PHOTOCATALYTIC REMOVAL OF PHENOL AND BASIC BLUE 3 (BB3) USING ZnO/C_3N_4 UNDER OUTDOOR LIGHT IRRADIATION

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by

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LIST OF ABBREVIATIONS

AOPs	Advanced oxidation processes
BB3	Basic blue 3
CB	Conduction band
C_3N_4	Carbon nitride
CO_2	Carbon dioxide
HCl	Hydrochloric acid
H_2O	Water
H_2O_2	Hydrogen peroxide
HPLC	High performance liquid chromatograph
HRTEM	High Resolution Transmission Electron Microscopy
L-H	Langmuir-Hinshelwood
O_2	Oxygen
NaOH	Sodium hydroxide
NHE	Normal hydrogen electrode
SEM	Scanning Electron Microscope
TiO_2	Titanium dioxide
TOC	Total organic carbon
UV	Ultraviolet
UV-vis DRS	Ultraviolet-visible Diffuse Reflectance Spectra
VB	Valence band
XRD	X-ray Diffraction
ZnO	Zinc oxide

LIST OF SYMBOLS

		Unit
C	Concentration at time t	mg/L
C_0	Initial concentration	mg/L
e^-	Electron	-
E_g	Energy band gap	eV
h^+	Holes	-
h	Planck's constant	eVs
$HO_2^{\bullet}$	Hyperoxyl radical	-
hv	Photon energy	-
K	Adsorption equilibrium constant	L/mg
k_{app}	Apparent rate constant	1/min
k_r	Reaction rate constant	mg/L/min
$O_2^{\bullet -}$	Superoxide radical anion	-
OH^-	Hydroxyl ion	-
$\bullet OH$	Hydroxyl radical	-
r	Reaction rate	mg/L.min
R^2	Correlation coefficient	-
zpc	Point charge zero	-
λ	Wavelength	nm
θ	Bragg's angle in degree	-

PENYINGKIRAN FENOL DAN BASIC BLUE 3 (BB3) MELALUI PEMFOTOMANGKINAN MENGGUNAKAN ZnO/C_3N_4 DI BAWAH PENYINARAN CAHAYA LAMPU LUARAN.

ABSTRAK

Pencemaran persekitaran telah menjadi masalah yang besar terutamanya kepada negara-negara membangun. Pencemaran air oleh pelbagai jenis bahan yang berbahaya boleh mengakibatkan impak yang negatif kepada persekitaran. Proses Pengoksidaan Lanjutan (AOP) telah diketahui mampu untuk merawat air yang telah tercemar sebelum dilepaskan. Di antara proses tersebut, pemfotomangkinan heterogen oleh pemangkin ZnO telah menarik minat sejak akhir-akhir ini. Walaubagaimanapun, masalah besar yang dihadapi oleh ZnO adalah kadar penyatuan semula pasangan e^-/h^+ yang tinggi yang boleh mengurangkan degradasi pemfotomangkinan. Jadi, gandingan ZnO dengan C_3N_4 yang mempunyai jurang tenaga yang rendah boleh menghalang penyatuan pasangan e^-/h^+ ini. Oleh itu, dalam kajian ini pemangkin ZnO/C_3N_4 dengan pelbagai peratusan berat C_3N_4 (0.7-4.9 berat%) telah berjaya disediakan melalui kaedah pengisitepuan yang mudah. Objektif kajian ini adalah untuk mensintesis dan mencirikan pemangkin ZnO/C_3N_4, untuk menilai kesan proses parameter ke atas degradasi pemfotomangkinan fenol dan *basic blue 3* (BB3), untuk mengetahui pemineralan bahan pencemar di bawah keadaan terbaik, dan untuk mengesahkan proses kinetik pemfotomangkinan bahan pencemar di bawah keadaan terbaik. Bagi sampel yang terhasil; Pembelauan Sinar-X (XRD), Mikroskop Penghantaran Elektron Beresolusi Tinggi (HRTEM), dan Spectrum UV-vis Pantulan telah digunakan untuk pencirian. Keputusan XRD menunjukkan penambahan C_3N_4 di dalam penyediaan pemangkin tidak menunjukkan puncak sepadan dengan C_3N_4 mungkin disebabkan oleh kandungan C_3N_4 yang rendah. Keputusan SEM mendedahkan permukaan pemangkin kurang dipengaruhi oleh berat C_3N_4. Walaubagaimanapun, imej HRTEM menunjukkan bahawa hubungan yang rapat antara ZnO dan C_3N_4 sememangnya terbentuk dan hal ini berfaedah kepada degradasi pemfotomangkinan. Kemudian, aktiviti pemfotomangkinan untuk ZnO tulen dan pemangkin yang disediakan telah diuji untuk degradasi fenol dan BB3. Tiga pembolehubah proses telah dikaji; kesan beban pemangkin, kesan kepekatan awal bahan cemar, dan kesan bendalir pH. Keputusan menunjukkan semua pemangkin ZnO/C_3N_4 yang disediakan mempamerkan aktiviti yang lebih baik berbanding ZnO tulen terutamanya pemangkin dengan 3.5 berat% ZnO/C_3N_4 yang menunjukkan penyingkiran tertinggi peratusan. Keadaan optimum bagi beban pemangkin didapati pada 1g/L dan 0.5 g/L masing-masing untuk fenol dan BB3. Selain itu, kedua-dua bahan pencemar menunjukkan penyingkiran tertinggi peratusan pada kepekatan awal 5 mg/L dengan peratusan 99.4% dan 89.6% masing-masing untuk fenol dan BB3. Degradasi fenol paling bagus adalah pada pH 5.7 (99.4%) sementara untuk BB3 pada pH 7 (96.7%). Pada keadaan terbaik di atas, analisis TOC menunjukkan hanya 56.5% dan 63.6% penyingkiran TOC telah dicapai masing-masing untuk fenol dan BB3. Kinetik bagi degradasi fenol dan BB3 turut dikaji. Keputusan menunjukkan bahawa kinetik bagi kedua-dua bahan pencemar ini mematuhi model Langmuir-Hinsheilwood (L-H). Akhir sekali, pemangkin 3.5 berat% ZnO/C_3N_4 mempunyai kebolehulangan dan keupayaan pemisah yang bagus mencadangkan potensi penggunaanya di dalam rawatan air sisa.

