Original Article: Photocatalytic Degradation of Organic Pollutants under Visible Light Irradiation

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ABSTRACT

In recent years, the applications of nanoparticles separately and independently of nanotechnology have made significant progress, for example, the production of nanoparticle photo catalysts has significantly increased the catalytic efficiency of certain materials, and the variety of their applications has been developed. The spread of pollutants in surface water and groundwater has become an important issue worldwide due to population growth and the rapid development of industrialization. Therefore, it is necessary to control the harmful effects of pollutants and improve environmental conditions. Recently, the use of nanoparticles to remove environmental pollution and remove organic pollutants has caused photo catalysts and their potential applications to be widely considered. Photo catalysts are materials that receive energy from a specific wavelength of light and cause a reaction to occur. The catalytic principle of visible light is based on the visible light irradiation light catalyst, the capacity band of the catalyst is from the electron transfer of the ground state of light to the conduction band, the generation of holes born from light and photo electronics, the holes of light with water molecules to produce hydroxyl free radicals, electrons and molecule reactions Oxygen produces superoxide anion and holes, hydroxyl radicals, and superoxide anion production. Reactive oxygen species can break down odor molecules, organic matter, bacteria, and other pollutants into water, carbon dioxide, and other small molecules. A small amount of N, S and P in organic matter produces nitrate, sulfate, phosphate, etc. after decomposition, to play the effect of detoxification, deodorization and sterilization.

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Introduction

The term photo catalyst refers to catalysts that are activated in the presence of light. Most of these materials are semiconductor solid oxides that create an electron-hole pair by absorbing light photons [1]. This electron-hole pair can react with the molecules that are on the surface of these particles and create specific applications. For a photocatalytic reaction to occur, it is necessary to perform 4 steps:

1- Absorption of light energy to produce electron-hole pairs.

2- Separation of excited charges (positive charge of hole and negative charge of electron).

3- transfer of electrons and holes to the surface of the photo catalyst [2].

4- Using the charges on the surface for oxidation and reduction reactions.

In the third stage of the reaction, a large part of the electron-hole pairs is recombined in the path of movement or on the surface. As a result of this combination, the absorbed electron energy is released as heat or light. This will reduce the efficiency of the photo catalyst. Excited surface charges that have a longer lifetime allow oxidation and reduction reactions to occur [3]. What is called photo catalysis in this process. For example, it can be the destruction of organic pollutants in water. Where after absorption of sunlight or artificial lights, the degradation reaction takes place spontaneously from a thermodynamic point of view. In addition to providing a thermodynamic shortcut, a photo catalyst changes the reaction pathway, thereby improving the reaction kinetics. A photo catalyst accelerates the thermodynamics and kinetics of a chemical reaction [4].

Existing photocatalytic processes

Part I: shows photosynthesis (the most successful act of natural photo catalysis). This process, as an intelligent result of billions of years of evolution of nature, has been the main source of our energy supply. Carbohydrates are the main products of these photocatalytic reactions [5].

Part II: You see a type of microalgae that synthesizes unique chemicals, such as H2, ethanol, and glycerol, through reactions similar to what happens in plants, but when it comes to artificial photosynthetic systems, there are many choices. There is before us.

Part III: Synthetic photo catalysis processes can be separated in two general ways. When the reduction and oxidation reactions are deliberately not separated, we see the cheap system shown in part (C). This group includes heterogeneous and homogeneous catalyst reactions, but a competitive strategy for this mode is to physically separate the sites where the reduction and oxidation reactions occur. That is, what you see in part (D). Of course, it is not necessary to use an electrode for this purpose, and these places can be separated with smart measures. In fact, the main difference in systems 3 and 4 is the separation of the place where the oxidation and reduction reactions occur, with a reasonable distance (more than 100 nm) [6].

The ability to degrade pollutants by photo catalysis depends on several factors:

1- Dimensions and morphology of the photo catalyst: all chemical reactions occur on the surface. Therefore, the size of the particle and the morphology of the photo catalyst have a significant effect on the amount of surface area and consequently the degradation rate of pollutants. Research has shown that nanostructured materials with dimensions less than 20 nm show very different physical and chemical properties compared to their bulk scale. Therefore, they are very important in this field. Reducing the size of the particles increases the energy gap of semiconductors, but in general, by reducing the size of the particles, the surface area of the photo catalyst material increases and it will have a greater ability to absorb pollutants and more photons. Therefore, the negative effect of increasing the energy gap is neutralized in this way [7].

