PHOTOCATALYTIC DEGRADATION OF METHYL ORANGE USING TiO_2 IMPREGNATED ACTIVATED CARBON

ABUBAKAR MUHAMMAD

UNIVERSITI TEKNOLOGI MALAYSIA

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I dedicated this thesis to my beloved mother, father and wife for their support and encouragement. I'm also grateful to my fellow friends and colleagues for their help and advice during the entire research making it a success.

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ABSTRACT

Photocatalytic active TiO_2 impregnated activated carbon TiO_2/AC with various ratios were prepared by sol-gel method. Methyl orange (MO) was used as target pollutant to test the activity of the catalysts under two different light sources. The catalysts were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) and Brunauer-Emmett-Teller (BET). The TiO_2/AC catalyst was found to be more effective than prepared TiO_2 for degradation of methyl orange in both light sources. The activated carbon adsorbability and TiO_2 photoactivities increase the catalytic performance of the catalyst. Optimization of parameters such as light sources (ultraviolet and visible light) and amount of catalysts for the photocatalytic degradation of the target pollutant were evaluated. FESEM and XRD results suggest better TiO_2 distribution, increase in particles morphologies from spherical to bulky particles and the increment in the amount of anatase when AC was increased accordingly. The bond formation was observed in the FTIR while Ti-O-C suggests a conjugation between the bulk AC and TiO_2. The formation of TiO_2/AC catalyst with an optimum AC ratio (TiO_2-50AC) reveals great potential in complete decolorization of methyl orange. Results obtained show that activated carbon gives great impact on the activity of TiO_2 especially for 50 wt.% that exhibited degradation of 99% methyl orange.

ABSTRAK

Fotopemangkinan aktif TiO_2 dan pemangkin TiO_2/AC dengan pelbagai nisbah berat karbon teraktif (AC) telah disediakan melalui kaedah sol-gel. Metil oren (MO) digunakan sebagai bahan pencemar untuk menguji aktiviti pemangkin dibawah dua sumber cahaya yang berbeza. Pemangkin telah dicirikan menggunakan pembelauan sinar-X (XRD), mikroskop imbasan elektron (SEM), Transformasi Fourier inframerah (FTIR) dan Brunauer-Emmett-Teller (BET). Pemangkin telah didapati lebih berkesan daripada TiO_2 yang disediakan untuk menguraikan metil jingga dengan kehadiran kedua-dua sumber cahaya. Sinergi yang diperkenalkan oleh kebolehserapan karbon teraktif dan fotoaktiviti TiO_2 meningkatkan prestasi pemangkin. Kesan parameter seperti sumber cahaya (UV dan cahaya nampak) dan jumlah pemangkin kepada degradasi fotopemangkinan bahan pencemar sasaran telah diuji. Keputusan SEM dan XRD menunjukkan kesan pengagihan TiO_2 yang lebih baik, peningkatan zarah morfologi daripada zarah sfera kepada yan lebih zarah besar, dan kenaikan dalam bilangan fasa anatase apabila AC digunakan. Pembentukan ikatan dicirikan melalui FTIR, sementara Ti-O-C menunjukkan konjugasi antara AC pukal dan TiO_2. Keputusan yang diperolehi ini menunjukkan bahawa karbon teraktif memberi pengaruh ke atas aktiviti TiO_2 terutamanya bagi 50 wt.% pemangkin yang menunjukkan degradasi metil oren sebanyak 99.0%.

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LIST OF ABBREVATIONS

AC	-	Activated Carbon
Å	-	Armstrong
BET	-	Brunauer-Emmett-Teller
eV	-	Electron Volt
FTIR	-	Fourier Transform Infrared
FESEM	-	Field Emission Scanning Electron Microscopy
MO	-	Methyl Orange
nm	-	Nanometer
SEM	-	Scanning Electron Microscopy
TiO_2	-	Titanium Dioxide
XRD	-	X-ray diffraction
%	-	Percentage
^{o}C	-	Degree centigrade
wt	-	Weight

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

The process of photocatalysis is conventionally defined as the acceleration of the rate of a chemical reaction, induced by the absorption of light with the presence of catalyst or coexisting molecule [1]. The substrate absorbed photons of light (ultraviolet or visible) along its surface generating valence band holes and conducting band electron. The oxidizing holes are formed when electrons from the valence band are being upgraded to the new energy level, the holes react with water molecules to produce reactive radicals. Electron promoted from the new energy level to the conducting band formed conducting band electrons which react with oxygen molecule to produce superoxide. The radicals formed react with organic pollutant on the surface of the photocatalyst and decompose it into harmless products. Once the reaction has begun the molecules generated by the oxidation of the organic pollutant can be adsorbed on the catalyst and oxidized again due to the constant formation of HO? radical during the irradiation period.

