

# Sequential Dual Coagulation and Photo-Fenton Oxidation for Real Distillery Wastewater Treatment

Khyle Glainmer N. Quiton\*, Ian Carlo T. Abareta, Cyrus Alexander D. Vizon, and Michelle C. Almendrala

School of Chemical, Biological, and Materials Engineering and Sciences, Mapua University, Intramuros, Manila, Philippines

Email: kgnqiton@mapua.edu.ph (K.G.N.Q.); ictabareta@mymail.mapua.edu.ph (I.C.T.A.);

cadvizon@mymail.mapua.edu.ph (C.A.D.V.); mcalmendrala@mapua.edu.ph (M.C.A.)

\*Corresponding author

Manuscript received November 6, 2023; revised February 2, 2024; accepted February 6, 2024; published July 19, 2024

**Abstract**—Distillery effluent leads to extensive surface water and groundwater pollution. Removal of various contaminants and color from this type of effluent has attracted great attention from environmental and aesthetic point of view. Distillery Wastewater (DWW) is hard to dispose due to its dark brown color, high ash content, low pH, undesirable viscosity, hydrophilicity, and high levels of Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). The treatment of DWW has become challenging with conventional treatment methods. With this, a unique hybrid treatment method utilizing a dual coagulation process followed by photo-Fenton oxidation under UV-C light irradiation was investigated for their combined treatment capabilities on the removal of COD, TSS, turbidity, and color from bioethanol DWW. The experimental design used a sequential experimentation approach based on the optimum result on the following sequence of optimizations: i) dual coagulant dosage using Aluminum Chlorohydrate (ACH) and Polydiallyldimethylammonium Chloride (PolyDADMAC); ii) dual coagulation settling time; iii) photo-Fenton  $\text{H}_2\text{O}_2$  concentration; and iv) photo-Fenton UV-C exposure time. The optimum dosage for the dual coagulation process is 90% ACH:10% PolyDADMAC with 5 h of settling yielding color and COD removal of 47.75% and 92.56%, respectively. Subsequently,  $245 \times 10^{-3}$  mol/L of  $\text{H}_2\text{O}_2$  concentration with a UV-C exposure time of 5 hours is optimum for the photo-Fenton process, yielding an overall color and COD removal of 94.25% and 99.81%, respectively.

**Keywords**—color removal, dual coagulation, Fenton reaction, molasses distillery wastewater, photo-Fenton, sequential, wastewater treatment

## I. INTRODUCTION

The growing environmental concerns about fossil fuels drive strong interest in the production of biofuels, with bioethanol being the most used and commercialized. Their effluent has a strong odor, High Chemical Oxygen Demand (COD), high Biochemical Oxygen Demand (BOD), melanoidin, low pH, and temperatures around 600 °C with high total suspended solids. Since the 2011 mandate by the Department of Energy (DOE) to increase bioethanol blend, 12 bioethanol distillery plants using sugarcane or molasses as feedstocks have already been established. Following the bioethanol blend mandate by DOE, bioethanol demand is expected to increase in the following years, with a projected demand of 2616.38 million Liters in 2040 [1]. A liter of ethanol generates about 10–15 L of distillery wastewater [1] and contains high Chemical Oxygen Demand (COD) ranging from 100,000 to 150,000 mg/L [2]. An example of these distilleries in the Philippines is the Roxel bioethanol plant in La Carlota, Negros Occidental. The Distillery Wastewater (DWW) they produce has a BOD of 6,000 to 9,000 mg/L in

this production plant, treated by anaerobic digestion. Despite lowering BOD levels to an acceptable level (50 mg/L), the problem arises such that anaerobic digestion cannot remove color. When introduced to bodies of water, melanoidin reduces sunlight penetration, decreasing dissolved oxygen within affected waters. While on land, it reduces soil alkalinity, which hinders seed germination [3]. Aside from melanoidin, plant polyphenols and caramels have a high chance of appearing in these wastewaters [4]. Alarmingly enough, 2% of the wastewater discharged is melanoidin, adding that for sugarcane molasses-based distilleries, only 6–8% ethanol is produced. To attest, Central Azucarera de Tarlac can make and recover ethanol by approximately 8% alcohol by volume while the remaining becomes DWW. The conventional DWW treatment via physicochemical and biological processes utilized in the country was already proven effective in removing high-content pollutants. However, these methods are ineffective in eliminating recalcitrant compounds due to their highly complex structure [5].

