Removal of organic pollutants from sugarcane stillage using UV-assisted Fenton process

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Abstract. Stillage or distillery wastewater have been reported as industrial effluent that are difficult to be treated as its discharge in the water bodies presents contamination with recalcitrant and non-degradable pollutants. Due to their complicated structure, stillage treatment process using traditional methods such as adsorption, coagulation, and flocculation is challenging. Fenton reaction has been found as an effective method to degrade these contaminants through hydroxyl radicals. In this study, the removal of pollutants in stillage was investigated using UV-assisted Fenton process. Experiments was conducted for 60 minutes in a batch reactor with initial pH of stillage 4.5, UV lamp of 395-400 nm, and constant speed of 250 rpm, while the dosages of H_2O_2 and Fe (II) were kept constant at 3.3 g/L and 0.6 g Fe/L, respectively. The profile of chemical oxygen demand (COD) removal, pH, temperature, and oxidation-reduction potential (ORP) was evaluated under three dilution factors of raw stillage (1/10; 1/25; and 1/50) during treatment process to investigate the effects of these parameters on treatment efficiency. It has been observed that initial COD of stillage had considerable effect on the performance of UV-photo-Fenton treatment, as higher dilution factor increases the removal efficiency of COD from stillage. The degradation of COD by UV-assisted Fenton was found to be suitably described by the pseudo-first-order kinetics. The results obtained from this work indicated that UV-Fenton can be introduced as a successful advanced treatment process for efficient degradation of stillage.
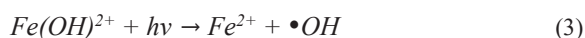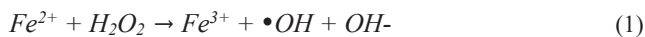
1 Introduction

In recent times, there has been a growing recognition of the significance of bioethanol biorefineries. Between 2000 and 2017, there has been a substantial tenfold increase in global biofuel production, soaring from 16 billion liters to 143 billion liters [1]. This surge is largely attributed to certain countries making a transition from fossil fuels to biofuels, with a particular focus on bioethanol. Bioethanol boasts numerous advantages when compared to fossil fuels, including being a cost-effective alternative, less detrimental to the environment,

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biodegradable, minimally toxic, and sourced from renewable resources. To transition away from fossil fuels and embrace alternative energy sources, bioethanol stands out as a highly promising choice. Nevertheless, it's worth noting that in the process of producing bioethanol, approximately 9-14 liters of liquid byproduct, commonly referred to as stillage or vinasse, are generated for every liter of ethanol produced [2, 3]. Generally, this wastewater is directly discharged to water bodies such as river and sewer. However, stillage attracted some concern related to the hazardous impact to the environment, as it contains emerging pollutants that are toxic to terrestrial and aquatic wildlife. Prior studies reported stillage is highly acidic and has a low pH due to the presence of organic acids [4]. Excessive organic matter in this wastewater can lead to elevated soil salinity and groundwater contamination. Furthermore, its chemical composition varies significantly, primarily determined by the raw materials employed in bioethanol production, such as sugarcane, sugar beet, molasses, corn, or cellulose. Its primary attributes include a dark brown hue, acidic pH levels ranging from 3.5 to 5.0, a substantial concentration of organic matter, and salinity with high levels of potassium (K), calcium (Ca), and magnesium (Mg) [5-7]. These characteristics may pose environmental challenges, underscoring the necessity for proper treatment. In addition, the complex characteristics of stillage causes limitations in applying methods to treat this wastewater [8]. Thus, an appropriate treatment technology is needed to be further investigated to ensure the sustainable and responsible handling of stillage and mitigating its environmental impact.

