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Photocatalytic restoration of liquid effluent from oil palm agroindustry in Malaysia using tungsten oxides catalyst

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ABSTRACT

In the current work, the photocatalytic treatment of palm oil mill effluent over tungsten oxides photocatalyst under ultraviolet-irradiation was evaluated. Characterization of fresh and used tungsten oxides photocatalyst was accomplished via X-Ray Diffraction, Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis, Ultraviolet–Visible Light Diffuse Reflectance Spectroscopy, and Fourier Transformed-Infrared Spectroscopy. Photocatalytic treatment of palm oil mill effluent was conducted to determine the effects of catalyst loading, longevity, and recyclability of the tungsten oxides photocatalyst, as well as the effect of pH alteration on palm oil mill effluent. During the photocatalytic reaction, the collected liquid sample was tested for chemical oxygen demand, pH, and colour intensity while the gaseous sample was analyzed via gas chromatography. The optimum catalyst loading was 0.5 g/L, corresponds to highest photocatalytic degradation (51.15%) and decolourization (96.21%). The pH alteration on palm oil mill effluent has negligible effect on its photocatalytic degradation with UV/WO_3 system. For longevity study, the optimum reaction time was 16 h, which achieved 84.70% photocatalytic degradation and 98.28% photocatalytic decolourization. From the recyclability study, it can be concluded that the tungsten oxides photocatalyst is suitable for photocatalytic decolourization of palm oil mill effluent, but not suitable for photocatalytic degradation. In addition, analysis of the gaseous product showed that the photocatalytic treatment has successfully degraded the organic pollutants in the liquid effluent into methane and carbon dioxide.

1. Introduction

According to Malaysian Palm Oil Council (MPOC, 2016), the oil palm industry in Malaysia presently accounts for 39% of production and 44% of exports for palm oil in the worldwide. Malaysia is the largest exporter of refined palm oil despite that it is the second-largest contributor to world production of the oil, behind only to the Indonesia. Although oil palm industry appears as one of the most structured agro-industry in Malaysia, the milling process can generate massive colloidal wastewater often known as palm oil mill effluent (POME). This is because a traditional milling process employs steam for sterilization process. Unfortunately, this process is a precursor to the formation of POME waste that is less environmentally-benign (Law et al., 2016). From the previous study, it was discovered that the processing of every ton of crude palm oil would produce approximately 2.5–3.75 tons of POME (Ahmad et al., 2003).

POME is a viscous, thick brownish and colloidal liquor that mainly consists of water (95–96%), total solids (4–5%, included 2% suspended solid) and oil (0.6–0.7%) (Wongfaed et al., 2015). Raw POME is acidic with pH ranging from 4 to 5, and is hot, as the milling process occurs at 80 °C–90 °C (Tabassum et al., 2015). POME is brownish as it contains appreciable amounts of lignin, tannin, humic acids, lipids and fatty acids that originate from industrial steam extraction (Saeed et al., 2015). A rapid expansion of palm oil production in Malaysia is generating large volume of POME wastewater. Without proper treatment, POME will inflict serious environmental pollution. Although POME is non-toxic, it possesses high chemical oxygen demand (COD) ranging from 15,000 to 100,000 ppm and high biochemical oxygen demand (BOD) that ranged from 10,250 to 43,750 ppm (Madaki and Lau, 2013). Indeed, COD and BOD are parameters that reflect the number of organic pollutants present in wastewater. Therefore, prior to discharge, the raw POME must be treated by POME treatment facility in order to

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meet the mandatory discharge standard to negate its environmental impact.

As stated by Malaysian Palm Oil Board (MPOB, 2016), prevalent POME treatment systems adopted by most of the palm oil mills in Malaysia are open ponding, open anaerobic digestion coupled with extended aeration, and closed anaerobic digestion coupled with the land application, specifically > 91% of palm oil mills in Malaysia opted for open ponding system (MPOB, 2016). The major drawbacks of open ponding system for treatment of POME are long hydraulic retention time (typically 66 days) for degradation, dissipation of greenhouse gas (namely CO_2 and CH_4) into the environment, the emanation of bad odour and land-intensive (*circa* 10–12 acres of land) (Ding et al., 2016; Tabassum et al., 2015). The discharge of POME above its permissible value is happening as enforcement is difficult; therefore, a more efficient and greener pathway is needed to degrade the organic pollutant. Tabassum and co-workers (Tabassum et al., 2015) highlighted several new POME treatment methods that have been studied, *viz.* ultrafiltration, membrane technology, coagulation, flotation, evaporation, adsorption, anaerobic and aerobic biodegradation. Although these techniques exhibit different mechanisms, their ultimate goals are to reduce the quantity of organic pollutant and to remove the colour. For instance, Amat and co-workers (Amat et al., 2015) employed membrane technology for polishing of anaerobically-treated POME, particularly 100% total organic carbon removal and 98% decolourization were accomplished with NF270 commercial membrane.

