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Review Article

A Review of Synthesis of an Efficient Photocatalyst for Photocatalytic Degradation of Organic Pollutants in Effluents

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ABSTRACT

In recent years, with the increase in the growing speed of industries and population, water pollution and environmental pollution is a major challenge for the scientific community, which needs a serious and real solution in the world. Because the discharge of wastewater containing toxic substances, solid waste or flue gases from factories is known as a serious problem for the sustainable development of human society. Therefore, in this paper, which is a review of recent studies on this subject, first, an introduction to the catalytic degradation of pollutants is provided, and then the researcher's studies are reviewed, and finally, a conclusion is provided. In conclusion, it is found that in photocatalytic processes, the catalyst dosage is very effective on the rate of pollutant degradation. As the catalyst dosage increases, the number of active sites absorbing the pollutant at the catalyst surface also increases. The increasing trend of dye removal with catalyst dosage can be attributed to the increase in surface area and the availability of more absorption sites. This process continues until it increases light absorption and the production of hydroxyl radicals. However, it is also noteworthy that at values above the optimum, the reaction rate decreases. In other words, if the catalyst dosage is too high, not only it is not effective on the dye removal process, but also causes more turbidity of the solution, which in turn prevents the penetration of light and the effectiveness of the photocatalytic process.

Keywords: synthesis; photocatalyst; organic pollutants; wastewater

1. Introduction

The importance and necessity of water resources for life on earth and the continuation of human civilization is obvious to everyone. Access to clean and affordable water is one of the most fundamental humanitarian goals and a major global challenge in the 21st century [1].

Unfortunately, human beings are causing harm to the environment through the growing number of industries, while they should take responsibility for the wise management and protection of natural resources and the idea that all beings are under the domination of human beings and human beings are the masters of creatures cannot be a justification for the exploitation and unsustainable use of the environment. Human beings should attempt to be at the center of a constructive and healthy life in harmony, interaction, and balance with nature [2].

Dye is one of the recognized organic pollutants in wastewater, which even in small amounts causes problems with the appearance and quality of water. Many dyes contain aromatic rings that are carcinogenic and mutagenic. Paint production in the world is estimated at about 700,000 to one million tons [3]. Dyes come from a variety of industries, including cosmetics, leather, paper, and the textile industry. Dyes are grouped according to their chemical structure into azo, anthraquinone, xanthine, acridine, etc. [4] And they are divided into reactive, acidic, direct, vat, etc. in terms of use [5].

Progress and expansion of science and engineering have alleviated or greatly improved many of the current problems with environmental pollutants by using nanosorbents, nanocatalysts, bioactive nanoparticles, and catalytic membrane with nanostructure and nanoparticles improving filtration among other products and processes derived from nanotechnology [6]. Photocatalytic degradation as the most compatible method of degradation is highly considered by researchers because its salient features include its

effectiveness and low consumption. Also in this process, organic pollutants are completely degraded and CO2 and H2O types are produced [7]. Carbon nanotubes attract a lot of attention due to their high electrical conductivity, thermal conductivity, tensile strength, and flexibility. Conventional methods for the synthesis of carbon nanotubes, arc discharge, laser ablation, chemical vapor deposition, sonochemical and hydrothermal synthesis, each of which has its advantages and disadvantages. Carbon nanotubes must be purified by a suitable method after the synthesis process. The method of synthesis and purification of nanotubes is an important parameter that has a great impact on product quality and is based on the type and application required of this material [8].

In photocatalytic processes, the catalyst dosage is very effective on the rate of pollutant degradation [9]. As the catalyst dosage increases, the number of active sites absorbing pollutant at the catalyst surface also increases. The increasing trend of dye removal with catalyst dosage can be attributed to the increase in surface area and the availability of more absorption sites [10]. This process continues until it increases the absorption of light and the production of hydroxyl radicals. However, it is also noteworthy that at values above the optimum, the reaction rate decreases. In other words, if the catalyst dosage is too high, not only it is not effective on the dye removal process, but also causes more turbidity of the solution, which in turn prevents the penetration of light and the effectiveness of the photocatalytic process [11].