Dyes are synthetic chemical that gives characteristic color to different materials. They are used in many industrial applications to give color for the final products. Industries such as cosmetics, plastics, food, paper and textile used dyes to color their products as an integrated part of the material [2]. They are also applied for

analytical purposes in chemical laboratories, biomedical and biological laboratories as biological stain [3]. Textile industries are among industries that have been ranked first in the usage of dyes. Therefore wastewater from textile industries consist of toxic dyes, heavy metals and sometime surfactants which poses serious health risk to human and the environment. Several classes of dyes are considered sources of carcinogens or mutagens uneasy to decolorize due to their complex structure and synthetic origin [4]. Dyes give permanent colors to fibers and resist fading upon exposure to sweat, light, water and many chemicals including oxidizing agents and microbial attack due to their chemical structure [5].

Dyes can be classified as cationic, anionic or nonionic type. Anionic dyes are being regarded as the direct and reactive acid dyes, cationic dyes are basic and the nonionic dyes are neutral. Both cationic and anionic dyes are water soluble, the nonionic or neutral dyes have a low water solubility, thereby exhibit hydrophobic character. The dye that mostly used on industrial scale are the azo, anthraquinone, sulphur, indigoid, trimethylphenyl and phthalocyanine derivatives, recently azo derivatives are the most used synthetic dyes in the industries [6]. The most problematic dyes are the brightly colored, water soluble reactive and acid dyes. They tend to pass through conventional treatment systems unaffected [7]. Physical and chemical treatment has been employed to minimize the toxic effect of these effluents due to the environmental problems impact by such pollutants.

Various approaches have been found in literatures dealing with the removal of dyes from industrial effluents. However, many of these methods which include direct precipitation, separation of pollutant, coagulation by chemical agent, ion exchange on synthetic adsorbent resin, reverse osmosis, ultrafiltration, adsorption on activated carbon and other adsorbents need further treatment in order to generate the adsorbent or to separate the purified effluent in the solution [8]. Most of the conventional methods create other secondary pollutants by transferring of organic compound from water to other phases [9]which further analysis has to be performed which is not cost effective. Alternatively, photochemical methods could be used in order to reduce the drawbacks mentioned above. Recent works have been dedicated

to the use of photocatalysis for the treatment of industrial effluent because of its ability to mineralized the target pollutant [10].

TiO_2 nanomaterials have played an important role in photodegradation of organic pollutants; it appears the most studied photocatalyst due to it cost effectiveness, photostability, abundance and high oxidizing power towards many organic pollutants [11, 12]. Despite these positive attributes, its application is limited due to its wide band gap (3.2 eV), difficulty of separating the catalyst TiO_2 from the solution and recombination of the photogenerated electron-hole pairs, this results in low efficiency of the photocatalytic reaction [13]. TiO_2 is effective in decomposing a wide variety of organic, inorganic and also toxic material in both liquid and gas phase systems however, energy band gap of pure TiO_2 of 3.2 eV limit its application only to ultraviolet light ($\lambda < 387$ nm, about 4% of the solar light). Various methods have been applied to improve the photocatalytic activity of TiO_2, two major categories which include chemical methods such as doping with non-metals, transition metals, dye sensitization, spatial structuring and rare earth metal doping [14]. The other method is to use physical approaches; introducing microwave or ultrasonic irradiation into TiO_2 photoreaction systems [15]. Activated carbon could be considered as a good support for TiO_2 to check out its drawbacks.

This is promising by the combination of the photocatalytic activity of the catalyst and adsorptivity property of the activated carbon. Commercial activated carbon is considered an effective adsorbent for liquid phase removal of organic pollutant [6]. However, its use is limited because of its high cost. Alternatively, activated carbon can be produced from waste materials from agricultural by-products [16] and wood industry, non-conventional waste from municipal and industrial activities . The use of waste materials for the preparation of activated carbon can be very useful to decrease waste disposal in the environment which could lead to other consequences. One of the major problems of using TiO_2 is the separation of the powder catalyst from the effluent at high concentrations which could contributes to catalyst coagulation and formation of aggregates [17].

The advantage of using activated carbon with TiO_2 is the ease at which the catalyst is separated from the bulk solution, high porosity, high surface area, high photostability and suitability of working at ambient temperature. Apart from activated carbon other materials such as clays [18], zeolite [19], silica, alumina [20], glass and nickel were used to improve the photocatalytic efficiency of the catalyst, but no significant contribution has been recorded. Activated carbon has been a promising for TiO_2 which can be attributed to the combine effect between the two materials. Sometimes interaction between TiO_2 and certain pollutant could cause coagulation, thereby, preventing large amount of UV or solar radiation from reaching the catalyst active centre. This lead to the reduction of the surface area of the catalyst [21], hence, reducing its photocatalytic activity. The activated carbon serves as an efficient adsorption trap for organic pollutant at the surface of the TiO_2, this leads to mass transfer of the pollutant to the catalyst surface where photoreaction occur. Enhancement of photocatalytic degradation of pollutants has been observed by activated carbon, which is attributed to the increase quantity of the substrate to come into contact with the catalyst through adsorption.