Advanced oxidation process (AOP) Fenton is considered as attractive and environmentally friendly water treatment techniques for the removal of pollutants because of their high chemical stability. In AOP Fenton, the contaminants can be converted into readily degradable small organic compounds (CO_2, H_2O, and inorganic ions) by generating highly reactive and non-selective hydroxyl radicals (•OH). AOP Fenton can be combined with ultraviolet (UV) illumination (photo-Fenton), ultrasound (sono-Fenton), or ozonation to increase the production of •OH [9-11]. UV-photo-Fenton method is considered as a promising hybrid treatment process for disposal of highly concentrated organic wastewater due to the UV light could accelerate the activation of oxidants [12, 13]. Furthermore, UV waves have a germicide effect on pathogenic microorganisms, virus, and bacteria [14]. UV-photo-Fenton process can be conducted using mercury, halogen, or fluorescent lamp as a source of UV light. The choice of key factors such as UV light sources, UV light types, and radiation time is crucial during the application of this method. Therefore, a suitable UV light source and irradiation time is needed to be investigated to get the optimum result. The mechanism of photo-Fenton reaction is shown in Equation (1) - (3) below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH- \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OH)^{3+} + \bullet OH \tag{2}$$

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + \bullet OH \tag{3}$$

In this study, a UV-assisted Fenton reaction was carried out to remove organic pollutants from stillage. Through the utilization of this approach, the objective is to subject the contaminants present in stillage to further degradation via hydroxyl radicals, rendering them more readily biodegradable. The objectives of this study are to investigate the performance of UV-photoFenton process based on its parameters such as pH, temperature, oxidation-reduction potential (ORP), and organic pollutants removal by varying dilution factor of the stillage samples. The UV-photoFenton process was also further assessed by evaluating the degradation kinetics using pseudo first-order model.

2 Methodology

2.1 Materials

The stillage for this study was kindly supplied by one of bioethanol industry in Yogyakarta, Indonesia which used sugarcane molasses as raw materials. Stillage was stored at 4℃ until it was used. Table 1 shows the main physical and chemical characteristics of the stillage used in this study. The chemical reagents used in this study included ferrous sulfate heptahydrate ($FeSO_4.7H_2O$, Merck), hydrogen peroxide 30% (H_2O_2 30% w/w, Merck), natrium hydroxide (NaOH, Merck), and aquadest.

Table 1. Chemical properties of stillage

Parameters	Units	Value
Chemical oxygen demand (COD)	mg/L	52,880
Biological oxygen demand (BOD)	mg/L	26,560
Iron (Fe)	mg/L	72.60
Potassium (K)	mg/L	560
Sulfate (SO_4)	mg/L	228

2.2 UV-photoFenton treatment

The UV-photo-Fenton experiments were performed in a lab-scale batch reactor with 1,000 mL capacity with UV-system installed in the top of reactor as shown by schematic drawing in Figure 1.
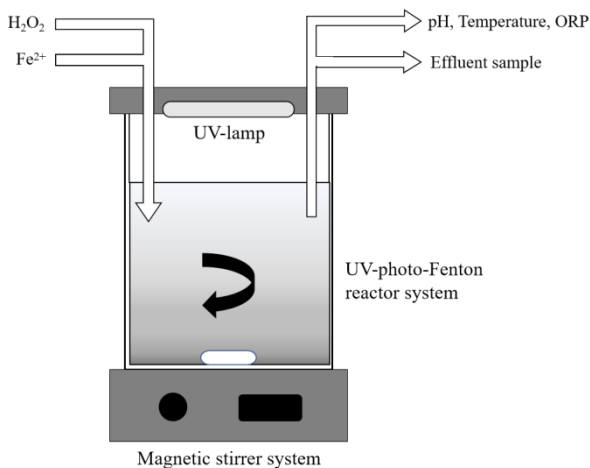

Fig. 1. Schematic diagram of UV-photo-Fenton reactor

In this study, three different dilution factors of raw stillage (1/10; 1/25; and 1/50) were used to investigate the effects of these parameters on treatment efficiency. The UV lamp (395-400 nm) was warmed up for 15 minutes and the reactor was loaded with 500 mL stillage solution (diluted accordingly with aquadest). Required amounts of $FeSO_4.7H_2O$ and H_2O_2

were added to the sample. The designed dosages of Fe (II) and H_2O_2 were kept constant at 0.6 g Fe/L and 3.3 g/L, respectively [15]. With initial pH 4.5, the solution was constantly agitated (250 rpm) by magnetic stirrer at ambient temperature for 60 minutes for the completion of the reaction. During the reactions, the pH values varied freely without any hand correction. At defined time intervals (15 minutes), samples were taken and analysed in terms of pH, temperature, and oxidation-reduction potential (ORP). After 60 minutes, the pH of the solution was then adjusted to 7 using NaOH (2M) to quench Fenton reaction. After precipitation, the samples were subjected for COD measurement.

