Effect of Catalyst Loading on Photocatalytic Degradation of Phenol by Using N, S Co-doped TiO₂

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Abstract. The study on the effect of catalyst loading of photocatalytic degradation of phenol by using N, S co-doped TiO₂ was investigated. The precursor of titania was Titanium (IV) isopropoxide (TTIP), while the sources of Nitrogen and Sulfur were ammonium nitrate and thiourea respectively. The photocatalyst were prepared by using dopant concentration at 1% of both Nitrogen and Sulphur that were prepared via sol-gel method. The photocatalyst were tested by different catalyst loading which were 1 g/L, 2g/L and 3 g/L. The gel obtained from the mixing process was dried and calcined at 600 °C. The performance of the photocatalyst were tested by using phenol as a model pollutant. The mixture of photocatalyst and pollutant was left under visible light for five hours for irradiation time. The experiment showed that catalyst loading of 3 g/L able to fully degrade phenol while 1 g/L and 2 g/L of photocatalyst degraded phenol at 69.9% and 96.2% respectively.

1. Introduction

Growing numbers of chemical industrial can produce tonnes of phenolic compounds in their effluent. Some of the examples are production of resins, coal conversion, petrochemical; and pharmaceutical industries [1,2]. The toxicity of phenol can affect aquatic microorganisms and can be lethal to fish at concentrations of 5 to 25 mg/L. Meanwhile, exposure towards human can cause damage towards internal organs. Hence, the World Health Organization (WHO) regulates the phenol concentration must not exceed 1 µg/L in drinking waters [2,3].

There are many treatments available to remove phenol completely by physical, biological and chemical means. One of the popular method of physical treatment is physical adsorption via activated carbons due to the effectiveness and low in cost [4]. The activated carbons can be made up of various materials such as wood, coconut shells, coal, date-pit, tamarind bean etc.[1,5,6]. Meanwhile, biological treatment of phenol is utilizing microorganisms from many genera which includes Pseudomonas, Bacillus, Aspergillus and others. The microorganisms are used in forms of pure, mixed culture and immobilized cells [7]. Other than that, the chemical treatment of phenol is via chemical oxidations by
using chlorine, ozone, hydrogen peroxide and potassium permanganate and chlorine dioxide are used to treat phenol [8].

Ozone (O$_3$) and hydrogen peroxide (H$_2$O$_2$) are capable in oxidizing inorganics to their higher oxidation while at the same time organic compounds are being oxidized into carbon dioxide and water. Since both methods have lower reaction rate if being used alone without ultraviolet (UV) radiation, the development of Advanced Oxidation Processes (AOPs) was applied to cater the problem. The UV rays were used with ozone or hydrogen peroxide to generate hydroxyl radicals which will cause the complete elimination of organic chemicals [9,10]. Some examples of AOPs in phenol treatment are photocatalytic degradation, electrochemical oxidation, photo-Fenton and sono-Fenton etc. [9]. In addition, photocatalytic degradation by titanium dioxide (TiO$_2$) and zinc oxide (ZnO) show promising results when it comes to phenol treatment. The usage of titania is very common because of the high efficiency, inexpensive and non-toxic [11].

According to Ahmed, Rasul, Martens, Brown, & Hashib (2010); photocatalytic activity of titania are reliant on surface and structural properties of the semiconductor in which including the surface area, crystal composition, particle size distribution, band gap and others. These factors have a huge impact on the adsorption behaviour during degradation of pollutants. Titanium dioxide photocatalyst are proven many times in treatment of organic pollutants despite its high band gap energy (3.2 eV) which requires UV light for photoactivity. By introducing other elements such as Nitrogen, Carbon, Sulphur and Ferum as dopant, the band gap energy can be reduced [13]. The photocatalytic degradation efficiency is highly dependent on the catalyst loading. The optimum catalyst loading can vary from 0.6 g/L of photocatalyst up to 2.5 g/L based on review by Ahmed et al. (2010)[12]. Past researches showed that the rate increased proportionally with catalyst loading but started to decrease at excessively high values as light scattering and screening effects tend to become lower. At high catalyst loading, the surface area of the photocatalyst tend to become lower because of agglomeration (particle-particle interaction) in which may affect the light absorption.

In this study, the effect of catalyst loading of photocatalytic degradation of phenol by using N, S co-doped TiO$_2$ was investigated. The photocatalyst was synthesised by using sol-gel method. The photocatalyst was characterized with XRD and FE-SEM and the degradation efficiency was tested at catalyst loading of 1 g/L, 2 g/L and 3 g/L under visible light.

