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Industrial Waste Treatment using TiO_2 Modified Clay as Adsorbent-Photocatalyst: Mini Review

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Abstract: Every year, the global industrial sector continues to experience rapid development, contributing to economic growth rates, especially in the textile industry. This has led to an increase in the amount of textile dye waste being distributed into the environment. One solution to address the issue of textile dye waste is by modifying clay with TiO_2 (TiO_2/clay) using degradation-adsorption techniques. In recent decades, the modification of clay minerals has become crucial due to their diverse potential as catalysts, adsorption media, and ion exchange agents. TiO_2 serves as a medium for ion insertion (intercalation), which enhances pore and surface area. This study explains the properties of clay, the photocatalytic properties of TiO_2, surface characteristics, and the photocatalytic/adsorption method on the TiO_2/clay composite. Various types of minerals have been inserted, such as rectorite, montmorillonite, kaolinite, vermiculite, and halloysite, between the layers of clay minerals through different methods and applications. The performance enhancement of tested dyes is carried out by doping metals into the photocatalytic/adsorption material.

Keywords: Clay, TiO_2, industrial waste, dye

1. Introduction

Industrial waste treatment is one of the crucial challenges in maintaining environmental sustainability. Every year, the global industrial sector continues to grow rapidly; however, behind this development, industrial waste poses a serious problem that needs to be wisely addressed. Industrial waste, especially from the textile industry, has the potential to pollute the environment if not properly managed. The use of colorants in the textile industry is one of the main sources of waste that causes environmental pollution. Textile dye waste may contain hazardous organic compounds that are difficult to degrade and can have negative impacts on aquatic ecosystems (Rashid et al., 2021). Therefore, efforts are needed to reduce the adverse effects of textile dye waste and seek environmentally friendly solutions.

Modification of clay has become an important alternative in material development. Clay possesses diverse potential to explore, such as its use as a catalyst, adsorption media, and for ion exchange (Kumari et al., 2022). Another advantage of clay is its ease of immobilization based on its textural structure and easy chemical modification. This allows clay to be adjusted according to specific purposes, such as particle size alteration, structural modification, and thermal properties. Research indicates that the modification process of clay can result in increased microporosity, leading to a larger surface area (Natsir et al., 2021). This advantage makes clay a stable choice for adsorbing pollutants in aquatic environments.

The utilization of clay as a renewable alternative material for colorant adsorption from textile industrial waste is highly relevant in addressing environmental pollution issues prevalent in Indonesia. Colorant waste poses serious problems as it exhibits high stability and is difficult to degrade in the environment due to conjugation of phi (π) electrons (Wen et al, 2019). Clay falls into the category of residual rocks (sediments) and comprises minerals like feldspar, olivine, pyroxene, amphibole, and mica. The insertion of TiO_2 into clay can enhance porosity and surface area through the ion intercalation process. Intensive research has been conducted on the development of TiO_2 as an effective photocatalyst.

TiO_2 as a semiconductor, has been widely used as a photocatalyst for organic waste degradation due to its inert and stable nature, as well as being a strong oxidizer. Doping methods have proven effective in activating the performance of TiO_2 under visible light by reducing its energy bandgap. The energy bandgap of TiO_2 in anatase phase is 3.2 eV (Peng et al., 2018). Doping is employed to modify the conductivity of semiconductor materials, and various types of dopants can be used, including sulfur, nitrogen, silver, manganese, copper, and aluminum (Pawar et al., 2023). Combining both photocatalyst and adsorbent in the organic pollutant degradation process can enhance the reaction efficiency. Moreover, the adsorbent does not need to be separated as the photocatalyst can degrade the pollutants adhered to the adsorbent in situ, ensuring the adsorption capacity remains optimal.

In this mini review, we will discuss the potential use of TiO_2-modified clay as an adsorbent-photocatalyst in industrial waste treatment. We will provide an overview of the latest research developments in this field, including approaches to modify clay with TiO_2, characteristics, and advantages of this composite, as well as its efficiency and effectiveness in addressing industrial waste pollution, particularly textile dye waste. It is expected that the findings of this mini review will contribute valuable information to the development of environmentally friendly and sustainable industrial waste treatment technologies. Innovative efforts like these are key to achieving the goal of environmental protection and improved industrial waste management in the future.