2.3 Analytical methods

Different parameters were measured to determine the effect of the Fenton treatments. The profiles of pH, temperature, and ORP values were measured and recorded by pH meter, thermometer, and ORP meters, respectively. COD of the samples were measured according to Standard Methods (APHA5220-D). Removal percentage of COD was calculated using the following equation:

$$\%COD\ Removal = \frac{c_0 - c}{c_0} \times 100\% \qquad (4)$$

c_0 : initial concentration of COD (mg/L)
C : residuals concentration of COD (mg/L)

3 Results and Discussion

3.1 Effect of dilution factor on organic pollutants degradation

Considering the complex characteristics and high content of organic matter in stillage, it is difficult to understand the degradation of the single compounds present in this wastewater. Thus, the organic pollutants in this research, were quantified using the measurement of chemical oxygen demand (COD), as this parameter provides an overall assessment of organic matter concentration. The impact of the UV-photo-Fenton treatment was assessed by examining the extent of COD removal. To explore how the initial COD influences COD removal efficiency, experiments involving three dilution factors of the stillage (1/10; 1/25; 1/50) were conducted. Figure 2 shows that dilution factor or initial COD of stillage had significant effect on the COD profile during UV-photo-Fenton treatment.
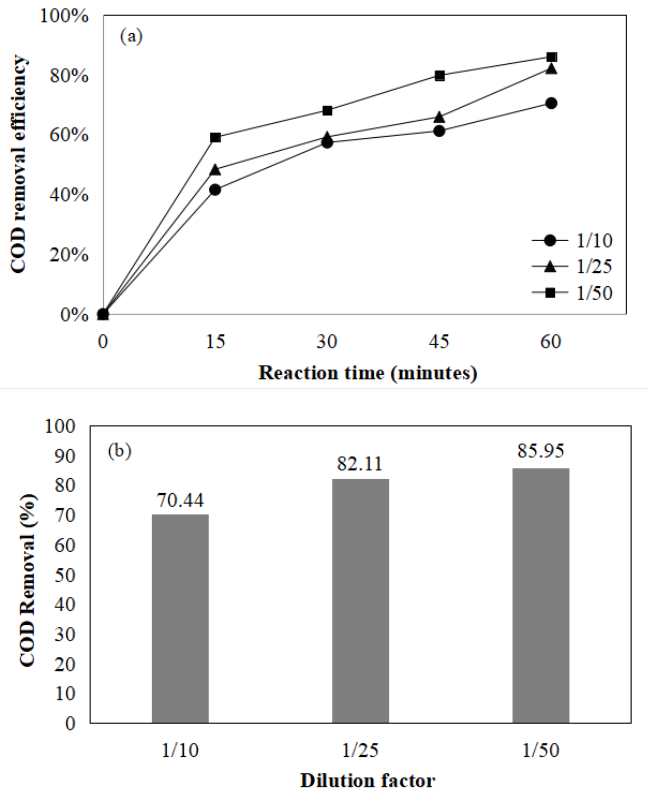
Fig. 2. Effect of dilution factor of stillage on the: (a) profile of COD removal efficiency and (b) total COD removal during UV-photo-Fenton treatment

As presented in Figure 2, COD removal of stillage after treated by UV-photo-Fenton reaction can reach around 70-85%. It is shown that the highest percentage of COD removal obtained at the highest dilution factor (1/50). It indicates that higher dilution factor increases the degradation of COD from stillage. During photo-Fenton reaction, the formation of hydroxyl radicals ($\cdot$OH) plays important role. Higher concentration of initial organic substrate in stillage requires higher amount of $\cdot$OH. Higher dilution factor means that the initial concentration of organic pollutants or COD in stillage is lower. Therefore, $\cdot$OH can effectively degraded the organic matters. Meanwhile in higher concentration, hydrogen peroxide added in solution could compete with organic matters to react with $\cdot$OH, which leads to undesirable consumption of $\cdot$OH [16].