2- Pollutant concentration: It is known that the amount of pollutant that can be absorbed on the surface of the photo catalyst material has a tremendous effect on the reactions. Because only the pollutants that are absorbed on the surface of the photo catalyst material have the ability to participate in photocatalytic reactions. Be careful that the concentration of the pollutant, which is present as a mass in all points of the solution, does not have a role in the yield of the reactions [8].

3- The concentration of the photo catalyst substance: the rate of destruction of pollutants strongly depends on the concentration of the photo catalyst. Increasing the concentration of the photo catalyst substance increases the active sites on the surface of these substances. Therefore, it leads to the formation of more electron-holes and ultimately more destruction. Of course, increasing the concentration of each photo catalyst substance can only partially improve the degradation rate [9].

4- Reaction temperature: To obtain the best performance, photocatalytic reactions must be carried out at a balanced temperature. Most photo catalysts perform optimally up to 80 degrees Celsius. At higher temperatures, in addition to increasing the amount of recombination, the absorption of pollutants on the surface of the photo catalyst material is disrupted. On the other hand, as the temperature decreases to zero degrees Celsius, the activation energy of the reactions increases and the reaction efficiency decreases. For this reason, it is better to consider the temperature range of 20 to 80 degrees Celsius as the optimal range for photo degradation of pollutants [10].

5- pH of the solution: changes in the pH of the solution change the surface charges of the photo catalyst particles and the potential of the catalytic reactions. Therefore, this parameter is effective on the intensity of pollutant surface absorption. For example, TiO^2 particles receive and lose protons in acidic and alkaline environments, respectively. That is, the surface of the titanium oxide structure has a positive charge in an acidic environment and a negative charge in an alkaline environment. Therefore, TiO^2 nanoparticles show higher oxidizing activity in acidic environment. It is necessary to pay attention to this parameter in the design and research on photo catalysts [11].

6- Inorganic ions: In most cases, polluted water contains some inorganic ions such as manganese, iron, zinc, copper, phosphate, nitrate, sulfate and chloride ions. These ions affect the photo degradation rate of organic pollutants by surface adsorption on the photo catalyst material [12].

7- Oxygen dissolved in water: Oxygen dissolved in water plays the role of electron acceptor in photocatalytic reactions. That is, it traps the excited electron in the conduction band and prevents its recombination with the hole. According to the research, oxygen dissolved in water does not have much effect on the amount of adsorption of pollutants on the TiO^2 catalyst surface [13].

8- Photo catalyst semiconductors: various semiconductors such as metal oxides and sulfides (TiO^2, ZnO, Fe^2O^3, WO^3, CdS and SnO^2) can act as photo catalyst materials due to their unique electronic properties. These materials have a full capacitance band and an empty conduction band. Semiconductor photo catalysts are the best choice for the degradation of organic pollutants for the following reasons:

- ✓ Being cheap.
- ✓ Being non-toxic or having low toxicity.
- ✓ Flexibility properties.

- ✓ Multi-electron transfer capability.

In addition to the mentioned advantages, these photo catalysts have their own limitations, including:

- ✓ A large energy gap that requires ultraviolet light to excite electrons by light.
- ✓ Instability in liquid environment that causes their chemical decomposition.
- ✓ High rate of electron-hole recombination [14].

The necessity of surface engineering of photo catalysts

The efficiency of a semiconductor photo catalyst is judged by various criteria. including:

- ✓ Semiconductor stability under irradiation.
- ✓ Quantum efficiency.
- ✓ Selectivity percentage of reaction products.
- ✓ Wavelength range response [15].