1.2 Problem Statement

Despite the attractive characteristics of TiO_2 mention earlier its wide band gap (3.2 eV) can only be excited by a small UV fraction of solar light, which account for less than 5.0% and 0.1% for both indoor lighting and solar light, respectively [22], making it impractical for use under sunlight/visible light. Another drawback of TiO_2 is the post-separation and recycling of the photocatalyst from the treated water prior to discharge. This separation process is important to avoid loss of the catalyst and importation of new contamination to the treated effluent [23]. This is accompanied by an additional operation cost and time extension. Also, high rate of electron-hole recombination which causes poor efficiency of the photocatalytic reaction.

Agricultural waste such as palm kernel shell, coconut shell, palm kernel fibre, saw dust, bamboo tree, cashew nut, almond shells, tomato stem and leaves, wild olive cores [24] are agricultural waste that have been successfully used in the production of activated carbon. The largest amount of palm kernel shell waste generated in Malaysia can be used as potential source of activated carbon that can be used with TiO_2 photocatalyst. Despite application of palm kernel shell as fuel, large amount are unutilized causing serious environmental problems. Malaysia as a leading palm oil producer and exporter in the world has an estimate of 4.6 million tons palm kernel shell waste annually [25] which create huge disposal problem. The environmental threat posed by this waste leads to several studies to make use of the palm kernel shell as the raw material for the preparation of activated carbon by several researchers [26].

The focus of this research is to develop a means to concentrate target pollutant around the TiO_2 particles and also to overcome the problem of post-separation of the photocatalyst in the slurry before disposal which add cost and time-consumption to the whole process. Both can be achieved by immobilizing the photocatalyst particles on activated carbon which ease the separation process. Activated carbon properties such as ability to adsorb variety of synthetic organic compound, long tradition of application in wastewater management and its capability of prolonging the separation lifetime of photogenerated electron-hole pair [27], thus increasing the rate of radical generation can be utilize to achieve a successful research. Even though there are a lot of research on improving the photocatalytic efficiency of TiO_2 using activated carbon support derived from agro-waste, only a few studies have been done on palm kernel shell activated carbon. A literature review showed that preparation and photocatalytic activity of immobilized composite TiO_2/palm kernel shell was not thoroughly investigated.

1.3 The objectives of this research are:

- Synthesize TiO_2 photocatalyst impregnated carbon from palm kernel shell using sol-gel method.

- Optimize operating parameters such as effect of chemical activation and calcination temperature of the immobilized photocatalyst.

- Characterize the synthesized TiO_2/AC and TiO_2 photocatalysts.

- Measure the photocatalytic activity of the TiO_2/AC and TiO_2 using methyl orange dye as the target pollutant.

1.4 Scope of the Study

In this research the preparation of titanium dioxide impregnated activated carbon was carried out. The activated carbon was produced from palm kernel shell (PSK) and impregnated with concentrated nitric acid as an oxidizing agent. The carbonization was accomplished by heating the material in a furnace at a temperature of 600^{o}C for 1 h. The TiO_2 was successfully synthesized by sol-gel method using Titanium(IV) isopropoxide as titanium dioxide precursor in the presence of Isopropanol and distilled water. The photocatalyst was calcined at 450^{o}C for 2 h.

Characterization techniques were used to characterize the samples using X-ray Diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform Infrared (FTIR), Brunauer-Emmett-Teller (BET) and UV-visible spectrometer. The above physicochemical techniques were correlated to the photocatalytic degradation of methyl orange.

1.5 Significances of this Study

This research will aim at study of the photocatalytic effect of activated carbon immobilized with TiO_2. The combined effect of adsorption by the activated carbon and photoreaction of TiO_2 will combined to produce a photocatalyst with high photocatalytic activity. The novelty of this research is the use of palm kernel shell (PKS) in the synthesis of TiO_2/AC catalyst, and the use of a locally homemade photoreactor for MO decomposition. The utilization of the waste for the preparation of activated carbon will help in reducing the environmental problem posed by PKS. The photocatalyst is expected to be a potential catalyst due to its ability to efficiently trap organic pollutant at the surface of the TiO_2, that leads to mass transfer of the pollutant to the catalyst surface where photoreaction occur. It is the goal of this research to synthesize a new material using palm kernel shell activated carbon immobilize with TiO_2 photocatalyst to check out the harmful effect of dyes in our environment.

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