3.2 Effect of dilution factor on UV-photo-Fenton performance

Various dilution factors of stillage (1/10; 1/25; 1/50) were experimentally evaluated in this study. As presented in Figure 3, dilution factor had considerable effect on the performance of UV-photo-Fenton treatment based on particular parameters: (a) pH, (b) temperature, and (c) oxidation-reduction potential (ORP).
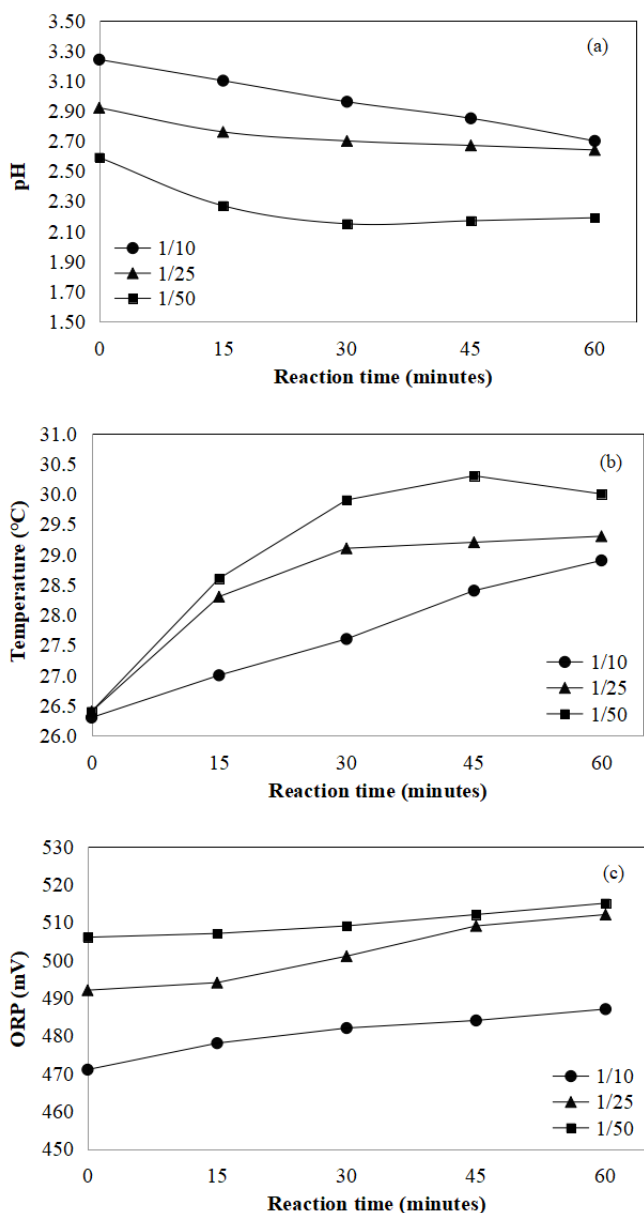
Fig. 3. Effect of dilution factor of UV-photo-Fenton performance in terms of: (a) pH, (b) temperature, and (c) oxidation-reduction potential (ORP) profile during reaction

The profile that occurred in the monitoring of pH, temperature, and ORP during UV-photo-Fenton reaction is presented in Figure 3. Figure 3(a) shows that the initial pH of the solution decreased by rising the dilution factor. Highest dilution factor (1/50) dropped pH of the solution from 4.5 (initial pH of raw stillage) to 2.6, while pH for dilution factor 1/10 and 1/25 were 3.2 and 2.9, respectively. This condition is in accordance with previous research findings that suggest the optimum pH for Fenton reaction is in the range of 2.5 to 5 [17, 18]. Based on the value of COD removal of stillage after being treated by UV-photo-Fenton, the

optimum condition in this study is obtained by dilution factor of 1/50 as 85.95% COD was successfully degraded.

