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A Review Study of Nanofibers in Photocatalytic Process for Wastewater Treatment

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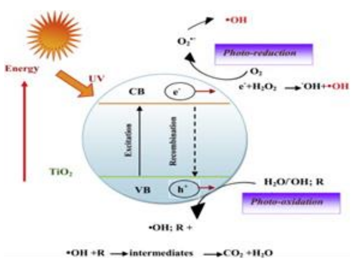
Graphical abstract



Abstract

Clean water resources are dwindling due to the rapid development of industrialization, population growth and long-term drought has become an issue worldwide. With this growing demand, various practical strategies and solutions have been adopted to yield more viable water resources. Over the last decades, a great deal of interest has been focused on the membrane and photocatalytic process of organic compounds present in water and wastewaters by using a catalyst in the form of nanoparticles or nanofibers. The paper presents an overview of the photocatalytic process and the application of using nanofibers in the process. Different modifications of photocatalyst are described. Advantages of the nanofiber application for photocatalytic process are discussed. Moreover a short introduction of producing the nanofibers using an electrospinning process is given.

Keywords: Nanofiber; photocatalytic; electrospinning; organic compound; wastewater

■1.0 INTRODUCTION

A few decades ago, the environmental issues about all the type of pollution have been reassessed under both regional and international level. The accumulation of the organic compounds and pollutants have been increasingly affected the environment because of the rapid development of progressing technology and the change of human way of life.[1] As the rapid urbanization in many countries nowadays, the problems of providing the clean and safe water to the growth population have been increasing. Wastewater will be best defined as any water that have been badly affected in quality which is contained liquid waste that is discharge from domestic residences, commercial properties, industry and others.

Disposal untreated waste water or minimal wastewater treatment of household and factories directly to drains and rivers has resulted in contaminated raw surface water. With the deterioration in water quality, the use of clean water for daily use such as cooking, washing clothes, cleaning the dirt, to drink and so on is impaired. The effect of increasing water pollution has also pose a danger to the health of living things whether human, animal or plant through poisoning and the spread of disease. There are many contaminants or a pollutant that can caused disease that is depends on the type of pollutants that present in the wastewater itself.

Current conventional wastewater treatment is incapable of treating all pollutants that presents in the water. There is no treatment technology that applies the same to all pollutants removal. Because of the environment nowadays become worse, membrane technology promising an innovation for treatment and reclamation as well as a leading process in the upgrade and expansion of wastewater treatment plant.[2] This kind of technologies become more attractive because of many advantages over conventional processes that can improved the purification in treating the wastewater.[3] Membrane technologies are looking forward to increase the effectiveness of treating pollutants in wastewater treatment but it has some limitations because of the fouling membrane that will reduce the permeate flux and efficiencies of the separation process.[4] The photodegradation of pollutants in the wastewater with the application of the photocatalysis have been compromising as the best technologies in treating the micropollutants and to reduce the membrane fouling problems.

Photocatalytic is one of the promising processes of advanced oxidation process (AOPs) because of the efficiencies, cheap and economical friendly in the treatment of toxic pollutants. AOPs are widely used for the removal of organic constituent from industrial and municipal wastewater. AOPs procedure are very promising technologies for treating a non-biodegradable or hardly biodegradable organic compounds which is very harmful that presents in wastewater.[5] When the suspension of the photocatalyst is higher the catalyst should be separated in order to increase the purity of treated water. Photocatalytic membrane reactors are a process of hybrid reactors which is the membrane and the photocatalyst is in a coupled process.[6,7] The membrane is playing a role as a separation process meanwhile the photocatalysis will play as the photodegradation of complex molecule into the simple molecule of pollutants. This type of process is simple, low cost and it is easy to handle in large scale for industrial applications.[8]

Photocatalytic process will involves the use of the semi-conducting material as a catalyst to absorb light. Nowadays, nanostructured is used as a catalyst in order to improve the process efficiencies because of the small particles will lead to a greater surface area for the reaction between pollutants and catalyst. Due to the higher active surface area, nanomaterial is lead to it ability for reducing the toxicity of pollutants to the safer levels and at a very reasonable cost.[9] Nanofibre membrane is one of the advance technology used because of the small pore size and has very large surface area to volume ratio. It also have a flexibility of it surface function and also the mechanical performance of nanofibre is high such as the tensile strength.[10,11] The excellent features of nanofibers technology is lead to the many important applications.

