

**PHOTOCATALYTIC PHENOL REMOVAL
IN PHENOL-UREA-FORMALDEHYDE SOLUTION
ON CYANAMIDE MODIFIED IRON (III) OXIDE**

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ON CYANAMIDE MODIFIED IRON (III) OXIDE

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*This work is dedicated to my beloved parents, Roslan and Noratipah,
as well as my little sister, Nur Aina Nabilah, who has always been there for me,
and has never doubted my dreams, and also to all my friends,
who has shared the joyful tears and get through the storms that we have
weathered. I love you all.*

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ABSTRACT

Phenolic resin waste contains harmful chemical compounds such as phenol, urea, and formaldehyde that need to be treated before disposal. In this study, a series of cyanamide modified Fe_2O_3 was prepared from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as the iron precursor and cyanamide (CYA) as the carbon and nitrogen source. The cyanamide modified Fe_2O_3 was used for photocatalytic removal of phenol in the mixture of phenol-urea-formaldehyde. X-ray diffractometry patterns showed the formation of Fe_2O_3 peak. The peak intensity decreased with the increased of cyanamide mol ratio. The addition of cyanamide decreased the band gap energy of Fe_2O_3 , showing that carbon and nitrogen-based material might act as a dopant. The presence of carbon species was confirmed by diffuse reflectance UV-visible and Fourier transform infrared spectroscopy, as well as thermogravimetric analysis, especially on sample with high mol ratio of cyanamide precursor. Photoluminescence study revealed that addition of low mol ratio of cyanamide successfully decreased the electron-hole recombination, while the addition of high mol ratio of cyanamide might block the emission sites of Fe_2O_3 . Scanning electron microscope images of the samples also confirmed that samples with high mol ratio of cyanamide have a flake-type structure that coated the surface of Fe_2O_3 . In the photocatalytic removal of phenol both under UV and visible light irradiation, all prepared samples gave better photocatalytic activity than the bulk Fe_2O_3 . The best activity was achieved on Fe_2O_3 -CYA(6) catalyst with the mol ratio cyanamide to iron precursor of 6, in which the percentage of phenol removal was 75 and 80% under UV and visible light, respectively. The high activity would be due to the success suppression of electron-hole recombination, decrease of the band gap energy, and the good interaction between phenol and emission sites of Fe_2O_3 -CYA(6) catalyst, as supported by the fluorescence quenching study. The photocatalytic activity for phenol removal decreased in the presence of urea, formaldehyde, and urea-formaldehyde since there were adsorption competition as well as reaction competitions, such as oxidation of formaldehyde and formation of phenolic resin.