For example, consider two semiconductor samples CdS and TiO^2. Cadmium sulfide has a small energy gap and can absorb radiant photons in the visible range, but degrades under radiation over time. On the other hand, TiO^2 is a very stable semiconductor, but since it has a large bandgap energy, it is only active in the UV range and is not efficient for visible applications. Meanwhile, only UV light includes only 10% of sunlight rays. Many limitations of semiconductors can be overcome by surface modification. 3 of the most important reasons for the necessity of surface modification in photocatalytic nanostructures are:

- ✓ Preventing recombination by separating the created charges.
- ✓ Excitability of semiconductor bandgap with visible light.
- ✓ Increasing the selectivity of reaction products.

There are various methods for surface modification of photocatalytic nanostructures, among which we can mention the creation of composite structures, core-shell structures and surface decoration [16].

In 2014, Heung Dong et al investigated the fabrication and characterization of CdSe/CdS/TiO^2 coaxial heterogeneous structure, which has potential application in photocatalytic decomposition and degradation of toxic water pollutants. CdSe/CdS is placed under double layer continuously on TiO^2 nanotubes using absorption reaction and ion layer reaction and electrochemical atomic layer deposition, which has significant effects on visible light response efficiency and hydrogen production (Figure 1).

The detailed synthesis process and surface morphology, phase structure of elemental decomposition and photo electrochemical properties of the resulting composite films are shown. The photographic efficiency of the nanocomposite is 9.47% and the hydrogen production rate is 10.24% ml h/cm, both of which are a 7-fold increase compared to pure TiO^2 nanotubes [17].

In 2013, Trishaqosh and his colleagues prepared TiO^2 graphene, CdSe composite and then investigated the photocatalytic activity of the composite with organic dye solutions. The characteristics of the composites were investigated by X-ray diffraction, energy dispersive X-ray, electron microscopy and transmission electron microscopy. The increase in the degradation of methyl orange and Rhoda mine B was observed by measuring the decrease in concentration by UV spectrophotometer, the synergistic effect of graphene on CdSe and TiO^2 was shown, and at the end, the recyclability and stability of the composite were also shown.

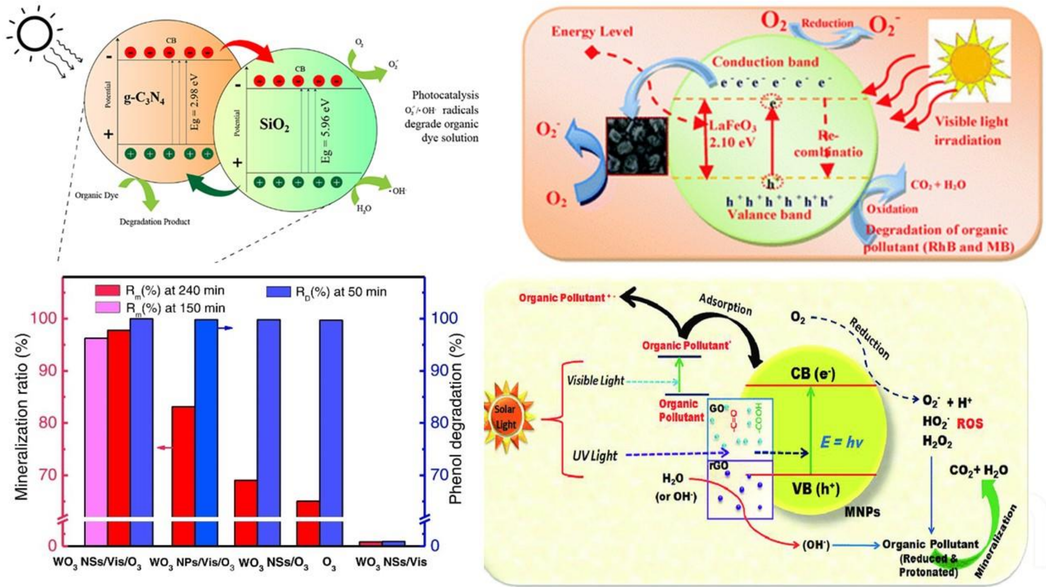

Figure 1. Photocatalytic Degradation of Organic Pollutants under Visible Light Irradiation

What is the photocatalytic property of titanium dioxide and what is its application?