Titanium dioxide (TiO_2) is an industrial substance with many applications in the cosmetics industry [12], solar cell manufacturing [13,14], medical and biomedical applications [15,16], and it is also known as a non-toxic and inexpensive catalyst for the elimination of water and air pollution [17,18]. Applications and physical and chemical properties of TiO_2 are directly affected by the final shape and size of the particles. Therefore, recent research has focused on the making of this substance with different morphologies and different phases [16,19]. TiO_2

crystals have three known phases of anatase, rutile, and brookite, among the existing phases, the anatase phase is the most used as a photocatalyst [20]. The spatial shape and some characteristics of these crystals are shown in Figure (1).

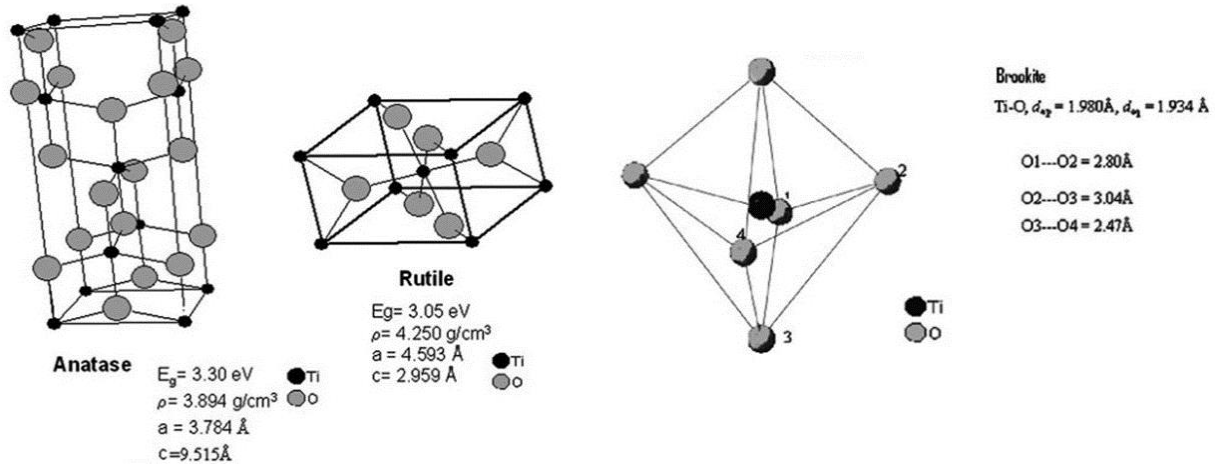

Fig. 1. Types of TiO2 crystals (21)

Dyes from wastewater of various industries such as food, textile, etc. are one of the most harmful and persistent contaminants in water that cannot be easily removed by conventional treatment methods [21,22]. Therefore, photocatalytic degradation of these dyes can be a useful method with high efficiency. For this purpose, TiO_2 is known as a suitable photocatalyst that has a good efficiency under UV light [20]. So far, different methods and raw materials have been used for the synthesis of TiO_2, and the use of each of these methods and materials has a great effect on the final structure of TiO_2. One of the problems in producing titanium oxide crystals by conventional methods is the long synthesis process and lack of control over the formed phases [23]. The sol-gel method is one of the most widely used methods for TiO_2 synthesis due to the lack of need for high temperature and pressure and its inexpensiveness [19]. Some researchers have used $TiCl_4$ as a source of titanium, which is a good choice for this purpose due to its high titanium content, and the results show that by this method, TiO_2 is formed in the anatase phase, which is the most suitable phase for

photocatalytic degradation. However, the production of dangerous by-products during the reaction is one of the disadvantages of using this substance [24].