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ABSTRACT

Environmental pollution has become a major problem especially for developing countries. Water contamination by various kinds of hazardous substances might give negative impacts to the environment. Advanced Oxidation Processes (AOP) are known to have the ability to treat the contaminated water before being discharged. Among them, heterogeneous photocatalysis by ZnO catalyst have attracted recent years. However, the major problem suffers by ZnO is a high recombination rate of e^-/h^+ pairs which can decrease the photocatalytic degradation. Thus, coupling of ZnO with small band gap value of C_3N_4 can prevent these recombination of e^-/h^+ pairs. Therefore, in this study ZnO/C_3N_4 catalyst with various C_3N_4 weight percentage (0.7-4.9 wt%) were successfully prepared by simple impregnation method. The objectives of this study are to synthesize and characterize the ZnO/C_3N_4 catalyst, to evaluate the effect of process parameters on photocatalytic degradation phenol and basic blue 3 (BB3), to determine the mineralization of pollutants under the best condition, and to validate the kinetic process of photodegradation of pollutants under the best condition. For the prepared samples; X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), High Resolution Transmission Electron Microscopy (HRTEM), and UV-vis Diffuse Reflectance Spectra (UV-vis DRS) have been used for characterization. XRD result showed that the addition of C_3N_4 in catalyst preparation gave no peak corresponding to C_3N_4 possibly because of the amount C_3N_4 was very low. SEM result revealed that the catalyst surface was less affected by C_3N_4 loading. However, HRTEM images showed that the intimate contact between ZnO and

C_3N_4 was indeed formed and it is advantageous for the photocatalytic degradation. Then, the photocatalytic activity of pure ZnO and as-prepared catalyst were evaluated for the degradation of phenol and BB3. Three process variables were studied; effect of catalyst loading, effect of catalyst loading and effect of solution pH for both phenol and BB3. The result showed that all the ZnO/C_3N_4 catalysts prepared catalyst exhibited better activity compared to pure ZnO especially with 3.5 wt% ZnO/C_3N_4 catalyst which showed highest removal percentages. The optimum catalyst loading was found at 1 g/L and 0.5 g/L for phenol and BB3, respectively. Besides, both pollutants showed the highest removal percentage at the initial concentration of 5 mg/L with the percentages of 99.4% and 89.6% for phenol and BB3, respectively. Degradation of phenol was found favor at pH 5.7 (99.4%) while for BB3 at pH 7(96.7%). At the best condition above, the TOC analysis revealed that only 56.5% and 63.6% of TOC removal for phenol and BB3, respectively. Kinetic degradation of phenol and BB3 also has been studied. The result showed that the reaction kinetic for both pollutants obeyed Langmuir-Hinshelwood (L-H) kinetic model. Finally, 3.5 wt% ZnO/C_3N_4 catalyst also has good repeatability and good separation ability suggested its potential application in wastewater treatment.

CHAPTER 1

INTRODUCTION

Water covers about ¾ of the earth's surface and its consumption contribute approximately 60 % - 70% of livings worldwide. Most of the human activities are dependable to the water as their main source. The growth of the human population and industries causes the increase of demand for fresh water while the sources of water supply remain constant. The quality of fresh water supply has been affected mainly due to the increased of industrial activities and human populations. In particular, developing countries have high potential to discharge more polluted water through domestic use and industrial activities. On the global level, the question of the fresh water supply has been a concern.