The photocatalytic property of titanium dioxide has been widely studied in recent decades since the discovery of water photolysis by titanium dioxide electrodes in 1972. Titanium dioxide has three main crystalline polymorphs in nature. Anatase, rutile, brookite, and rutile are the most common forms of titanium dioxide. There are different methods to evaluate the photocatalytic activity of a material. The most commonly used method is dye decomposition in aqueous solution under UV light due to its simplicity [18].

In this situation, the rate of decomposition of a suitable organic dye is used as a measure of activity. Physical properties such as particle size and surface area determine the effective area that will absorb dye before degradation. The physical mechanisms involved in such aqueous-based methods are different from gas-phase reactions. More advanced techniques use mass spectrometers to evaluate the photocatalytic activity of titanium dioxide in the gas phase. A photo catalyst is effective for heterogeneous gas-phase reactions that are efficient in generating radicals as a result of an absorbed photon. More advanced techniques use mass spectrometers to evaluate the photocatalytic activity of titanium dioxide in the gas phase [19].

Recent media reports have called photo catalysis the most important invention of the 21st century. Photo catalyst is a coating agent containing titanium dioxide as an active component. An oxidation-reduction chemical reaction occurs when light comes in contact with the photo catalyst. When the photo catalyst is applied to surfaces, it purifies the air to prevent surface contamination. In addition, this technology acts as a revolutionary catalyst for environmental protection. For example, using a photo catalyst to coat the exterior wall of a building allows the decomposition of exhaust gas (NOx).

It also prevents the accumulation of dirt caused by rainwater runoff. By coating the interior walls with such an agent, hazardous substances (VOC) and various microbes (influenza, mold, E. coli, Staphylococcus aureus, MRSA, etc.) that cause sick building syndrome are destroyed and rendered harmless. In fact, very important photo catalysts are found in our immediate environment. The process of photosynthesis used by plants is also an example of a photocatalytic reaction. Titanium dioxide is a semiconductor that produces electrons and electron holes when exposed to light. It then reacts with water and oxygen, to create hydroxyl radicals and reactive oxygen species that allow the degradation and breakdown of harmful substances, resulting in an effective self-cleaning effect [20].

When light and water come into contact with a surface coated with titanium dioxide, the surface becomes coated with a hydrophilic material. This super hydrophilic process removes surface dirt and water, to wash the surface of oil, dust and other similar contaminants. This phenomenon is seen when rain or other water comes into contact with the surface and as a result it is cleaned by itself.

Decomposition and release

Superoxide anion and hydroxyl radical, which lead to the transfer process of these electrons, can cause strong oxidative decomposition. This process breaks down organic compounds such as dirt and sticky oils, bacteria, harmful chemical gases, viruses and molds.

Advantages of the photocatalytic properties of titanium dioxide

The environmental benefits of photocatalytic coatings such as titanium dioxide (TiO^2) are suitable due to their potential application for the degradation of a wide range of substances and pollutants in the air. Photocatalytic active coating systems are able to reduce environmental pollution and clean the air. The technological and economic importance of photo catalysis has increased significantly in the last decade. Improvements in performance are strongly linked to advances in nanotechnology. Various applications have been developed from anti-fog, anti-microbial and self-cleaning surfaces, to water and air purification and hydrogen production from sunlight, and many more have made their way into commercial products [21].

Titanium dioxide photo catalyst not only destroys bacterial cells, but also decomposes the cell itself. Titanium dioxide photo catalyst has been found to be more effective than any other antibacterial agent. Because the photocatalytic reaction works even when cells cover the surface and bacteria are actively multiplying. It is expected that endotoxin produced during cell death is also degraded by photocatalytic action. Titanium dioxide does not degrade and exhibits a long-term antibacterial effect. In general, disinfection with titanium dioxide is three times stronger than chlorine and 1.5 times stronger than ozone. The air purifier using titanium dioxide photo catalyst can prevent the creation of soil, pollen, bacteria, viruses and harmful gases and helps clean the air by filtering 99.9% of pollution [22].

Titanium dioxide has recently developed various applications in the medical industry. Some of them are:

1- Drug delivery systems for cancer treatment: Cancer treatment with traditional chemotherapy can have disastrous effects on cells due to the toxic nature of these compounds. As a result, the focus on how nanotechnology can be used to diagnose and treat cancer has been of great interest. Currently, the most important challenge to be overcome is to reduce the side effects of nanotechnology-based pharmaceutical systems. The use of antibiotics has increased significantly worldwide [23].