ABSTRAK

Sisa resin fenolik mengandung kandungan bahan kimia berbahaya seperti fenol, urea dan formaldehid yang perlu dirawat sebelum dibuang. Dalam kajian ini, suatu siri ferum(III) oksida (Fe_2O_3) terubahsuai sianamida telah disediakan daripada $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ sebagai pelopor ferum dan sianamida (CYA) sebagai sumber karbon dan nitrogen. Ferum(III) oksida terubahsuai sianamida digunakan untuk fotopemangkinan penyingkiran fenol dalam campuran larutan fenol-urea-formaldehid. Corak teknik pembelauan sinar-X menunjukkan pembentukan Fe_2O_3 , di mana keamatan puncak berkurang dengan meningkatnya nisbah mol sianamida. Pertambahan sianamida mengurangkan tenaga ruang jalur Fe_2O_3 , menunjukkan bahawa bahan berasaskan karbon dan nitrogen berkemungkinan bertindak sebagai dopan. Kehadiran spesies karbon telah disahkan dengan menggunakan pantulan serakan ultra lembayung-cahaya nampak dan spektroskopi inframerah transformasi Fourier, serta analisis termogravimetri terutama pada sampel dengan nisbah mol sianamida yang tinggi. Kajian pendarcahaya menunjukkan bahawa pertambahan nisbah mol sianamida yang rendah berjaya mengurangkan penggabungan semula elektron-lubang, sementara penambahan nisbah mol sianamida dalam jumlah yang tinggi berkemungkinan menyekat tapak pemancaran Fe_2O_3 . Imej sampel daripada mikroskop pengimbas elektron juga telah mengesahkan bahawa sampel dengan nisbah mol sianamida yang tinggi mempunyai struktur berbentuk kepingan yang menyaluti permukaan Fe_2O_3 . Dalam fotopemangkinan penyingkiran fenol di bawah sinaran UV dan cahaya nampak, semua sampel memberikan aktiviti fotopemangkinan yang lebih baik daripada Fe_2O_3 pukal. Aktiviti terbaik diberikan oleh mangkin Fe_2O_3 -CYA(6) dengan nisbah mol sianamida kepada ferum 6, yang memberikan peratusan penyingkiran fenol masing-masing 75 dan 80% di bawah cahaya UV dan cahaya nampak. Aktiviti yang tinggi oleh mangkin ini disebabkan kejayaan penyekatan elektron-lubang, pengecilan aras jalur tenaga dan interaksi yang baik antara fenol dan tapak pemancaran mangkin Fe_2O_3 -CYA(6), seperti yang disokong dalam kajian pelindap kejutan pendarfluor. Aktiviti fotopemangkinan untuk penyingkiran fenol menurun dengan kehadiran urea, formaldehid dan urea-formaldehid kerana terdapat persaingan penyerapan dan juga persaingan tindak balas seperti pengoksidaan formaldehid dan pembentukan resin fenolik.

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LIST OF ABBREVIATIONS

arb.u	-	Arbitrary unit
cm	-	centimetre
DR UV-Vis	-	Diffuse Reflectance Ultra Violet-Visible
eV	-	Electron volt
FTIR	-	Fourier Transform Infra-Red
g	-	Gram
GC-FID	-	Gas Chromatography-Flame Ionization Detector
h		Hour(s)
K	-	Kelvin
kV	-	Kilovolt
min	-	Minute(s)
mL	-	Millimetre
nm	-	Nanometre
ppm	-	Part per million
s	-	Second
SEM	-	Scanning Electron Microscopy
TGA	-	Thermogravimetric Analysis
UV	-	Ultra Violet
XRD	-	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 General Background

Phenolic resin is one type of thermosetting resins containing phenol, formaldehyde and also urea. Phenolic resins have been used in vast applications, such as plastic industry (Whitehouse *et al.*, 1967), wood adhesives (Peshkova & Li, 2003), and communication equipment (Hirano & Asami, 2013). As one of the compositions in the phenolic resins, phenol has been recognized as the most common organic pollutants, which can be easily found in the industrial waste. Since phenol can act as a carcinogenic compound to the human being, the permissible exposure limit (PEL) stated by Occupational Safety and Health is around 5 ppm (United States Department of Labour, 1996). Due to the toxicity of the phenol, many studies have been focused on the degradation of phenol. There have been many researches conducted on various methods suitable in dealing with this pollutant, such as biodegradation (El-Naas *et al.*, 2009), adsorption (Caetano *et al.*, 2009), thermal decomposition (Chen *et al.*, 2008), catalytic conversion (Katada *et al.*, 1997), and emulsion liquid membranes (Correia & Carvalho, 2003) and emulsion pertraction technology (Urtiaga *et al.*, 2009). Another method that can be acknowledged is photocatalytic degradation method that is still stands as one the preferred methods in most of the studies, owing to its clean and environmentally safe process.

Photocatalysis has been proven to be one of the efficient methods in mineralization or removal of organic pollutant (Bandara *et al.*, 2001; Yang *et al.*,

2000; Zhang *et al.*, 2010). While there have been many reports on photocatalytic removal of phenol as a single target pollutant, less attention has been made on the removal of phenol in the presence of other organic pollutants, such as in the case of phenolic resins, which contained of phenol, urea, and formaldehyde. Furthermore, most studies reported that the efficiency of the photocatalyst was restricted only to the low concentration of phenol (Araña *et al.*, 2001). Therefore, photocatalytic removal of phenol in the presence of urea and formaldehyde was investigated in this study. For this purpose, development of a highly active heterogeneous photocatalyst that able to degrade phenol even in high concentration in the presence of other pollutants is very important.

On the other hand, iron (III) oxide (Fe_2O_3) has been recognized as a good catalyst for various chemical reactions. As it also has paramagnetic properties, it can be used as a good recyclable catalyst in heterogeneous catalysis. As example, Fe_2O_3 can be reused easily for at least five cycles by collecting the catalyst using magnet (Drbohlavova *et al.*, 2009). In addition to the paramagnetic properties, Fe_2O_3 is a semiconductor that has a band gap of 2.1 eV, suggesting that it might be a potential photocatalyst under visible light irradiation. Unfortunately, it was confirmed that even though Fe_2O_3 showed its efficiency in removing phenol from water under ultra-violet (UV) light irradiation, it was not active under visible light irradiation (Roslan, 2011). Since sunlight emits more visible than the UV light, development of visible light-driven photocatalysts is a very important approach in photocatalysis study. Therefore, the photocatalytic activity of Fe_2O_3 under visible light irradiation should be improved, such as by introducing other material that is active under visible light. One of such potential materials is carbon nitride (C_3N_4) that has been reported to have band gap of 2.66 eV and absorb light up to 460 nm (Wang *et al.*, 2009a).

The C_3N_4 can be prepared by a simple thermal polymerization method using various molecular precursors reported to prepare the g- C_3N_4 , such as melamine (2,4,6-triamines-triazine) (Zhang *et al.*, 2001), $\text{C}_3\text{N}_3(\text{NH}_2)_3$ (Gillan, 2000), s-triazine (cyanuric; C_3N_3) ring compounds such as $\text{C}_3\text{N}_3\text{X}_3$ ($\text{X} = \text{Cl}, \text{N}, \text{OH}, \text{NHCl}$) (Khabasheshku *et al.*, 2000), cyanamide (Thomas *et al.*, 2008) and urea (Lee *et al.*, 2012). There are several hypothetical phases of carbon nitride, which are alpha (α),

beta (β), cubic, pseudocubic and graphitic. Among of these phases, graphitic carbon nitride (g-C₃N₄) is the most stable phase at ambient conditions and possesses the smallest band gap due to the sp² hybridization of carbon and nitrogen forming the π -conjugated graphitic planes (Molina & Sansores, 1999). Since C₃N₄ has been reported to show good photocatalytic activity under visible light irradiation for various reactions such as water splitting (Yan *et al.*, 2012) and selective oxidation of alkene (Li *et al.*, 2011), several studies on the preparation of metal oxides modified by C₃N₄ have been investigated, such as In₂TiO₅ (Liu *et al.*, 2011) and ZnO (Wang *et al.*, 2011). These prepared metal oxides modified by C₃N₄ showed better photocatalytic activities under visible light irradiation than the non-modified metal oxides.

Among the precursors of C₃N₄ mentioned above, cyanamide is of interest. In addition to formation of carbon nitride, cyanamide has been reported as a good carbon and nitrogen source in the preparation of metal nitrides (Buha *et al.*, 2007), metal carbides (Li *et al.*, 2008) and metal cyanamide (Zhao *et al.*, 2013). Therefore, in this study, Fe₂O₃ was modified by cyanamide for the first time. During the thermal calcination process, cyanamide could be converted to C₃N₄ or other carbon and nitrogen-based materials, which would help enhancing the photocatalytic activity of Fe₂O₃.

1.2 Statement of Problem

Even though Fe₂O₃ has been recognized as potential photocatalyst in the photocatalytic degradation of phenol under UV light irradiation, it was reported that Fe₂O₃ suffered from the inability to work under visible light irradiation. Since visible light dominates 46% of solar light spectrum, the development of visible light-driven photocatalyst is highly desirable. Therefore, further modification needs to be conducted in order to improve the photocatalytic activity of Fe₂O₃ under visible light irradiation. Unfortunately, there is still no established method to modify the Fe₂O₃ due to the lack understanding on how to design the Fe₂O₃-based photocatalysts.