Recently, dual coagulant systems using organic and inorganic coagulant systems have been gaining attention for eco-friendly and cost-efficient wastewater treatment. At the same time, they are reducing the need for post-treatment as much as possible, with varying removal efficiency results. Combinations of coagulation and flocculation with different technologies, such as anaerobic digestion [6], aerobic [7], advanced oxidation [8], and electrochemical oxidation [9], have been extensively studied. Advanced Oxidation Processes (AOPs) are recent advancements in the research and development of wastewater treatment technologies brought about by increasing environmental concerns about various contaminants. AOPs generate strong oxidants such as hydroxyl radicals ( $\cdot\text{OH}$ ) to degrade recalcitrant organic pollutants [10]. The  $\cdot\text{OH}$  radicals generated are known for their high oxidation capability in wastewater treatment. Various AOPs have already been studied, but Fenton and photo-Fenton were the most effective, cost-efficient, and less-tedious methods for wastewater treatment when used alone or with other conventional methods [11]. Fenton reaction is known for its fast reaction rate, cost-efficient, and easy generation of  $\cdot\text{OH}$  radicals [12].

The application of the dual coagulation system using inorganic Aluminum Chlorohydrate (ACH) and organic Polydiallyldimethylammonium Chloride (PolyDADMAC) coagulants with UV photo-Fenton oxidation to treat real molasses-based DWW from the industry has not been documented.

The novelty of the current work focuses on the utilization

of the combination of ACH and PolyDADMAC with different coagulant ratio followed by UV-assisted photo-Fenton oxidation for the treatment of real DWW from an actual distillery plant in the Philippines.

Hence, this study aims to remove various parameters such as COD, TSS, turbidity, and color from bioethanol DWW via sequential dual ACH-PolyDADMAC coagulation and photo-Fenton oxidation under UV-C light irradiation. The results of the study will help in developing better alternatives for DWW treatment by utilizing the combined system of dual coagulation using inorganic and organic coagulants with photo-Fenton oxidation. Therefore, this will benefit distillery industries for a safer and cleaner DWW discharge that meets the scope of the general effluent standards.

## II. LITERATURE REVIEW

Conventionally, wastewater treatment has always used single coagulants to treat wastewater and utilized the jar test to evaluate the optimal pH conditions and dosage of the coagulants to bring out the most optimal removal efficiencies. Coagulants can be divided into two categories which are inorganic and organic coagulants. Using inorganic coagulants in high doses decreases the water's pH which is considered as a problem to be solved [13]. The water is added with acid to reach the optimum pH for the inorganic coagulant to perform at its peak. Excessive lowering of the pH may result in post-treatment for the water to lessen the inorganic coagulants in the system and raise the pH. The pH decrease is due to the formation of hydrogen ions that react with the wastewater's alkalinity examined. On the other hand, recent studies have shown that organic coagulants are more effective for wastewater treatment. Organic Polymer Flocculants (OPFs) have overcome the drawbacks of inorganic polymeric flocculants because OPFs are less affected by pH, temperature, contaminant salts, better water treatment efficiency, and less sludge yield [14]. For this reason, organic coagulants are, in certain aspects, a better alternative because they do not affect the water's alkalinity and pH. However, the effectiveness of these coagulants and determining which is better is still debatable. A study comparing unconventional organic coagulants, Cofloc, C29510 Kemipol, and Sedifloc 575, to conventional inorganic coagulant, PIX113 with polymer A110 dosing showed the capabilities of organic coagulants to match the convention in terms of removal efficiency for COD as well as Total Suspended Solids (TSS) [14]. However, it is inefficient in removing color in DWW as it often requires a high dosage of coagulants depending on the effluent being treated [14].

Inorganic ACH and organic PolyDADMAC coagulants have found to be effective in the remediation of different contaminants in water and wastewater. According to the study of Verma et al., ACH can reach 91% decolorization efficiency in the treatment of silk dye bath effluent [15]. In addition, the turbidity of Greater-Zab river water was reduced from 2000 NTU to 3.3 NTU using 1.6  $\mu\text{L/L}$  of ACH under pH 7.36 and 30 min of sedimentation time [16]. