

**PHOTOCATALYTIC REMOVAL OF PHENOL USING SUPPORTED
NANO-TiO₂ DOPED WITH LANTHANUM**

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NANO-TiO₂ DOPED WITH LANTHANUM**

by

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LIST OF SYMBOLS

| Symbol | Description | Unit |
|------------|----------------------------------|-------------------|
| C | Phenol concentration at time t | ppm |
| C_o | Initial phenol concentration | ppm |
| C | Velocity of light | m/s |
| CB | Conduction band | - |
| dC/dt | Derivative of concentration | mg/L.min |
| E_g | Band gap energy | eV |
| e_{cb}^- | Electron in conduction band | - |
| e_{vb}^- | Electron in valence band | - |
| h | Planck's constant | eVs |
| $h\nu$ | Photon energy | - |
| h_{vb}^+ | Hole in valence band | - |
| HO_2 | Hyperoxyl radical | - |
| k | Reaction rate constant | mg/L.min |
| K | Adsorption equilibrium constant | L/mg |
| k_{app} | Apparent rate constant | min ⁻¹ |
| mol % | Mol percent | - |
| O_2^- | Superoxide anion | - |
| OH^- | Hydroxide anion | - |
| OH | Hydroxyl radical | - |
| pH_{pzc} | Point of zero charge | - |
| R^2 | Coefficient of correlation | - |
| R | Reaction rate | mg/L.min |

| | | |
|----------|-------------------|-----|
| <i>T</i> | Time | min |
| VB | Valence band | - |
| wt% | Weight in percent | - |

Greek Symbols

| | |
|----------|--|
| | Bragg's angle (degree) |
| | Alpha |
| Å | Angstrom (1×10^{-10}) |
| δ | Angular width of half-maximum intensity (radian) |
| | Wavelength of the UV lamp (nm) |

LIST OF ABBREVIATIONS

| | |
|--------------------------------|---|
| AOP | Advanced oxidation process |
| BET | Brunauer-Emmett-Teller |
| BaSO ₄ | Barium sulphate |
| CB | Conduction band |
| CO ₂ | Carbon dioxide |
| EDX | Energy dispersive X-ray |
| FTIR | Fourier transform infrared spectroscopy |
| HCl | Hydrochloric acid |
| HPLC | High performance liquid chromatography |
| H ₂ O | water |
| KBr | Potassium bromide |
| La | Lanthanum |
| La ₂ O ₃ | Lanthanum oxide |
| MMT | Montmorillonite |
| NaOH | Sodium hydroxide |
| N ₂ | Nitrogen gas |
| O ₂ | Oxygen |
| SEM | Scanning Electron Microscope |
| TiO ₂ | Titanium dioxide |
| UV | Ultraviolet |
| UV-vis | UV-vis spectrophotometer |
| VB | Valence band |
| XRD | X-ray diffraction |

**PENYINGKIRAN FENOL MELALUI PEMFOTOMANGKINAN
MENGUNAKAN NANO-TiO₂ YANG DISOKONG DIDOP DENGAN
LANTANUM**

ABSTRAK

Titanium dioksida (TiO₂), memainkan peranan utama dalam jenis rawatan ini kerana ciri-ciri yang istimewa yang dipunyainya seperti kos yang rendah, lengai, tidak bertoksik dan juga sangat stabil. Walaubagaimanapun, beberapa pengubahsuaian perlu dilakukan untuk menambah baik kekurangannya. TiO₂ komersial, Degussa P25 fotopemangkin telah diubahsuai dengan mendopkan bersama lantanum menggunakan kaedah impregnasi basah dan sekatgeraknya ke atas gel silika. Fotopemangkin ini telah berjaya disintesis untuk mendegradasi bahan organik tercemar yang terpilih, iaitu fenol, secara berkesan di bawah cahaya UV menggunakan sistem reaktor berkelompok. Fotopemangkin ini telah dicirikan menggunakan Mikroskop Imbasan Elektron (SEM), Spektroskopi serakan tenaga X-ray (EDX), Pembelauan sinar-X (XRD), Brunauer-Emmett-Teller (BET), Spektroskopi UV-Vis dan Spektroskopi Fourier Transform Infrared (FTIR). Pengubahsuaian pada TiO₂ telah meningkatkan fotoaktivitinya disebabkan oleh perubahan dalam jurang jalur tenaga, penggabungan semula electron – lubang positif, saiz kristal, luas permukaan serta kitar semula fotopemangkin. Amaun pendop lantanum untuk fotopemangkin yang terbaik ialah 2.0 mol% (La:Ti) manakala bagi gel silika sebagai sokongan pula iaitu dalam nisbah berat ialah sebanyak 3:1 (Ti:Si). Fotopemangkin ini dikenali sebagai 2.0 La-TiO₂/ gel silika. Keputusan dalam degradasi pemfotopemangkinan fenol adalah sehingga 98% berbanding dengan TiO₂ P25 komersial 57.9% sahaja dalam masa 4 jam dengan menggunakan cahaya UV A. 2.0 La-TiO₂/ gel silika juga terbukti mempunyai

kebolegunaan yang sangat baik selepas tiga kali penggunaan dan juga keupayaan mendapan yang efisien. Pelbagai parameter operasi seperti kepekatan awal fenol, pH awal fenol dan juga dos fotopemangkin dikaji. Hasil kajian menunjukkan bahawa keadaan yang terbaik adalah seperti berikut: kepekatan awal fenol 10 ppm, dos fotopemangkin sebanyak 1.0 g / L nilai pH awal fenol sebanyak 5.3. Kinetik untuk degradasi pemfotopemangkinan fenol juga telah dikaji dengan menggunakan model Langmuir-Hinshelwood. Keputusan menunjukkan bahawa kinetik tindak balas untuk kajian ini mematuhi kinetik pseudo-pertama dengan nilai k (pemalar kadar tindakbalas) dan K (pemalar keseimbangan penjerapan) sebanyak 1.149 mg / L.min dan 0.0106 L / mg masing-masing.