In this work, all experiments were conducted at ambient room temperature, as previous research has indicated that the temperature of wastewater has minimal impact on the efficiency of COD removal in Fenton's oxidation [19]. From Figure 3(b), the temperature of solution was typically increased during 60 minutes. The highest temperature (30°C) was reached by stillage with dilution factor of 1/50, while other dilution factors (1/10 and 1/25) raised the solution temperature less than 3°C.

UV-photo-Fenton process involves both reduction and oxidation reactions. Thus, variations of ORP values were presented during the process. Analysis of the ORP values could be linked to the production of •OH during the reactions. The ORP values typically increased during the reaction for all dilution factors as shown by Figure 3(c), while the highest ORP was achieved by stillage sample with dilution factor 1/50. The ORP, which was initially 506 mV, increased to maximum ORP value of 515 mV, which indicated high oxidizing condition during photo-Fenton reaction that correlated to the high amount of •OH generated from hydrogen peroxide in the solution [20].

3.3 Kinetic study of degradation process

The decreasing concentration of organic pollutants (COD) in this study can be considered as degradation process by UV-photo-Fenton reaction. The profile of COD removal percentage value as a function of time were used to evaluate the kinetic of degradation process of organic pollutants in this study. The kinetics for oxidation of the organic pollutants by UV-photo-Fenton process can be represented as follows:

$$\frac{dC_p}{dt} = -k_p C_p C_{\cdot OH} \tag{5}$$

Thus, the data related to COD removal (from Figures 1) can be analyzed using the pseudo-first order equation:

$$ln\frac{[C]_0}{[C]} = k_1 t \tag{6}$$

C_0 : initial concentration of COD (mg/L)
C : residuals concentration of COD (mg/L)
k_1 : constant of pseudo-first order equation (min^{-1})
t   : time (min)

The pseudo-first order rate constant is derived by determining the slope through a linear least-squares fit applied to the logarithmic plot of the data. The results of kinetic study is presented in Figure 4, while calculated rate constants k_1 and correlations coefficients R^2 were summarized in Table 2.
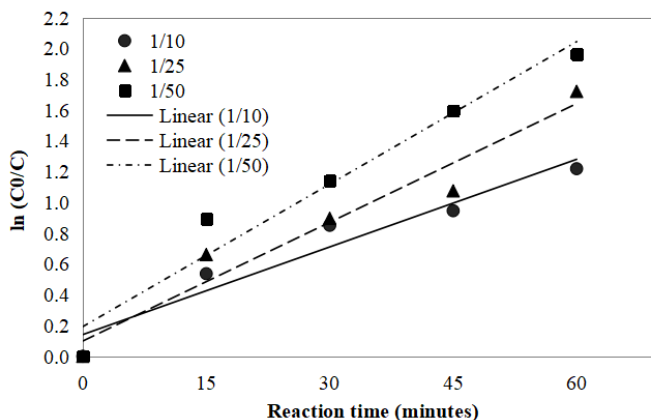
Fig. 4. Kinetic study of COD degradation process for various dilution factors of stillage samples

Table 2. Experimental results for COD degradation process of stillage using UV-photo-Fenton

Dilution factor of stillage	k_1 (min^{-1})	R^2
1/10	0.019	0.9330
1/25	0.0257	0.9486
1/50	0.0309	0.9551

As depicted in Figure 4, when examining the degradation profile of COD using logarithmic values, it becomes evident that all reactions follow the typical equation for pseudo-first order reaction kinetics. Table 2 shows the summary of constant value of degradation rate (k_1) of COD at various dilution factors of stillage. In order to compare kinetic study, the kinetic model providing the best fit was determined by the highest R^2 associated [21, 22], which was showed that the highest k value was obtained at dilution factor of 1/50.

4 Conclusions

The treatment of stillage from bioethanol industry by the UV-photo-Fenton oxidation reaction was considered in this study. Various dilution factor of stillage samples was used to investigate its effects on treatment efficiency. In this work, the degradation of organic pollutants (COD) from stillage is effectively achieved. The best dilution factor and optimum condition for stillage to be treated using UV-photo-Fenton was 1/50 which achieved 85.95% COD removal. The degradation process of COD using UV-photo-Fenton was well described by the pseudo-first order kinetics. The degradation rate constants (k) increased with rise of dilution factor of stillage samples.

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