2.0 PHOTOCATALYTIC

2.1 Overview of the Photocatalytic Process

Photocatalytic oxidation nowadays have been pledging as the valuable process for air and water purification because of the capability to degrade an organic pollutants without using chemicals to produce harmless products.[12,13] This advanced oxidation process (AOPs) has a variety of reactions such as organic synthesis, water splitting, photoreduction, hydrogen transfer, gaseous pollutant removal and others.[14,15] Generally, photocatalytic process will undergo the degradation process of the photocatalyst by the production of hydroxyl compounds (OH radical). The molecule or a solid excited their electrons whenever it absorbed light usually from the UV light and shows their ability in donate or accept electrons. The electrons will undergo both a better oxidising and reducing agent that is involved the conducting medium which is water that will generate highly reactive hydroxyl radical and super oxide oxygen radical to entrapped the organic pollutants and produce the harmless water and carbon dioxide.[16-19]

The basic principles of photocatalytic process by using a semiconductor as a photcatalyst started at the semiconductor electronic band structure. Bandgap is a gap in a perfect crystal where no electrons state can exists which is present between the highest occupied energy band (valence band, vb) and the lowest empty band (conduction band, cb). The electron from valence band will be transferred to the conduction band whereas the bandgap energy that is absorbed by semiconductor particles is lower or same with the photon of energy. The electron promotion from vb to cb is simultaneously generated the electrone hole in the valence band. The electrone that have been promoted to the conduction band (e_{cb}^-) will recombine with the electrone hole in the valence band whether on the surface or in the particles. Otherwise, the electron combination can trapped in the surface that will react with the donor (D) or acceptor (A) species adsorbed. This process is happening only in a few nanoseconds.[12-15]

The electron and hole pair generated from the light absorption is producing a better oxidising and reducing agent that is give away a very reactive hydroxyl radical ($OH^\bullet$) and a very superoxide oxygen radical ($O_2^{\bullet -}$). The OH radicals will entrapped the organic pollutants molecule and the molecule will be decomposed to form the harmless water and carbon dioxide. The contribution of superoxide oxygen radical ($O_2^{\bullet -}$) is quite smaller rather than the formation of OH radicals ($OH^\bullet$) makes it less important to initiate the oxidation reactions.[20]The Equation (1) to (3) showed the general process of photocatalytic process that including the electron excitation of the semiconductor photocatalyst.

TiO_2/semiconductor + hv $\rightarrow TiO_2\ (e^-) + TiO_2\ (h^+)$ (1)

$TiO_2\ (h^+) + H_20 \rightarrow TiO_2 + OH^\bullet + H^+$ (2)

Organic contaminants + $OH^\bullet$ $\rightarrow$ Intermediate $\rightarrow CO_2 + H_2O$ (harmless) (3)

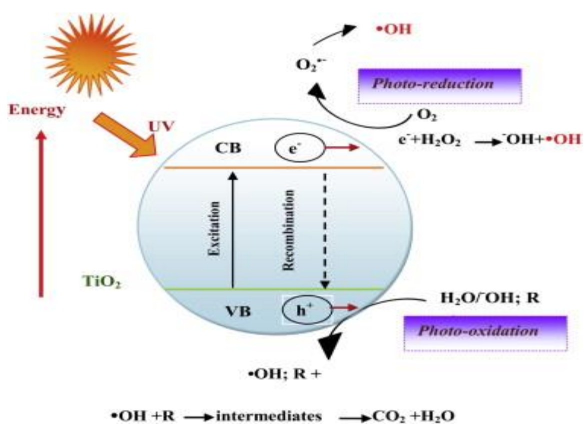


Figure 1 Schematic diagram illustrating the principle of photocatalytic process[21]

2.2 TiO2 as a Photocatalyst

Photocatalyst is important because of it is effectively detoxify the harmful organic pollutants. Good semiconductor photocatalyst will lead to the better photocatalytic process result. There is many type of semiconductors catalyst that is used such as from the chalcogenide type of oxides (titanium dioxide, zinc oxide, silicon dioxide, zirconium dioxide, and others) or sulfides (cadmium sulfide, zinc sulfide and others).[15] Among many type of semiconductor catalyst, titanium dioxide (TiO2) is the very active catalyst under the ultraviolet (UV) light radiation. TiO2 become the most potential semiconductor catalyst in photocatalytic process because of it trait as the higher photactivity, high stability, economically cost, strongly oxidizing conditions and others.[17, 18] TiO2 photocatalyst come in three type of crystal structure which is rutile, anatase and brookite. Rutile and anatase phase are lot have been reported because of the practical interest and the high reaction activity.[22]

