved the best responses for color removal, with thermodynamic research showing that degradation occurred through a physical adsorption mechanism.

The catalytic reaction reported an increasion in level in response to the growing temperatures. Divyasri et al (2021), discussed the qualified of TiO_2 nanotube doped with N and F by either anodizing a Ti material in NH_4F and NH_4Cl solutions. They realized which annealing the doped TiO_2 nanotube arrays in an N_2 atmosphere significantly decreased the problem of F atom repair, resulting in greater photocatalytic activity forward into methyl orange. While also, a degradation process using heterostructure as a bridge among photogenerated electron-hole pairs was developed, which was found to be able to degrade 99.9% of Methylene Blue and Rodhamin B solution. Photocatalytic decomposition of a large variety of dyes is sufficient. Even so, it is commonly challenging to validate photocatalyst productivity by evaluating its capability to degrade a specialized dye. The conditions affecting the photocatalytic activity depend on the type of catalyst and dye used.

An immediate comparison of different photocatalysts operating under different conditions is complicated. Additionally, it demonstrated surface research methods by using analysis based on optimization. The observational value was compared to the predicted value, indicating the optimum models consistency. The application of a response surface method can significantly improve the productivity required to obtain the maximum dye decolorization efficiency.

The composite material was produced by effectively combining TiO_2 nanotubes with nanomaterials of platinum class metals (Pd, Ru, and Pt). Additionally, the improvement of sample electrodes working as photoanode and cathode in a photoelectrocatalytic reaction has been investigated.

The effect of platinum class metal (Pt, Pd, and Ru) modification on the activity enhancement of pure TiO_2 nanotubes has been investigated by photocatalyst degradation of 10 ppm MO in the presence of visible light (>420 nm). After 4 hours of reaction, only 4.5% of MO was removed from the pure TiO_2 nanotubes, which related to the electrochemical method, and had greater efficiency for the same reaction time. TiO_2 nanotubes-Ru had the highest efficiency of 85.8%, which is more than the Platinum and Palladium electrode with 45% and 75% efficiency in the methyl orange degradation process (Li et al.,2019).

The combination $AgInS_2$ with TiO_2 nanotubes was degraded Methyl orange used the simple SILAR technique at deposition rates of 2, 3, and 4 cycles. The findings showed of distributed $AgInS_2$ nanoparticles are attached to the surface and inside of TiO_2 NTs. The electrodes visible light sensitivity is significantly improved when the TiO_2 nanotubes were sensitized with $AgInS_2$ nanoparticles. Under visible light irradiation, the TiO_2 nanotubes-$AgInS_2$ with 3 cycles SILAR method photoelectrode exhibits increased photocurrents and increased the photocatalytic activity. Comparable research with pure TiO_2 nanotubes carried, and the degradation rate of less than 10%.
TiO_2 nanotubes-$AgInS_2$ has the greatest photocatalytic activity of these samples, with a degradation rate of 79% under the same irradiation period. According to directing electrons to the conduction band of TiO_2 nanotubes-$AgInS_2$ with three deposition cycles significantly improve the photon efficiency and reduce the rate of electron-hole recombination by injecting TiO_2 with fluorine, visible light activity enabled, and the formation of electron-hole pairs improved, and greater productivity compared to traditional photocatalysts (Razali et al ., 2017). The efficiency of 38% for 2 hours in visible light irradiation.

The degradation of dye in a photocatalytic process was investigated in various cases. The photocatalytic reaction produced no hazardous substances and pursued Kinetics of a pseudo-first order. Temperature increases increased the rate of decolorization, so while increases in pH reduced the rate (Sanjaya et al.,2018). Table 4 summarizes the specific dopants and sensitizers involved with the use of TiO_2 as a photocatalytic activity. The enhanced visible light activation methods, the origin of visible light activity, and the electronic structure of various visible light active TiO_2 photocatalysts.

Additionally, it has might be effectively used to develop new photocatalysts capable of enhancing photocatalytic performance advances in UV and visible light driven dyes degradation applications. Finally, different methods for identifying suitable methods that promote light absorption and electron-hole separation to enhance photocatalytic activity are described.