Bayan et al explained that the use of antibiotics has increased following the coronavirus disease (COVID-19). These materials enter the environment from various routes such as pharmaceutical industry wastewater, hospital wastewater, and human and animal waste.

Wastewater treatment plants have been identified as the main source of antibiotics entering the environment. These pollutants, their metabolites and their degradation products can negatively affect the environment and human health through migration or accumulation. Side effects include:

- ✓ Nausea.
- ✓ Vomiting.
- ✓ Skin rash and colitis with antibiotics.

Since antibiotics are not fully metabolized in the body after administration, about 30-90% of the 300,000 tons of antibiotics in the world remain active after excretion. Therefore, many active antibiotics are dispersed in the environment every year. The amount of antibiotics has been reported from ng/L in surface water to micrograms/liter in sewage treatment plants and hospital effluents. This amount can reach mg/liter in pharmaceutical wastewater [24].

2- Vancomycin: Vancomycin is the most common glycopeptide antibiotic among other antibiotics. It is used as a last line of defense against serious diseases such as endocarditis, pneumonia and meningitis. The use of vancomycin has increased in German hospitals, especially in the southern regions of this country. As a result, resistance to vancomycin increased from 11.2% in 2014 to 26.1% in 2017. Furthermore, the concentration of vancomycin in French rivers was 9 ng/L. This value was 1.6 and 37.3 micrograms/liter in the treated effluents of French hospitals. According to Laverman's report, vancomycin removal efficiency during UV and activated sludge treatment processes was 52% and 28%, respectively [25].

In addition, Qiu et al., the highest concentrations of vancomycin in Chinese pharmaceutical factories were 54.90±5.97 mg/L and 46.32±3.60 mg/L at the inlet of treatment plants and 0.04 ± 0.04 50 mg/L and 0.04±0.24 mg/L in the final effluent. As an antibiotic, vancomycin may have acute or chronic toxicity to bacteria, algae, invertebrates, and fish in the aquatic environment. A large number of antibiotics are non-degradable and can survive in aquatic environments for long periods of time. The wastewater treatment plant is ineffective in removing antibiotics and there are studies whose experimental results indicate the limitation of treatment methods in the decomposition of pharmaceutical products. The mentioned reasons show that new treatment methods are needed to remove antibiotics from different water environments. As a result, there is an increased interest in methods that convert such materials into non-toxic materials. Among wastewater treatment methods, advanced oxidation processes (AOPs) can degrade organic compounds by hydroxyl radicals under UV or visible light in water and wastewater treatment [26].

AOPs can be divided into heterogeneous and homogeneous systems. The catalyst used in heterogeneous processes is a semi-conducting material. Semiconductors such as heterogeneous photo catalysis based on titanium dioxide (TiO2) are widely used for the degradation of antibiotics from aqueous media. Applying UV or visible light to a semiconductor creates electron-hole (e/h) pairs in the conduction (CB) and valence (VB) bands of the semiconductor, respectively. The generated electrons (e^-) can reduce dissolved oxygen, to produce superoxide radicals.

Conversely, holes (h^+) can oxidize water molecules or hydroxyl anions to produce hydroxyl radicals. These powerful reactive radicals can then attack the organic pollutants, break them into smaller pieces and eventually turn them into water or carbon dioxide. TiO^2 is widely used as a photo catalyst in pharmaceutical wastewater treatment.

It has excellent photocatalytic activity, wide availability, non-toxicity and high surface-to-volume ratio. TiO^2 as a semiconductor has a large energy gap (3.2eV). It also has chemical stability in operating conditions and very high oxidation capacity of the holes created on the valence bond [27].

Therefore, it is widely used as the main material of photocatalytic reactors, but the photo degradation of organic compounds with TiO^2 is limited due to the low rate of electron transfer to oxygen. Also, the recombination of e^-/h^+ produced by TiO^2 is limited. Its performance in photo degradation experiments and photocatalytic activity decreases significantly, which increases the cost of the method. In addition, it has a narrow photocatalytic region (< 400 nm) that can absorb only a small fraction of sunlight. 2 to 3%. Poor adsorption, low surface area, rapid recombination of electron-hole pairs and difficulty in solution separation lead to significant limitations in the use of TiO^2 from solution. On the other hand, hydroxyl radicals are short-lived. As a result, they must react immediately after production. Dispersion of TiO^2 particles on clinoptilolite creates a larger surface than TiO^2 alone [28].