The two TiO2 crystal structure are commonly used in the photocatalytic activity. Anatase phase shows the great potential in the photocatalytic activity rather than rutile structure because of the small particle size and higher photocatalytic activity.[23] The rutile and anatase phase of TiO2 are made of octahedron but the different is on the mode of arrangement and the distortion effect. The three-dimensional framework between the two structures is different in term of the edge share bonding. In rutile phase, the octahedrons link by sharing an edge along the c axis to form chains for the three-dimensional formation meanwhile the anatase phase just sharing the edge bonding among the octahedrons itself[22]. Although the anatse phases show a greater photocatalytic activity, the mixed structure between the two crystallographic structures become a fascinating effect in higher photocatalytic activity.[24] There is been reported that a product of Degussa, P25 (TiO2) powder which contained ~80% of anatase phase and ~20% of amorphous and rutile phase showed the great photocatalytic activity.[25] The mixture of the two crystal structure is not well studied because of the exact percentage of the crystal phase is changeable.

The TiO2 powders contain both anatase and rutile structure can be prepared by applying two methods. One of it is by applying heat treatments to the partial conversion of anatase phase that is will be converted into the rutile phase. One of the study have been reported that the used of starting powder which is the pure anatese TiO2 powder that is heated in aerobic atmosphere in a hour at different temperature. The second method is by applying the physical mixing of the rutile and anatese phase powder while distinguish the ratios. In this method, the rutile powder that is consists of 1.5% of anatase phase will be used. The presented anantase phase will be removed by the treatment with 10% of Hydrogen fluoride (HF) solution for a day. The powder need to be thoroughly washed by water after the treatment to remove the unwanted particle which is fluorine atom to generate the pure rutile powder. Water at certain ration will be added to the mixed powder between the pure rutile and anatase powder and sonicated for 30 minutes.[26] The powders contain bot pure rutile and anatase phase is become a promising effects on higher photocatalytic activity although the ratio of the anatase powder is low rather than rutile percentage.[27]

2.3 TiO2 Photocatalyst Modification

There are various efforts done by the researchers to increase the photocatalytic activity and efficiencies in treating water. The most interesting modification to enhance the phtocatalytic efficiency is modified the photocatalyst surface. One of the ways to improve the effectiveness of the TiO2 photocatalyst is by doping the metal and non-metal ion into TiO2 surface.[28-30] This can be proven by the use of the loading of platinum black and copper dopped on TiO2 photocatalyst is enhancing the photocatalytic activity in order to degrade phenol.[31,32] The TiO2 catalyst is more effective and efficient in order to absorb visible light by implanted chromium ion onto TiO2 photocatalyst by using high-voltage acceleration technique.[33] Hydrogen plasma treatment is used to reduce the TiO2 photocatalyst is expecting to increase the catalyst efficiency to utilize solar energy because of this treatment creates a new absorption band in the visible light region that will increase photocatalytic activity.[34] TiO2 structure that is chemically modified by substituting with sulphur anions resulting in high activities of the degradation of methylene blue, 2-propanol in aqueous solution and partial oxidation of adamantine.[35]

TiO2 catalytic activity can be improve by increase the specific surface area of its photocatalyst and it is depend on it crystal size. The specific surface area is inversely proportional to the catalyst crystal size. So that, when the crystal size of the catalyst is small, the specific surface area will become high.[36] There is many ways to make a TiO2 nanoparticle preparation such as microemulsion,[37,38] hydrothermal crystallization, chemical precipitation and sol-gel.[39] Nanoparticles, nanotubes, nanofibers and others type of nanotechnologies application are providing a very fascinate properties such as higher purity, greater surface area, greater size uniformity and many mores. There are various methods on producing nanoparticle of the titanium dioxide in order to increase the photocatalytic activity. One of the methods on producing the nanopowders is by preparing via sol-gel method and titanium tetraisopropoxide (TTIP), distilled water and ethyl alcohol as a starting material.[40] In order to synthesis high-purity anatase TiO2 powder nanocrystals, one of the researches introduces one-step method which is combining hydrolysis-precipitation and alchothermal process. The objective is to produce the high crystallinity and large surface area of the titanium dioxide.[41] Microemulsion is one of the methods to produce the Tio2 nanoparticle where TiO2 nanoparticles formed when the titanium tetraisopropoxide was dropped into the microemulsion solution. The hydrolysis reaction between TTIP in organic solvent and water in core of microemulsion will formed the TiO2 nanoparticle.[42] There is little method on producing the TiO2 nanofibers. The most commercialize methods nowadays have been used is electrospinning process.