Tabel 4. Modification and Best Condition of TiO_2 nanotubes photocatalyst using dopant metal, non-metal, and sensitizer for degradation synthetic dyes waste

Photo electrode	Methode TiO_2 NT	Light source	Pollutant	Result	Reff
TiO_2 NT-Cu	Hydrothermal	Visible light	Methylene orange	The performance of the Cu doped TiO_2 nanotubes has been analyzed in the presence of sunlight for the degradation of 90% methyl orange.	(Razali et al.,2020)
TiO_2 NT-Ag	Anodization	UV light	Orange II	Orange II 20 ppm was successfully degraded with optimum loading of dosage 0,5% of TiO_2-Ag.	(Zulfikar et al .,2018)
TiO_2NT-Fe	Anodization	Visible light	Congo Red	The greatest catalytic endurance 91% for its decoloration of Congo red.	(Zafar et al., 2020)

Photo electrode	Methode TiO_2 NT	Light source	Pollutant	Result	Reff
TiO_2 NT-6Ni/4Cr	Hydrothermal	Visible light	Methylene Blue	The co-doped TiO_2 with 6Ni/4Cr showed higher photocatalytic activity of 95.6% and high stability toward MB degradation.	(Shaban et al.,2019)
TiO_2 NT-CeO_2	Hydrothermal	Visible light	Methylene Blue	The analysis reported that the maximum degradation is 93.4% and the best parameters temperature is 160 °C.	(Quang et al.,2018)
TiO_2 NT-PbS	SILAR deposition	Visible light	Amido Black	Decoloration has been removed 75% of Amido Black after 30 SILAR deposition cycles.	(Hajjaji et al., 2020)
TiO_2 NT-Se	Anodization	Visible light	Rhodamine B	RhB successfully degrade 73.27%.	(Muzzakar et al.,2019)
TiO_2 NT-B	Anodization	Visible Light	Methylene Blue	Methylene blue successfully egraded 34% for 2 hours.	(Szkoda et al 2016)
TiO_2 NT-NaOH	Template	UV Light	Rodhamin B	After 60 minutes of UV light irradiation, the degradation rate of RhB on TiO_2NT-NaOH was 69.8%	(He et al., 2019)
TiO_2 NT-Gd	Anodization	UV light	Methyl Orange	Under ideal conditions (60V 10 h) MO was degraded 95,8%.	(Li et al.,2020)
TiO_2 NT -$CuInS_2$	SILAR deposition	UV-Vis light	Rodhamin B	$CuInS_2$ successfully sensitized TiO_2 NT degraded of RhB 97,37%	(Yan et al., 2019)
TiO_2 NT-$AgInS_2$	SILAR deposition	Visible light	Methyl Orange	The highest photodegradation MO rate achieves 79% with 3 SILAR optimum condition	(Zhang et al., 2017)

3. Conclusion

This paper highlights the modifications of TiO_2 nanotubes, which are regarded as the most exciting and valuable photocatalyst to enhance the photocatalytic activity in dyes wastewater treatment while attached to UV-Vis radiation. Furthermore, TiO_2 non-modified applies only to medium concentrations of pollutants because it has low efficiency and cannot perform under the visible parts of the solar spectrum. This article gives a thorough update and research focused on several fundamental difficulties while also emphasizing the achievements achieved to enhance the surface-electronic structure of titania significantly. Several methods for enhancement of TiO_2 photocatalyst have been established to reduce recombination, including metal doping, nonmetal doping, and sensitizer. We have evaluated the impacts of ideal dopants on the photocatalytic efficiency of modification TiO_2 nanotubes. The removal efficiency of azo dyes using sensitizer, metal, and TiO_2 doped with nonmetal ions is incredibly attractive. Due to the increased photocatalytic activity, low toxicity, and stabilities of modified TiO_2 photocatalysis, it is expected for industrial applied in the future. This strategy effectively removes dyes from textile wastewater, thus further resolving contaminated water concerns. To improve the processing of synthetic dye waste by photocatalytic besides modified the photocatalyst, several strategies will be used to save energy and costs. It would have minimized the waste generated and reuse the waste in the production process. Then, it would have to increase the quality of the final product and reduce waste formation. Lastly, forbid the use of toxic raw materials to prevent

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