2. Studies conducted

Abbasi and Farrokhnia in 2020 conducted a study entitled "synthesis of 2D-2D photocatalyst g-C3N4/Fe3O4/TiO2 and investigation of its performance in methylene blue degradation using the design of Box-Behnken model experiment. In their research, g-$C_3N_4/Fe_3O_4/TiO_2$ has been successfully prepared by reflux and thermal compression methods. The activity of the prepared photocatalysts has been successfully prepared by studying the degradation kinetics of reflux and thermal compression methods. The activity of prepared photocatalysts has been investigated by studying the degradation kinetics of organic pollutants of methylene blue. In order to achieve the optimal effective parameters, the response surface methodology (RSM) has been used. The degradation mechanism using g-$C_3N_4/Fe_3O_4/TiO_2$ photocatalyst has shown that the presence of 5% weight of iron oxide in the photocatalyst structure reduces electron-hole recombination, and transfers electron between two semiconductors and accelerates the degradation of methylene blue [25].

In 2021, Rezaei and Moturi conducted a study entitled "photo catalytic ozonation used for the treatment of water and wastewater: a review". Their study aimed to describe photo catalytic ozonation as a combination of two different techniques for hydroxyl radical generation; photo catalysis and ozonation, and to highlight its advantages for water and wastewater treatment compared to these two technologies. An extensive review on the mechanisms, kinetics and economic aspects of photo catalytic ozonation has been performed to explore the synergistic effects produced by applying this oxidation method to the degradation, mineralization and detoxification of different organic pollutants in aqueous media. The influence of experimental parameters such as pollutant concentrations, ozone

dose, photo catalytic load and properties, solution pH and temperature, irradiation wavelength and intensity and the effect of the presence of some substances on the efficiency of photo catalytic ozonation is discussed. Finally, plasma-induced photo catalytic systems are introduced as a new approach for handling photo catalytic ozonation treatments

In 2011, Khameneh Asl et al. Conducted a study entitled "The Effect of Synthesis Process on the Microstructure and Photo catalytic Behavior of Zinc Oxide Nanopowders. In their research, zinc oxide nan powders were prepared using solo thermal processes and chemical methods with the help of microwave and ultrasonic and the physical characteristics of the powders were found using BET X-ray diffraction and scanning electron microscopy. Then, using photo spectroscopic data and red dye reagent and measuring the dye removal per catalyst unit in the reaction under ultraviolet light, the amount of catalytic activity of the samples was obtained. The results showed that the samples obtained from the solo-thermal process with hollow structure had the highest amount of dye removal per time unit, which could be due to the appropriate length and type of bond in the crystal surface plates to absorb and decompose the dye molecule [26,27].

Shamekhi and Aghajani in 2017 conducted a study entitled "Green Synthesis of Zinc Oxide Nanoparticles Using Rubia Tinctorum Extract and Investigating Its Photo catalytic Effect. In their study, zinc oxide nanoparticles were synthesized by aqueous extract of Rubia tinctorum by coprecipitation method. The synthesized nanoparticles were examined by X-ray diffraction (XRD) scanning electron microscopy (SEM) and Fourier transform of infrared spectroscopy (FT-IR). Furthermore, the synthesized nanoparticles were used as a photo catalytic agent to degrade methyl violet. Photo catalytic results show that 92% of the degradation is done in the presence of synthesized zinc oxide nanoparticles. In addition, the

results of electron microscopy showed that the extract had a significant effect on reducing the size of zinc oxide nanoparticles [28].

Akbari and Sharifnia in 2017 conducted a study entitled "fabrication of ZnO photo catalyst using soluble combustion synthesis method". In their research, soluble combustion was made using synthesis method. In order to investigate the morphology, structural and optical properties of the photo catalyst, the analyses of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), UV–visible (UV-Vis) spectrophotometry, and photoluminescence (PL) spectroscopy were used. The analyses carried out showed the fabrication of ZnO wurtzite with a particle size of approximately 500 nm and without impurities and structural defects [29].

Ramezani Haratmeh et al. in 2018 conducted a study entitled "hydrogen production during a photo catalytic process in a solar reactor". In their research, according to the weather conditions of the country in different seasons of the year, solar energy has been used as a sustainable source to provide the energy needed to break down water molecules. Considering the existing solar systems that are mainly used, in this research, a solar point concentrating collector is designed and built, and using the geometric design performed for the solar reactor and the sensors for detecting the intensity of light and temperature embedded in this system, during the day, the collecting plate is positioned in a direction that concentrates the maximum amount of sunlight at one point and provides the maximum energy required to perform the photo catalytic reaction during the day to the solar cavity cylindrical reactor [30].