■3.0 ELECTROSPINNING

3.1 Nanofiber by Electrospinning

The drastically decreasing of the polymer fiber diameters from micrometres (µm) to nanometres (nm) have change the fascinating characteristics on the fibers surface such as flexibility of the surface functionalities and also providing a very large surface area to volume ratio. The fiber changes also producing the superior mechanical performance such as on the fiber stiffness or tensile strength.[11] The higher surface of reaction and others broad properties of the fiber make it one of important candidates in many applications. Electrospinnnig is one of the commercial uses to turn out the microfiber polymer into the nanofiber polymers. This technology is a simple method in the fabrication of the ultrafine fibers with a very small diameter.[43] The basic principle of the electrospinning process is when the high voltage supply is charged into the polymer solution droplet to induce the projection of the liquid droplet and will be solidified on the collector plate in order to produce the nanofibers.

3.2 Precursor Solutions

In order to prepare the nanofibers, the most important thing is the electrospinning solution. The preparation of the electrospinning precursor solution needed inorganic precursor and a solvent. The solution prepared used only precursor and solvent cannot be directly electrospin because of the hydrolysis rate of the metal alkoxide will be changing rapidly and the rheological properties will become an appropriate make it hard to control the electrospinning process.[44] In order to control the hydrolysis rate of the precursor solution, the additive such as catalyst will be added but in a small portion. The rheological properties that are an appropriate can be adjusted by adding the polymer. The typical spinnable precursor solution includes the alkoxide metal or organic precursor, polymer, additive and relatively volatile solvent.[45-47] There are many reports regarding the preparation of the preparation of TiO2 nanofibers by electrospinning because of TiO2 become most promising semiconductor in photocatalytic process with many modifications to improve the properties of the nanofibers itself.

3.3 Electrospinning

Electrospinnig is one of the methods to produce nanofibers which are diameter (10-100 nm) which is a very simple and versatile technique. The basic setup for the electrospinning process required the nanofiber collector (Al or Si wafer).[44] The precursor solution that is prepared will be loaded into the syringe pump with a spinneret at the tip. The high voltage power (kV/cm) will be supplied at the spinneret to yields an electrical field. The collector plate will be placed several centimetres (cm) from the tip. The viscous solution will be feed through the spinneret at a constant and slow rate usually below than 1mL/hr and it will be controlled by the syringe pump. The droplet from the spinneret will become highly electrified immediately and the induced charges are evenly dispersed at the liquid surface.[48-50] The charged fiber will be deposited on the collector plate because of the electrostatic attraction. The as-spun nanofibers will be kept in the air to complete the hydrolysis reaction. Titanium dioxide is one kind of ceramic nanofiber that is generate from the expansion of electrospinning technology. Generally ceramic nanofibers are elctrospin the ceramic precursor but with the present of the polymer compound to adjust the rheological properties of the precursor solution. To produce the pure anatase TiO2 nanofiber, the excess polymer will be burned by undergo the calcination process at high temperature at a certain time.[51]

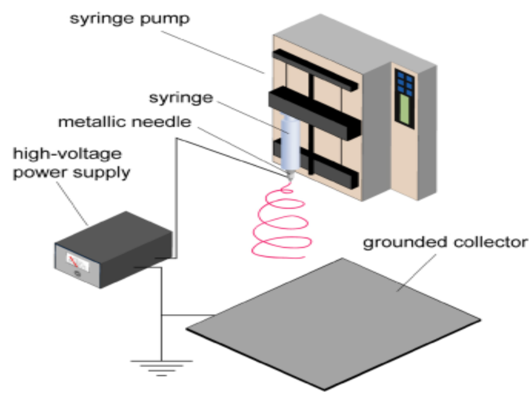


Figure 2 Schematic of a typical setup for electrospinning process[52]

4.0 NANOFIBER IN PHOTOCATALYTIC PROCESS

4.1 Nanofiber

Nanofiber comes in a very small particle diameter which the diameter is less than one micron. This kind of nano compound has been used in many applications such as air filtration, water treatment application and many more.[53] Nanofibre are produced from a variety of polymers either from organic or inorganic polymer such as polyvinylalcohol, polyurethanes, polyimides, co-polymers, polymers contained an additives, silica and others. Nanofibres also have been used in many applications. One of it is textile industry which is the end uses is in textile fabrics.[54] The nanofibers properties are different from the other type of fibers like conventional fiber and melt blown fibers. The fiber diameter of the nanofiber is much smaller compared to the melt blown and conventional fiber. The smaller size of fiber diameter, the filtration efficiency becomes high because of high surface area for the reaction.[55] Table 1 describe the differences between the typical dimension of conventional fibres, melt-blown and nanofibres.