PHOTOCATALYTIC REMOVAL OF PHENOL USING SUPPORTED NANO-TiO₂ DOPED WITH LANTHANUM

ABSTRACT

Titanium dioxide (TiO₂), plays a main role in this treatment due its special characteristics such as inert, non- toxic and also very stable. However, some modifications have to be done to improve its limitation. Commercial TiO₂, Degussa P25 photocatalyst was modified by doping with lanthanum using wet impregnation method and immobilized onto silica gel. It has been successfully synthesized in order to degrade chosen organic pollutant, phenol, effectively under UV light using a batch reactor system. The photocatalyst has been characterized using Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), UV-Vis spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR). The modification on TiO₂ has enhanced its photoactivity due to change in the energy band gap, electron-hole recombination, crystalline size, surface area and also reusability of the photocatalyst. The best dopant loading of lanthanum is 2.0 mol % (La:Ti) while for silica gel as a support is 3:1 (Ti/Si) weight ratio for the photocatalyst. The photocatalyst is known as 2.0 La-TiO₂/ silica gel. The result in phenol photocatalytic degradation was up to 98% compare to commercial TiO₂ P25 alone 57.9% within 4 hours using UV A light. The 2.0 La-TiO₂/ silica gel also proven to have an excellent reusability after the three time of usage and sedimentation ability. Various operating parameters such as initial phenol concentration, initial phenol pH and also photocatalyst loading dosage were examined. The results showed that the best conditions are as follows: initial concentration of 10 ppm, photocatalyst loading 1.0 g/L, and initial phenol pH 5.3. Kinetic for

photocatalytic degradation of phenol also has been studied using Langmuir-Hinshelwood model. Result showed that the reaction kinetic for this study followed pseudo-first order kinetic with k (reaction rate constant) and K (equilibrium adsorption constant) value of 1.149 mg/ L.min and 0.0106 L/ mg respectively.

CHAPTER 1

INTRODUCTION

1.1 Water and human

The birthplace of human, Earth, consists of 70% water and 30% land. Water covers more than land on our Earth crust and shows that how much it is important to living things. Without water, one of the main source in order for living things keep on surviving and live, many consequences will be faced. Dehydration, main worries that pops out in our mind if we are lack of water resources. Day by day, our water supply is shortening, mainly by water pollution besides population growing and also climate change. Due to water contamination, human health is affected and in danger. It is not a surprise when there is a shortage of freshwater supply for us and also to the ecosystems. Yet, this phenomenon already occurred in some of the developing countries. A research survey from United Nation, reported that two out three from Earth population will be facing water-scarce regions by 2025 (Ganoulis, 2009).

There are many types of pollutant which is destroying the natural environmental water. Most of them were wastes released from industries, and some from urban areas. Hydrocarbon compounds, herbicides, textile dyes, alcohols, detergents, surfactants and more being released and disrupting our natural waterways such as rivers, lakes and oceans (Bahnmann, 2004). Even worse is the release of inorganic compounds such as mercury, nickel, cadmium, lead and also biological contaminations which are bacteria's and viruses (Bhattacharyya and Gupta, 2008, Zan *et al.*, 2007, Pigeot-Rémy *et al.*, 2012). According to a statistic, about 70% wastewater were being released into existing water supplies and untreated from industries in developing countries (UN-WWAP, 2009).

Among all pollutants, phenol is one of the main contributor in harming our nature water, which discharged from various industries such as petrochemical, oil refining, paper mills, pharmaceuticals and herbicides (Chiou and Juang, 2007). In 2009, the demand in petrochemical industries has expanded and so the worldwide production of phenol has risen up to 8 million tonnes per year (Mcmanamon *et al.*, 2011). Phenol extremely toxic organic compound and soluble in water easily (Kujawski *et al.*, 2004). Due to its toxicity, human and aquatic life is a major concern. This part will be discussed later in Chapter 2 in a very detail.

Therefore, it has become main priority to treat waste like phenol to accomplish environmental law in order to save the ecosystems and also for the human betterment. Up to now, there are several ways of treating wastewater which has been developed. There are physical, biological and chemical which have been applied. All these method have their advantages and disadvantages in treating wastewaters.

1.2 Wastewater treatment methods

Previously, conventional wastewater treatment such as filtration, sedimentation were applied to treat wastewater (Padmanabhan *et al.*, 2006). Next, various technologies have developed such as adsorption, coagulation, membrane filtration, electrolysis and biological processes (Gogate and Pandit, 2004). However, these treatments consume higher energy and operating cost, chemicals and even worst is that the waste is concentrated into solid and sludge where it is producing a secondary waste which has to be considered again (Gaya and Abdullah, 2008). Another method which has been used is chlorination where it kills bacteria's and viruses, or disinfect them. Unfortunately, there were undesired byproduct such as chloroform or trihalomethanes being produced too which are carcinogenic to human health (Yang and Cheng, 2007).