In recent decades, supporting semiconductors on different substrates has increased their photocatalytic efficiency. Zeolites have attracted more attention due to their unique uniform pores and straight channels among different supports. Among the zeolites, natural clinoptilolite is more economical and environmentally friendly.

This zeolite, due to its unique structure, uniform pores, low price, high purity, high ion exchange capacity, low density, large surface area, high degree of crystallinity, ability to absorb molecules and ions, as well as its availability in Iran, was used in the present study. Attention has been paid. The adsorption capacity of this zeolite places organic pollutant molecules near the surface of the catalyst, where hydroxyl radicals are generated. As a result, the photo degradation efficiency increases [29].

Another advantage of zeolite is that it prevents condensation of TiO^2 in heterogeneous photocatalytic processes, which increases the effective surface area of the semiconductor (TiO^2). Zeolite also has a strong electric field that prevents the recombination of electron/hole pairs through the distribution of generated electrons in the material. Therefore, it shows more activity compared to other carriers. So far, more than 100 types of zeolites have been found in nature. Clinoptilolite is not toxic to the body and passes through the entire digestive tract without absorption. This material is stable in different environmental conditions and can withstand temperatures above 4500 degrees celsius. It is also resistant to alkaline and acidic conditions without any degradation.

Effects of different operating conditions on vancomycin degradation rates

1- pH effect: pH is a significant parameter in photocatalytic processes that affects the degradation of organic compounds. Photocatalytic properties such as surface charge, particle size and particle aggregation are strongly influenced by solution pH. Knowing the charges accumulated on the surface of the catalyst or adsorbent helps us to optimize the acidity of the solution to achieve the best signal [29].

The photo degradation process is carried out on the surface of the catalyst. Then, the surface charge of the catalyst and the pH of the surrounding solution play an essential role in the catalytic efficiency. In general, before pHzpc (zero-point charge), the catalyst surface has a negative charge that can absorb the protons produced in the water splitting process from the solution around the catalyst.

Due to the presence of hydroxyl anions in the adjacent solution, its pH increases and the surface of the catalyst receives a positive charge.

According to the study of Rezaei et al., when pHS > pHpzc, the surface of the catalyst has a positive charge that absorbs the hydroxyl anions of water. This process leads to receiving a net negative charge by the catalyst surface and lowering the pH of the contact solution. The pHzpc for TiO^2-clinoptilolite was found to be 6.5. At pH values lower than 6.5, TiO^2-clinoptilolite has a positive charge, which makes vancomycin have a higher degradation efficiency. On the contrary, the TiO^2-clinoptilolite catalyst becomes negatively charged at higher pH values. Although hydroxyl radicals can be formed, they are destroyed without having a chance to react and destroy vancomycin molecules. Therefore, vancomycin removal efficiency decreases with increasing pH values, which were consistent with Petrella et al.'s study [30].

Mehrabadi et al showed that when the repulsive force between the catalyst surface (negative charge) and free electrons (negative charges) increases at pH> pHzpc, a decrease in the rate of pollutant photocatalytic degradation and absorption is observed. Since the surface charge of the catalyst strongly depends on the pH of the solution, the effect of pH on the rate of photo degradation was studied in the range of pH 3-11.

Discussion

A threefold increase in the removal of organic pollutants from wastewater

According to the researchers of Malayer University, when titania crystallizes, three different phases are created. Anatase is one of the phases of titania, which has higher photocatalytic and antibacterial properties than the other two phases, rutile and brookite. This phase is much more effective in removing pollutants than the other two phases. The stability of anatase phase at high temperatures is one of the attractiveness of researchers. Because at a temperature higher than 600 degrees, this phase changes to the rutile phase. In this research, the influence of titania doping with silicon (Si) and zirconium (Zr) on the stability of anatase phase formed at high temperatures has been investigated. Also, investigating the photocatalytic property and the rate of decomposition of the organic pollutant methylene orange by the said nanocomposite under visible light irradiation, were among the features considered in this research [31].