Table 1 Typical dimensions of conventional fibres, melt-blown fibres and nanofibres

Fibres	Fiber Diameter (µm)	Linear Density (dtex)	Specific surface (m^2/g)
Coneventional	10-40	1-30	ca. 0.2
Melt blown	1-5	ca. 0.01	ca. 2
Nanofiber	0.05-0.5	ca. 0.0001	ca. 20

4.2 Nanofiber in Photocatalytic Process

Titania used in photocatalytic process have made a great semiconductor in eliminating organic or inorganic pollutants compound in water and air. Titania is chosen as photocatalyst because of its higher band gap make it has higher photocatalycally activity.[56] Modifying the photocatalyst is not only changes the mechanism and kinetics under radiation but also introduces visible light activity. Each of the photocatalyst modification will influence the photocatalytic activity depending on the test substrate and the process condition. The most spectacular modification on Tio2 photocatalyst is with the uses of the nanofibers. The uses of nanofibers in photocatalytic activity will increase the specific surface area of the energy absorption from UV light. Nanofiber will also increase the photodegradation efficiency when there is bigger surface contact between the catalyst and the pollutants that need to be removed. Past few years, many researchers work on the degradation of dye pollutants in industry. The most effective way is by using the photocatalytic process and TiO2 as a photocatalyst.[57] One of the researchers does an improvement of TiO2 photocatalyst when they are using porous TiO2 nanofibers to enhance the surface volume ratio to improve photocatalytic activity and the efficiency increase up to 76.65% after 1 hour irradiation.[58] Photocatalytic is also use in the removal of the pharmaceutical waste. The improvement of the photocatalyst is lead to the higher removal efficiencies. The photocatalytic oxidation of cimetidine in increased from 42% to 90% whenever the thickness of TiO2 nanofiber is increasing. This is also showed that, the nanofiber application in photocatalytic process give a better result.[59] Many application have been used nanofiber to improve the performance such as the degradation of organic pollutants from industrial wastes, treatment of produces water in oil nad gas production industries, disinfection of water and living space also indoor air pollutant treatment.[60]

4.3 Advantages of Nanofiber

Nanofibers represent many advantages in many applications especially in photocatalytic process while treating organic pollutants. The higher surface to volume ratio of the nanofiber gives a higher impact on pollutant degradation. This can be proven when the photodegradation between naphthalene/anthracene by zinc oxide (ZnO) nanofiber showed the high rate constant.[61] The strength of the nanofiber is also high and it is comparable with a commercial Teflon (PTFE). The strength of the nanofiber membrane is independent of the direction in dry condition.[62] Fouling membrane is one of a serious problem because of the decreasing in filtration efficiency, increase in energy consumption due to frequent chemical washing. Nanofiber prepared a full surface exposure to UV or solar light that is effectively eliminates the fouling membrane.[63] Nanofibers have one dimension that is many time longer than the other type of nanomaterial is providing a defined flow pattern along the longer dimension which contribute to the higher photocatalytic efficiency[60]. The nanofiber membrane is also giving an advantage on the membrane distillation. The nanofiber membrane surface will increase the hydrophobicity of polymeric material thus increased the membrane distillation.[64] The high porosity of the nanofibers will improve the water separation and increase the efficiency of the water treated. The application of the nanofiber is not only focused in the photocatalytic process but also in the other applications such as in tissue engineering, air filtration, drug delivery system and others.

■5.0 CONCLUSION

Photocatalytic posses high capability in the wastewater treatment. The utilization of titanium dioxide (TiO2) as a photocatalyst give e very fascinating result in photodegradation of pollutant in air or water. Photocatalyst modification have been done to improve the photocatalytic activity. Nanomaterial are of a great interest for a variety of applications. Among the nanomaterial use, nanofiber is resulting in high photocatalytic activity because of the high surface area and high mechanical strength. Electrospinning is one of the succesfull technology to produce a very fine nanofiber. The uses of nanofiber give many advantages to improve the performance of many applications. So that, nanofiber are the most efficient in the many application especially in photocatalytic process.

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