It is envisaged that photocatalysis could offer a promising new treatment method for POME by the virtue of its green approach and excellent performance in degradation of organic pollutants (Cheng et al., 2015, 2016; Ng and Cheng, 2015, 2016; Ng et al., 2016). For the details, Cheng et al. (2015) studied the photocatalytic degradation of POME using Pt-doped TiO_2 catalyst within a timeframe of 8 h, whereby 90.0% and 11.0% photodegradation were accomplished for 100-W visible and UV light irradiation respectively. Cheng et al. (2016) and Ng et al. (2016) proved that photocatalysis treatment of POME using Ag-doped TiO_2 is viable, in which catalyst used in both studies were synthesized via different preparation methods. Ng and Cheng (2015) reported photomineralization of POME over UV-responsive TiO_2 photocatalyst while Ng and Cheng (2016) undertaken quite a similar work except that ZnO was used. Photocatalysis pathway shows significant decomposition of organic pollutants via by utilizing light energy from solar spectrum to activate semiconductor photocatalyst (Kondarides, 2010). Significantly, there are voluminous review papers detailing major breakthroughs in photocatalysis field. To name a few, Kou and co-workers (Kou et al., 2017) have outlined comprehensive strategies to enhance the photocatalytic performance of photocatalysts via modification of their band gap, shape, and surface morphology, as well as synthesizing composites. In addition, Putri and co-workers (Putri et al., 2016) have discussed the physicochemical properties of graphene oxide (GO) as an efficient carbocatalyst in photocatalytic applications.

Tungsten trioxide (WO_3) recently gains increasing attention as it can absorb visible or UV light (Shukla et al., 2016). WO_3 is an n-type semiconductor oxide with a band gap energy in the range of 2.5 eV–3 eV (Shukla et al., 2016). It has several notable features that are advantageous for photocatalysis, *viz.* high stability during irradiation, cheap, non-toxic, exhibits strong absorption in solar spectrum and resilient towards photo-corrosion (Kumar and Rao, 2015; Shukla et al., 2016; Usami et al., 2012). It is a well-known fact that the solar spectrum consists of 46% visible light and only 5% of UV light, hence previous research works mainly concern on the photocatalytic treatment using WO_3 under visible light illumination. Research discovers that WO_3 is an excellent visible light photocatalyst due to its narrow band gap energy. Ghasempour and co-workers (Ghasempour et al., 2015) reported that > 92% of *E. coli* bacterial inactivation was obtained after 24 h of photoinactivation using visible light/WO_3 system. However, the effectiveness of photocatalytic degradation using WO_3 under UV-irradiation has been rarely discussed. It has been proved before that WO_3 also possesses significant photocatalytic activity, even under UV-irradiation, with 50% conversion of NO in about 20 min (Luévano-Hipólito et al., 2014).

Specifically, this research aims to study the photocatalytic treatment of POME over WO_3 photocatalyst under UV-irradiation. The physicochemical properties of WO_3 photocatalyst prior and after the photocatalytic reaction was obtained via four insightful characterization techniques, *viz.* X-Ray Diffraction (XRD), UV–Vis Diffuse Reflectance Spectroscopy (UV–Vis DRS), Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX), and Fourier Transform Infrared Spectroscopy (FTIR). Simultaneously, the photocatalytic treatment of POME was performed to study the photocatalytic activity of WO_3 from the aspects of catalyst loading, pH alteration, longevity, and recyclability. Throughout the photocatalytic reaction, the collected liquid sample was tested for COD, pH, and colour intensity while the gaseous sample was analyzed via gas chromatography (GC).

2. Materials and method

2.1. Photocatalyst, chemicals, and POME sample

Tungsten oxide (WO_3) with a purity > 99% used in this study was purchased from Acros Organics Company while the high range COD reagent (20–1500 mg/L) was procured from Hach Company. Zero-grade oxygen gas was used as an O_2 source in photocatalytic treatment whereas acetone (CH_3COCH_3) with a purity > 99.5% was diluted to 0.1 M for the use as a washing agent for spent WO_3 in recyclability study. The POME in this study was collected from a settling pond of a local mill located in Kuantan, Malaysia to avoid the variation in POME composition.

2.2. Pre-treatment of POME sample

During sampling process, the POME waste was stored in a black, air tight container to prevent stray light exposure and was immediately transported to the laboratory. Fresh POME liquor with approximately 400 ppm COD concentration was impenetrable to light; hence, it needs to undergo vacuum filtration twice to eliminate solid suspensions. For vacuum filtration purpose, Whatman Grade 1 qualitative filter paper with 125 mm diameter and mean pore size of 11 μm made from cellulose material was employed. Subsequently, it was further diluted with deionized water to 200 ppm of COD concentration. In order to prevent pre-photocatalytic reaction disturbance like microbial-biodegradation from occurring, the pre-treated POME liquor was stored in a 4 °C chiller, a method that was employed by Cheng and co-workers (Cheng et al., 2015).

2.3. Characterization of fresh and post-reaction WO_3 photocatalysts

The UV–Vis Diffuse Reflectance Spectroscopy (UV–Vis DRS) was performed for fresh WO_3 and used WO_3 (without washing with 200 mL of 0.1 M acetone). For UV–Vis DRS analysis, the UV–Vis spectra of WO_3 were generated on a Perkin Elmer Lambda 1050 UV/Vis/NIR Spectrophotometer that was equipped with a snap-in integrating sphere. The instrument can measure the optical absorbance of photocatalysts at wavelengths that ranged 200–900 nm. Subsequently, the Knee method introduced by Bhatnagar and Subrahmanyam (1982) was employed to determine