2. Properties of Clay

Clay is an abundant natural material that has drawn the attention of researchers in recent decades as an effective adsorbent to address environmental pollution issues. The unique adsorption properties of clay, such as its large surface area, negative surface charge, and variations in crystal structures, make it a promising subject of study for the removal of various pollutants from the environment. Recent research has demonstrated the diverse chemical properties of clay, involving its micro and crystal structures, such as montmorillonite, kaolin, and illite, which play crucial roles in the adsorption process. Moreover, several researchers have successfully enhanced the adsorption efficiency of clay through physical and chemical modifications, including thermal processing, chemical activation, and the addition of binding agents. Clay has also been applied in various environmental pollution remediation applications, such as the removal of heavy metals, pesticides, dyes, and other organic pollutants, as well as in water and soil remediation systems. However, some challenges remain to be addressed, such as the regeneration and recycling of clay after its use as an adsorbent. With the substantial potential of clay as an environmentally friendly and cost-effective adsorbent, future research should focus on further development to achieve a cleaner and healthier environment through the efficient and sustainable utilization of clay as an adsorbent.

Clay consists of octahedral layers (O) of either brucite ($Mg(OH)_2$) or gibbsite ($Al(OH)_3$) and tetrahedral silica layers (T) stacked on top of each other. Montmorillonite is a clay mineral widely distributed in Indonesia and is unique due to its swelling ability, high cation exchange capacity, and interlayering capability (Fatimah et al., 2010). Based on its unique properties, montmorillonite contained in bentonite can be modified to obtain alumino-silicate compound products with improved physicochemical properties. These physicochemical properties include crystallinity, surface acidity, and thermal stability, which are essential requirements for an adsorbent (Tomczyk et al., 2020).

The surface area and pore volume of clay can be enhanced through acid activation (Torres-Luna & Carriazo, 2019). This treatment depends heavily on the strength of the acid, as well as the time and temperature of the system. Chemical changes occurring in the clay structure during the activation process create octahedral voids in the crystal lattice, leading to the addition of Lewis acid (Giraldo et al., 2017). The optimal acid activation process acts as a charge balancer, where protons from the acid replace exchangeable cations such as Na^+ and Ca^{2+} located between the two layers (Kang et al., 2014).

3. The Properties of TiO_2

The photocatalytic properties of TiO_2 have attracted the attention of scientists and researchers in various fields, especially in environmental treatment applications. TiO_2 is an inorganic compound consisting of titanium (Ti) and oxygen (O). It has three main phases: anatase, rutile, and brookite, with anatase and rutile being the most extensively studied in the context of photocatalysis. Anatase exhibits superior photocatalytic properties compared to rutile due to its larger band gap, which allows for the generation of more electron-hole pairs (electron-hole pairs) when exposed to sunlight.

Several factors influence the efficiency of TiO_2 photocatalysis, including crystal form and particle size, light intensity, pollutant concentration, and solution pH. The primary applications of TiO_2 photocatalytic properties are in drinking water treatment to remove soluble organic compounds, heavy metals, and pathogenic bacteria, as well as in industrial waste treatment to degrade hazardous organic compounds before disposal into the environment. TiO_2 can also be used in photocatalytic reactors for air purification, eliminating pollutants such as volatile organic compounds (VOCs) and PM2.5 particles.

The photocatalytic properties of TiO_2 as a photocatalyst have demonstrated significant potential in environmental treatment applications. Its high efficiency, relatively low cost, and ability to eliminate harmful pollutants make it an attractive alternative for sustainable solutions in addressing current environmental challenges. Although promising results have been achieved, further research is still needed to enhance efficiency and optimize the use of TiO_2 in various environmental treatment applications. TiO_2 is widely used as a photocatalyst due to its inert nature, good thermal stability, resistance to high temperatures, and relatively good catalytic activity. The photocatalytic activity of TiO_2 can be enhanced by modifying its structure, surface area, and particle size through doping (Byranvand et al., 2018). Due to its semiconductor structure with a relatively large band gap (3.2 eV), which accelerates photocatalytic reactions, TiO_2 is also extensively used in photodegradation processes (Divya et al., 2019).