The preparation of titania-based three-component nanocomposite, the possibility of removing organic pollutant up to three times compared to pure titania, the possibility of anatase phase stability up to 1000 degrees Celsius are among the results obtained by these researchers in this research. The industries of removal of organic and mineral pollutants and wastewater treatment of petrochemical factories are among the cases where the results of this research can be applied. Considering that the main applications of titania nanoparticles are in the photocatalytic field and are related to the anatase phase, in this research we focus more on the stability of this phase at high temperatures and the effect of contaminating titania with Si and Zr elements on the photocatalytic properties and the rate of methylene decomposition [32].

Orange has been investigated under visible light irradiation. If the rutile phase is placed in a small amount (10-20%) next to the anatase phase, it will help to increase the photocatalytic property of titania. Also, impurity of the titania network with the help of metal cations can prevent or increase the presence of the rutile phase. These factors depend on the radius of the cations used and how they are placed in the space network of titania.

At the beginning of our research, we investigated the elements affecting the photocatalytic properties and stability of the anatase phase, and finally two elements, Si and Zr, were chosen to contaminate titania. Then, nanocomposite compounds with different percentages were prepared and the decomposition rate of the organic pollutant methylene orange was measured under visible light irradiation and in the presence of the desired compounds [33].

Then the optimal combination that results in the highest amount of decomposition was selected. Finally, the optimal composition was subjected to heat treatment at high temperatures, in order to investigate the stability of the anatase phase and its photocatalytic properties at high temperatures. The results showed the stability of anatase phase up to 1000 degrees Celsius, which was one of the most important and significant results in this research.

By producing these materials in the form of nanocomposite, the specific surface of nanoparticles increases and the absorption centers increase. As a result, this increases the photocatalytic properties. Over the past 20 years, research and development in the field of photo catalysis has been very impressive. One of the important applications of photo catalyst disinfection technology is the destruction of organic pollutants in the water and air flow. It is considered as one of the so-called advanced oxidation processes of AOP [34].

Important mechanical and kinetic aspects and some requirements for efficient photo catalysts in water treatment are considered. Since the relatively high cost of producing light from electricity used for water purification is one of the most important drawbacks, especially for the rapid commercialization of photocatalytic water purification units, solar photons have been used for many years with great success. have been used. Undoubtedly, the photo catalyst process will play an important role in sustainable wastewater treatment processes in the next few years. There are many products that can potentially be used on a daily basis that can have significant benefits for improving the air we breathe [35].

Using the TiO2 photo catalyst process to remove organic pollutants

Pollutants classified as persistent organic pollutants are of great concern to the scientific community due to their persistence in the environment. The TiO^2 photo catalyst disinfection process is based on a great potential as a purification technology. It appears to be a low-cost, environmentally friendly and sustainable technology for the removal of POPs in wastewater. However, this technology has some major technical obstacles that hinder its commercialization, including:

- ✓ Inadequate use of visible light.
- ✓ Low adsorption capacity for hydrophobic pollutants.

The uniform distribution in aqueous suspension system suffers from the problems of TiO^2 particle recovery after water treatment. To improve the efficiency of TiO^2 photo catalyst, many studies are conducted with the aim of eliminating the limitations mentioned above. The performance of various TiO^2 photo catalyst disinfection processes is based on the degradation of POPs [36].

Removing micro pollutants from water with a new method

Organic pollutants such as drugs, pesticides, and hormones, even at the nanoscale, contaminate drinking water in ways that pose significant risks to humans, animals, and the environment. In particular, the steroid hormones estrone, estradiol, progesterone, and testosterone can cause biological damage in humans and wildlife. Therefore, the European Union has determined the strict minimum quality standards for safe and clean drinking water, which should also be considered in the development of new water purification technologies. "The challenge for science is to develop more sensitive methods for targeting hormone molecules," says Prof. André Iris Schoffer, head of the Institute for Advanced Membrane Technology (IAMT) at KIT. The main problem is that steroid hormones are very difficult to detect in water [37].