2. Methodology
2.1. Preparation of Photocatalyst via Sol-gel Method
The N, S co-doped TiO$_2$ photocatalyst was prepared by using Titanium (IV) isopropoxide (TTIP) as the titania precursor while using ammonium nitrate (NH$_4$NO$_3$) and thiourea (CS(NH$_2$)$_2$) were used as nitrogen and sulphur sources respectively. Ethanol (C$_2$H$_5$OH) and analytical reagent (AR) grade of acetic acid (CH$_3$COOH) were used in the present study as solvents. The amount of NH$_4$NO$_3$ and thiourea were weighed based on the dopant concentration which were 1% nitrogen and 1% sulphur. The dopants were added with 180 mL deionized water and 20 mL acetic acid and labelled as Solution A. On the other hand, 60 mL TTIP were dissolved in 200 mL ethanol and labelled as Solution B. The Solution A was added to Solution B in a dropwise manner with constant stirring for an hour. Later, the solution was left stirred at 200 rpm by using magnetic stirrer for another 2 hours until gel was formed. The gel was covered with aluminium foil and left 24 hours for aging phase. The gel was dried in oven at 100 °C until fully dried. The dried photocatalyst were ground and calcined at 600 °C for 3 hours at 5 °C/min as the heating rate.

2.2. Characterization of Photocatalyst
The photocatalyst were characterized by using X-ray Diffractometer (XRD model: Rigaku Ultime IV) with a Cu Kα radiation. The scanning rate of XRD was 5°/min in a 2θ range of 20 – 80° to analyse the phases of the crystals. The morphologies of the photocatalyst were observed by using Field Emission-Scanning Electron Microscope (FE-SEM, model DSM 982 Gemini Supra 40VP).
2.3. Photocatalytic Degradation Study
The photocatalytic degradation was carried out by using phenol prepared with the starting concentration of 15 mg/L and volume of 100 mL. Later, 1g/L of photocatalyst was weighed and added to the solution. The solution was placed inside a photoreactor equipped with 24W Philips Compact Fluorescent Lamp (CFL) at the height of 6 cm from the beaker which acted as a visible-light source. The solution was stirred in the dark for 30 minutes to ensure in equilibrium state. The solution was left stirred for five hours and 5 mL sample was collected in every 30 minutes interval. The collected samples were centrifuged for 10 minutes at 10,000 rpm to separate phenol and the photocatalyst. The concentrations of phenol were recorded to determine the degradation rate. The steps were repeated for 2 g/L and 3 g/L of catalyst loading.

The quantifications of phenol were analysed by using rapid colorimetric estimation by Martin (1949). The reagent will turn from yellow to reddish colour in the presence of phenol. The solutions were left for 15 minutes followed by absorbance measurement at wavelength of 510 nm. The degradation efficiencies of phenol were calculated by using Equation (1).

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\eta = \frac{C_o - C_t}{C_o} \times 100\%
\]

where:
- \(\eta\): phenol degradation efficiency
- \(C_o\): initial concentration of phenol
- \(C_t\): concentration of phenol at specific time

3. Results and discussions
3.1. Characterization of Photocatalyst
The X-ray diffraction (XRD) pattern for the N, S-TiO\(_2\) photocatalyst is shown in Figure 1. The XRD pattern is used to determine the phase constitution and the crystallite size of the photocatalyst [15]. From the result, characteristic peak at 2\(\theta\) = 25.356\(^o\) was obtained that represent anatase phase (JCPDS file number = 01-089-4921). There are no trace of rutile and brookite phases which is favourable because anatase has better photocatalytic activity than other phases [16,17].

![Figure 1. XRD patterns of 1.0% N, S-TiO\(_2\) (fitting well with JCPDS file number 01-089-4921)](image)

The surface morphology of the photocatalyst by FE-SEM can be referred in Fig. 2. The figure shows spherical particles, unevenly sized and agglomeration occur at certain area. The agglomeration can occur due to the formation of solid bridge between surface hydroxyl groups during drying process or
combination of particles after being exposed to high temperature while calcination [18,19]. Agglomerated particles is undesirable because of reduction the surface area of the photocatalyst and eventually affecting the degradation performance of phenol [17].

Figure 2. Surface morphology of N, S-TiO$_2$ photocatalyst depicted by FE-SEM.