Photocatalysis is a process of combined photochemical reactions that require light and a catalyst to accelerate chemical transformations. When TiO_2 is exposed to light (λ <385 nm), it generates electrons (e-) and positive holes (h+), which can initiate chemical reactions on its surface. The electrons then interact with oxygen, producing $O2^-$, while H+ interacts with water, generating hydroxyl radicals (Maulidiyah et al., 2017). If a semiconductor absorbs energy equal to or greater than its band gap energy, electron excitation (e-) occurs from the valence band (VB) to the conduction band (CB), resulting in the formation of positive holes (h^+) and electrons (Salim et al., 2023). Photocatalysts can convert organic pollutants into biodegradable compounds with low molecular weight. During UV light irradiation, electron-hole pairs (e^- and h^+) are absorbed from light by the photocatalytic semiconductor. These charges can lead to recombination or separation at the surface of the photocatalytic semiconductor. Photocatalytic processes have been extensively studied in wastewater treatment using TiO_2 nanoparticles (Al-Mamun et al., 2019).

TiO_2 exhibits weak adsorption capability in degrading target compounds. Its dispersion property throughout the solution leads to suboptimal contact between TiO_2 and pollutants. To enhance adsorption capacity, TiO_2 can be modified with polarized minerals that have high adsorption abilities. The polarization of clay minerals using TiO_2 as a base material has been widely applied in photocatalysis as it is believed to activate the oxidation of organic pollutants in water (Horikoshi & Serpone, 2020). TiO_2 can be embedded onto the crystal lattice of clay minerals, thereby enhancing the ability to absorb liquid waste. The surface area and pore size of pillared bentonite can be further enlarged through etching processes. The choice of materials as polarization agents should serve a dual role, not only to increase the surface area but also as a catalytic agent to degrade organic pollutants in wastewater (Mishra et al., 2018).

4. Surface Characterization of TiO_2/Clay

The purpose of this clay is to enhance thermal stability, increase the quantity and types of pores, specific surface area, and surface acidity of the clay by adding metal hydroxide polycations to the clay layers. Furthermore, calcination will convert the polycations into rigid metal oxide clusters, thus preventing the damage to the clay layers (Zunino & Scrivener, 2022). Interlayering into the clay structure results in increased surface area, basal spacing, and surface acidity, which will affect the adsorption capacity of the pillared clay mineral (Szymanski et al., 2014). These studies also explain the significant differences in adsorption capacity between pillared and non-pillared clay minerals. The main reasons for modifying clay minerals are their abundant availability, suboptimal utilization, low heat capacity, as well as the quantity and size of clay mineral pores. Several clays have been reported to be modified with photocatalysts, including:

4.1 Synthesis of TiO_2/rectorite Nanoparticles

The synthesis of TiO_2/rectorite nanoparticles through sol-gel calcination has been reported (Zhang et al., 2011). The average size of TiO_2/rectorite is around 10 nm. A lattice edge distance of 0.35 nm observed corresponds to the (101) anatase step reflection. The interaction of TiO_2 precursor with rectorite particles up to a certain extent damages the rectorite structure (Zhang et al., 2008), resulting in some peeled rectorite fragments. TiO_2/rectorite exhibited successful photocatalytic activity under UV light irradiation in the decomposition of Acid Red G anionic dye. Even after five photocatalytic cycles, the photocatalytic activity was entirely retained, possibly due to the highly porous structure and large specific surface area of TiO_2/rectorite.

4.2 Synthesis of TiO_2/Montmorillonite Nanoparticles

The synthesis of TiO_2/Montmorillonite nanoparticles using the hydrolysis method has been reported (Zhang et al., 2008). The intercalation of precursors into the Montmorillonite interlayer damages the Montmorillonite structure to a certain extent, resulting in some single-layer and multi-layer peeled sheets. Hydrogen bonding and Van der Waals forces absorb precursor molecules on the outer surface of the peeled silicate layers. TiO_2 nanoparticles have formed within the Montmorillonite interlayer and on the Montmorillonite surface during the precursor hydrolysis process.

4.3 Synthesis of Aluminum-Doped TiO_2/Montmorillonite

The synthesis of Aluminum-doped TiO_2/Montmorillonite using the impregnation method has been reported (Fatimah et al., 2010). The increase in specific surface area due to the formation of titania particles is also demonstrated by the TEM image. Large aggregates of titania particles were observed for Aluminum-doped TiO_2/Montmorillonite. Similar results were reported for titanium-pillared montmorillonite (Yoda et al., 2004).