For every quintillion water molecule there is one hormone molecule. This concentration is very low. Using conventional water treatment technologies, wastewater treatment plants can neither detect nor remove micro-pollutants and organic pollutants. So researchers at IAMT and KIT's Institute of Microstructure Technology (IMT) are working on new methods to not only detect and measure micro pollutants, but also to remove them. A new and promising photocatalytic process. The scientists coated a commercially available large-pore polymer membrane with Pd(II) porphyrin, a photosensitive molecule containing palladium that can absorb visible radiation.

Exposure to simulated sunlight initiates a chemical process that produces so-called singlet oxygen. The scientists were able to reduce the concentration of estradiol, the most biologically active steroid hormone, by 98% from 100 to 2 ng/L [38].

Removal of pollutants using photocatalytic nanotubes

The researchers of the University of Tehran, in collaboration with the researchers of the Polytechnic University of Milan, Italy, have synthesized these materials in the form of nanotubes in order to improve the photocatalytic performance of titanium oxide nanoparticles. These nanotubes, which were produced on a laboratory scale, to remove impurities, nowadays photocatalytic processes based on sunlight have attracted a lot of attention for their application in various fields. Some semiconductor metal oxides are classified as photo catalyst materials. Among metal oxides, titanium dioxide with a special crystal structure is known as a photo catalyst material with high efficiency [39].

In many previous researches, titanium oxide nanoparticles in the form of powder have been used and evaluated. Modifying and producing these photocatalytic materials with different shapes and methods can improve the photocatalytic performance of these materials. According to Hamed Eskanderlou, project manager, the aim of this research was to synthesize titanium dioxide nanotubes with high photocatalytic activity under visible light irradiation [40].

Also, the performance of these nanotubes in the process of removing organic pollutants from water environments has been evaluated. Referring to the structures of anatase and rutile as two different structures of titanium dioxide, he said: the structure of anatase has a higher photocatalytic activity than the structure of rutile. Therefore, in this research, studies were focused on the synthesis of titanium dioxide nanotubes with pure and stable anatase structure at high temperature. He also noted: the electrochemical method of anodic oxidation was used as a fast, easy and cheap method for the synthesis of titanium dioxide nanotubes [41].

Also, silver and palladium noble metal nanoparticles were used to further increase the photocatalytic properties of nanotubes. In the continuation of the stages of synthesis, evaluation and application of the mentioned nanotubes, Skanderlo explained as follows: first, titanium dioxide nanotubes were grown on a titanium sheet by the electrochemical method of anodic oxidation in the presence of fluoride base electrolyte [42].

In the next step, in order to increase the photocatalytic activity of nanotubes under visible light irradiation, silver and palladium nanoparticles were placed on the surface of nanotubes using the chemical reduction method. Next, the obtained nanotubes were subjected to X-ray diffraction (XRD) test for structural evaluation. Finally, the photocatalytic activity of titanium dioxide nanotubes under visible light irradiation and electric current was investigated in removing the organic pollutant paranitrophenol from the aqueous environment [43].

The results of the studies indicate that there is a significant relationship between the photocatalytic activity of titanium dioxide nanotubes and their crystal structure. Also, the loading of palladium and silver nanoparticles on nanotubes will increase the photocatalytic activity of nanotubes due to the electron-withdrawing properties of noble metals [44].

Conclusion

Today, the progress of industrial technologies and the ever-increasing population have caused a severe problem called environmental pollution, which is a serious threat to human life and health. There are many physical and chemical methods to reduce and remove colored pollutants from industrial wastewater, such as ultrafiltration, coagulation, absorption on activated carbon, ion exchange and oxidation methods. Although these methods are relatively effective in removing pollutants, the main drawback of these methods is the formation of secondary waste materials. In fact, these methods are not destructive processes and only transfer pollution from the aqueous phase to the solid network. One of these methods is advanced oxidation, which causes the complete destruction of pollutants based on the photocatalytic process. With the increase of industrial pollution, the cost of pollutant destruction by UV-based photo catalysts increases and faces a decrease in efficiency. In other words, using a clean and low-cost source of solar energy and active perovskite Nano photo catalysts in the visible region can be a better alternative.

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