3.2. Effect of Catalyst Loading on Photocatalytic Degradation of Phenol
The effect of catalyst loading on photocatalytic degradation of phenol were studied by using the amount of catalyst of 1 g/L, 2 g/L and 3 g/L. The photocatalytic degradation of phenol against time is shown Figure 3. From the figure, the concentrations of phenol declined gradually but increased at some point. The increased of concentrations of phenol might be because of the separation process between phenol and photocatalyst. During separation via centrifuge, the residue of the photocatalyst powder may still left inside the sample and affect the light penetration during quantification of phenol.

The fastest degradation of phenol at 3 g/L in which took only 4.5 hours to complete and had the steepest slope. On the other hand, the other catalyst loading were unable to degrade within the given irradiation time. By using Equation (1), 3 g/L of photocatalyst loading shown the highest photodegradation performance which is 100.0%. Whereas 1 g/L and 2g/L of photocatalyst loading resulting in 69.9% and 96.2% degradation of phenol respectively.

The results suggest that the degradation performance increase proportionally with the catalyst loading which is comparable to a review by Ahmed et al. (2010) which state the optimum loading of phenol by using titania photocatalyst was 2.0 g/L using UV light as the light source. Therefore, it can be surmised that doping Nitrogen and Sulphur to TiO$_2$ at the highest loading (3 g/L) corresponds to highest phenol degradation rate as energy band gap of TiO$_2$ is reduced allowing visible light as the light source. The best catalyst loading for N, S-TiO$_2$ is 3 g/L. However, at higher catalyst loading, the degradation efficiency can be expected to decrease because of agglomeration and thus lower the photocatalytic activity.
4. Conclusions
N, S-TiO$_2$ photocatalyst was prepared via sol-gel method at dopant concentration of 1%. The characterization of photocatalyst shows anatase phase transformation of TiO$_2$. From FE-SEM results, the surface of the photocatalyst was unevenly sized and agglomeration occur at certain areas. The photocatalyst was tested for effect of catalyst loading on degradation of phenol. The catalyst loading of 3 g/L able to fully degrade phenol and taken the least time to complete the degradation.

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References
[1] Al-jiboury K F C 2013 Adsorption of Phenol from Industrial Wastewater using Commercial Powdered Activated Carbon
[2] Al-Khalid T and El-Naas M H 2012 *Crit. Rev. Environ. Sci. Technol.* **42** 1631–90
[3] Banerjee A and Ghoshal A K 2011 *Int. Biodeterior. Biodegradation* **65** 1052–60
[4] Dakhil I H 2013 Removal Of Phenol From Industrial Wastewater Using Sawdust *3* 25–31
[5] El-Naas M H, Al-Zuhair S and Alhaija M A 2010 *Chem. Eng. J.* **162** 997–1005
[6] Kulkarni, Sunil J and Kaware J P 2013 *Int. J. Sci. Res. Publ.* **3** 1–5
[7] Basha K M, Rajendran A and Thangavelu V 2010 Recent advances in the Biodegradation of Phenol : A review *1* 219–34
[8] Diya’Udeen B H, Daud W M A W and Abdul Aziz A R 2011 *Process Saf. Environ. Prot.* **89** 95–105
[9] Babuponnusami A and Muthukumar K 2011 *Clean - Soil, Air, Water* **39** 142–7
[10] Oller I, Malato S and Sánchez-Pérez J A 2011 *Sci. Total Environ.* **409** 4141–66
[11] Velasco L F, Parra J B and Ania C O 2010 *Appl. Surf. Sci.* **256** 5254–8
[12] Ahmed S, Rasul M G, Martens W N, Brown R and Hashib M A 2010 *Desalination* **261** 3–18
[13] Sikirman A, Krishnan J and Mohamad E N 2014 Appl. Mech. Mater. 661 34–8
[14] Martin R W 1949 Rapid Colorimetric Estimation of Phenol 1419–20
[15] Yu C, Cai D, Yang K, Yu J C, Zhou Y and Fan C 2010 J. Phys. Chem. Solids 71 1337–43
[16] Rahimi R, Safalou Moghaddam S and Rabbani M 2012 J. Sol-Gel Sci. Technol. 64 17–26
[17] Hamadanian M, Reisi-Vanani a. and Majedi a. 2010 J. Iran. Chem. Soc. 7 S52–8
[18] Sikirman A, Krishnan J, Jai J and Senusi F 2014 Adv. Mater. Res. 894 245–9
[19] Krishnan J, Mohamad E N and Hadi A 2014 Adv. Mater. Res. 661 63–7