5. Photocatalytic-Adsorbent Activity of TiO_2/Clay Composites

The degradation of organic materials based on photocatalytic-adsorbent processes is a developed method using materials produced by manufacturers, such as TiO_2 Degussa P25 and ZnO powder. To enhance the photocatalytic power, they are combined with clay, which plays a role in increasing the surface area and pore volume of the clay through acid activation (Kibanova et al., 2009). This treatment is highly dependent on the strength of the acid, the time, and the temperature of the system. The chemical changes that occur in the clay structure during the activation process result in octahedral vacancies in the crystal lattice, leading to the addition of Lewis acid (Bijang et al., 2015).

The pillared material can be compounds inserted between clay layers, where the distance between adjacent layers at the time of material insertion creates a porous structure with increased layer spacing. The improved catalytic properties through immobilization may also be due to the force field between the support and TiO_2 particles, which prevents the recombination of electron-hole pairs (Barbosa et al., 2015). The reaction occurring during the synthesis process of clay/TiO_2 is schematically. The surface's ability to adsorb positively or negatively charged species depends on the proton concentration of the solution. In this case, the surface charge characteristics of clay minerals are essential in understanding the adsorption and/or desorption mechanisms of contaminants such as dyes (Li et al., 2013).

This type of clay has been widely applied as a photocatalytic/adsorbent material by incorporating the semiconductor TiO_2. Based on literature research, we found that various types of minerals have been inserted between clay mineral layers using various methods and applications, such as rectorite, montmorillonite, kaolinite, vermiculite, and halloysite (Table 1). Furthermore, the addition of metal doping to photocatalytic/adsorbent materials can also enhance the performance of each tested dye.

Table 1. Synthesis and photocatalytic/adsorbent activity of UV and visible light responsive TiO_2/clay composites.

Nanocomposite	Synthesis Method	Model Dye Pollutant	Ref.

TiO_2/Rectorite	The preparation via the sol-gel process without the calcination step	Acid red G	(Zhang et al., 2011)
TiO_2/halloysite	Prepared by employing the low-temperature synthesis of crystalline TiO_2 on halloysite nanotube	Rhodamine B	(Li et al., 2013)
Sulfur-TiO_2 /montmorillonite	Syntesized by pillarization method	Methylene blue	
Vanadium-TiO_2 /montmorillonite	Prepared by a sol–gel process	Sulforhodamine B	(Chen et al., 2011)
N-S codeped TiO_2/ montmorillonite	Synthesized by impregnating	4BS	(Zhang et al., 2008)
Fe_3O_4-TiO_2/montmorillonite	Prepared by a single step of hydrolysis	Methylene blue	Zhang et al., 2014)

TiO_2/Montmorillonite doped with sulfur has been successfully achieved through the pillaring method (Natsir et al., 2020). In this study, sulfur doping was varied. The addition of sulfur dopants to the TiO_2 matrix could reduce the energy gap to 3.2 eV. The resulting photocatalytic/adsorbent performance was optimum in the sulfur-doped TiO_2/Montmorillonite composite (mass of the material 0.5 g), which exhibited an adsorption capacity of 0.337 mg.g-1 with an adsorption efficiency of 93.87%, while the optimal degradation ability was 94.94% at 0.341 $mg.g^{-1}$. The composite of TiO_2/Montmorillonite doped with sulfur holds great promise in textile waste treatment in the future, using an environmentally friendly adsorption-degradation approach. The overall capability of the TiO_2/clay composite is better than that of pure TiO_2 photocatalysts, mainly due to the presence of TiO_2 photocatalysts within the composite. The generation of hydroxyl radicals in the reaction system is enhanced by the presence of TiO_2/clay, as these radicals are not only produced from water photocatalysis but also generated on the surface of the photocatalyst.

Conclusions

This specific clay mineral has found extensive use as a material for photocatalysis and adsorption through the incorporation of TiO_2 semiconductors. Different techniques and applications have been employed to insert various types of minerals between the layers of clay minerals, including rectorite, montmorillonite, kaolinite, vermiculite, and halloysite. Furthermore, the introduction of metal doping to the photocatalytic/adsorbent material has been shown to enhance the degradation efficiency of the tested dyes.

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Conflicts of Interest
The authors declare no conflict of interest.

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