Modification of Fe_2O_3 so that it can act as visible light-driven photocatalyst is still one challenging problem. Cyanamide is used in this study since the polycondensation process of cyanamide may lead to the formation of C_3N_4 as well as other carbon and nitrogen-based materials such as CN and NCN. This study is the first investigation on the effect of cyanamide modifier on the properties and photocatalytic activity of Fe_2O_3 . Therefore, it is still unclear and needs to be clarified if cyanamide precursor may improve the efficiency in the electron charge transfer process of Fe_2O_3 under visible light irradiation. Some parameters, such as effect of the ratio of cyanamide to Fe_2O_3 need to be explored in order to get fundamental understanding on designing the Fe_2O_3 -based photocatalysts.

While the potential ability of Fe_2O_3 photocatalyst has been recognized for photocatalytic removal of phenol, the potential photocatalytic activity of Fe_2O_3 -based photocatalysts to remove phenol in the presence of other compounds is still needs to be clarified. In addition, efficiency of phenol removal in high concentration remains unclear and further investigations need to be conducted. In the present study, the first photocatalytic degradation of phenol in the presence of urea and formaldehyde over novel Fe_2O_3 -based photocatalysts is carried out. Effect of some parameters, such as the ratio of urea or formaldehyde to phenol, on the photocatalytic activity of the Fe_2O_3 -based photocatalysts to remove phenol is still unclear and needs to be revealed.

1.3 Objectives

The main objectives of this study are:

1. To synthesize novel Fe_2O_3 -based photocatalysts that are active in the visible light region.
2. To investigate the properties of the new Fe_2O_3 -based photocatalysts.

3. To study the photocatalytic activity of the Fe_2O_3 -based photocatalysts for phenol removal under UV and visible light irradiation in the presence of urea and/or formaldehyde.

1.4 Scope of the Study

The scope of this study is shown below. For preparation of Fe_2O_3 -based photocatalysts, iron precursor used was $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. As the modifier, cyanamide was used with the mol ratio of cyanamide to iron precursor within the range of 2 to 10. The synthesis of Fe_2O_3 -based photocatalysts was carried out using one pot oxidation method at temperature of 823 K with rate of heating of 2.2 K min^{-1} . The prepared Fe_2O_3 -based photocatalysts were characterized by X-ray diffraction (XRD), diffuse reflectance (DR) UV-visible spectroscopy, photoluminescence spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and elemental analyzer. The photocatalytic activity of the prepared Fe_2O_3 -based photocatalysts was tested for removal of phenol in the presence of urea, formaldehyde, and urea-formaldehyde at room temperature. The mol ratios of phenol to urea and formaldehyde used were 1:1 and 1:300, while for phenol-urea-formaldehyde were 1:1:1 and 1:300:300. All of the reactions were conducted under both UV and visible light irradiation for 25 h. The products of photocatalytic reactions were analysed and determined by a gas chromatography equipped with flame ionization detector (GC-FID).

1.5 Significance of Study

Modification of Fe_2O_3 with cyanamide would result in a novel series of materials. Therefore, this study is important in the point of view of material science. Since Fe_2O_3 -based materials were used as a photocatalyst, this study will also give contribution in the photocatalysis science. The study on the ability of Fe_2O_3 -based photocatalysts to remove phenol into non-hazardous compound will be a stepping

stone for other researchers to explore the use of Fe_2O_3 -based photocatalysts for other reaction such as conversion as well as the use of other photocatalysts for removal of phenol. Therefore, this study will give better knowledge and understanding on both photocatalyst and photocatalytic reaction.

Study on the removal of phenol in the absence and presence of other organic pollutants, such as urea and formaldehyde by photocatalytic reaction is very important in the point of view of green technology to reduce environmental problems. As we know, phenol is one of the most toxic compounds found in industrial waste water. It is expected that the findings from this research will enrich our knowledge on the fundamental studies of converting toxic organic compound in industrial waste water into non-hazardous compound, thus minimizing the harmful effects towards human being.

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