In 2020, Faghani et al. conducted a study entitled "determining the optical and structural properties of TiO_2/SiO_2 and ZnO/SiO_2 composite films using sol-gel method". In their research, the properties of silicon dioxide composite films with titanium dioxide and also

silicon dioxide and zinc oxide generated by sol-gel method were investigated. In this work, the effects of de-stressing temperature on the optical and structural properties of SiO_2 thin films are discussed in detail. TiO_2/SiO_2 and ZnO/SiO_2 composite films were prepared by sol-gel dip coating method. Surface morphology, crystal structure of thin films and characteristics of synthesized SiO2/TiO2 and SiO2/ZnO nanoparticles were investigated using visible-UV spectroscopy, scanning electron microscopy (SEM) by analyzing elemental X-ray diffraction (EDX) and X-ray diffraction (XR). FESEM images showed that the coating of SiO_2 on the nanoparticles increased their size by about 30 nm. For the photo catalytic activity by investigating the degradation and dye removal of azo congo red (CR) dye with artificial UV light, the photo catalytic activity of both types of SiO2 nanoparticles was somewhat reduced. However, the photo catalytic activity of ZnO nanoparticles completely disappeared after coating with SiO_2 [31] .

In 2021, Manian et al. conducted a study entitled "synthesis of titanium dioxide nanoparticles by the combustion gel method and investigating its photo catalytic properties on methylene blue dye". In their study, 2 TiO_2 nanoparticles with a particle size of 10 to 20 nm were prepared using the combustion gel synthesis method. It was then calcined for 90 minutes at 480 °C to remove organic matters and enhance the properties of the crystal lattice. The generated phases and the size of the crystals were investigated using X-ray diffraction test. In order to investigate the photocatalytic properties of the prepared nanoparticles, methylene blue was used as a pigment and using ultraviolet light as a stimulating agent and a device for recording variations in the concentration of methylene blue in solution, the amount of dye degradation in the presence of TiO_2 nanoparticles under ultraviolet radiation for 70 minutes was investigated [32].

Yousefi et al. conducted a study in 2021 entitled "kinetics and equilibrium absorption of methylene blue in plants left in aqueous solution". The biological absorption of methylene blue (MB) from aqueous solution by leaf debris and pericarp fiber was investigated in batch experiments. The effects of contact time, initial MB concentration, pH and biomass dose on absorption capacity were investigated. Moreover, kinetic and equilibrium models were used to fit the experimental data. Equilibrium data were analyzed using Freundlich and the Langmuir isotherm. The results show that the uptake capacity increases until it reaches equilibrium after 10 minutes. Contact time, in addition, the amount of megabytes absorbed per gram of bio sorbent increases with pH in the pH range of 2-5, but tends to decrease in the pH range of 7-10. Under optimal conditions, equilibrium absorption data are accurately repeated. Sent by a quasi-second-order kinetic model. The results show that the Langmuir model best describes the absorption of methylene blue on three bio sorbents at neutral pH and ambient temperature, the maximum absorption capacity is 24.2, 33.3, and 41 milligram megabytes per gram of bio sorbent for SMPF, ROG, and RTN, respectively. Thermodynamics of the studies showed spontaneous and endothermic absorption with ROG and SMPF residues but exothermic with RTN. Their results clearly show that RTN, ROG, and SMPF act as effective absorbents for methylene blue removal [33].

3. Conclusions

According to the studies, it was found that in photo catalytic processes, the catalyst dosage is very effective on the rate of pollutant degradation. As the catalyst dosage increases, the number of active sites absorbing the pollutant at the catalyst surface also increases. The increasing trend of dye removal with catalyst dosage can be attributed to the increase in surface area and the availability of more absorption sites. This process continues until it increases light absorption and the production of hydroxyl radicals. However, it is also noteworthy that at values above the optimum, the reaction rate decreases. In other words, if

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