1.1 Industrial Water Pollution

Nowadays, water pollution becomes the main threat and challenge that a human must face. Water pollution occurs because of emission of pollutants (particles, chemicals or substances that cause water to be contaminated) are discharged directly or indirectly into water system without proper treatment. Pollutants enter into the water system mainly by human causes or factors. Daily human activities introduce pollutant and wastes into the river and streams, lakes, groundwater aquifers, and oceans. These pollutants eventually will affect the groundwater system and become dangerous for human consumption. These contaminants mainly contributed from the textile industry, haloalkanes, aromatic compounds, alcohol, detergents and surfactants, agriculture wastes like insecticides, herbicides and pesticides (Gordon and Jules, 2009), inorganic compounds like heavy metals like mercury, nickel, and lead (Fenglian *et al.*, 2011; Ming *et al.*, 2012); and pathogens like bacteria and fungi (Vinu and Madras, 2012). Although these contaminants may exist at trace levels, they can change the quality of drinking water and can cause adverse effects to the environment and human health.

Phenol and basic blue 3 (BB3) are among of the hazardous pollutants released to the environment. They are contributed from many industrial activities especially from agriculture industries. Phenol and its derivatives have been known for their toxicity and carcinogenicity and they are highly resistant to many degradation processes including conventional biological and chemical treatment (Tassalit *et al*., 2008). Severe illness like leukaemia and some serious organs malfunction may arise if exposes in high concentration of phenol. Dyes can cause serious environmental problem since they have low biodegradability in a water system that causes a high potential threat to the environment (Fatimah *et al*., 2011). The release of colored waste even in trace quantities is highly desirable as it reduces the penetration of light into the water, thereby decreasing the efficiency of photosynthesis in aquatic plants. This in turn causes the ecosystem of streams to be seriously affected.

1.2 Advanced Oxidation Process

Recently, AOPs have received considerable attention for the complete destruction of contaminants. AOPs become a promising technology for wastewater treatment containing non-easily removable organic compounds. AOPs include photocatalysis system like the combination of semiconductor and light, and semiconductor and oxidants (Kansal *et al*., 2009). The research regarding AOP in wastewater treatment also has been reported by several authors. The AOP have been developed include heterogeneous catalysis, ozonation, Fenton processes, and oxidation by H_2O_2 (Vilhunen *et al*., 2010; Andronic *et* al., 2011; Rosal *et al*., 2011; Wu *et al*., 2011). Heterogeneous catalysis, among the advanced oxidation processes (AOP) is a process successfully used to oxidize organic pollutants present in the aqueous systems. Heterogeneous photocatalysis offers a number of advantages as the following:

a) Destroying contaminants by decomposing into non-toxic substances with the aid of light irradiation.

b) Environmentally friendly materials can be employed as a semiconductor catalyst.

c) Photocatalytic activity can be conducted under mild condition.

d) Complete mineralization of organic pollutants without producing secondary pollutants.

Despite having some advantages in destroying organic pollutants, heterogeneous photocatalysis also have some disadvantages which are less active and selective compared to homogeneous catalysis. On the other hand, heterogeneous catalysis also suffers from the leaching of the catalyst during its use and recycle, leading to deactivation of catalyst (Erica *et al*., 2005).

1.3 Semiconductor Coupling

Due to the fact that the catalyst makes use of light to enhance the degradation of organic pollutants in the presence of semiconductors, several attempts have been made in this field. Semiconductors like TiO_2, ZnO, and Fe_2O_3 can be used to act as sensitizers for light-induced redox-processes. As stated by Hofmann *et al.* (1995), this process occurs because of the electronic structure of the metal atoms in chemical combination, which is characterized by filled valence band (VB) and empty conduction band (CB). Upon irradiation with the energy equal or more than the band gap energy, this semiconductor molecules absorb the photon light energy, hence the electrons in the valence band excited to the conduction band. In order for the semiconductor to catalyse the reaction, the recombination of e^-- h^+ must be prevented as much as possible.

After the discovery of water splitting by Fujishima and Honda (Fujishima and Honda, 1972), TiO_2 have been extensively investigated as the potential catalyst for degradation of organic contaminants by many researchers. However, ZnO has been found to be a potential catalyst in the photocatalysis research area because of the comparable band gap energy of ZnO with TiO_2 (3.2 eV). ZnO offers several advantages over TiO_2 in photocatalytic research area which are:

a) Can absorb a large fraction of the solar spectrum (Yulong *et al*., 2013).

b) A good electron donor with high optical activity and stability (Kanika *et al*., 2013).

1.4 Problem Statement

Removal of environmental contaminants by light-driven photocatalytic activity has received considerable attention in recent years since the demand of the fresh water supply are critical (Song *et* al., 2014). In the past researches regarding semiconductors have been investigated like ZnO, WO_3, ZnS, Fe_2O_3, CdS and $SrTiO_3$ as well as coupled semiconductors. However, producing a good catalyst may require extensive research regarding their separation efficiency. One way to improve the photoactivity of catalyst is by increasing the separation efficiency and form a composite powder between two semiconductors. A good catalyst must possess high activity, ability to utilize visible and/or near-UV light, photostable (durable) and reusable, chemically and biologically inert and cheap (Chen *et al*., 2008).

Among the available catalysts, ZnO is a popular catalyst used in the photodegradation of organic and inorganic compounds because of its high activity, low cost and non-toxicity. ZnO also have been reported to have higher photocatalytic activities both in air and aqueous media (Kansal *et al*., 2010; Wahab *et al*., 2013). However, the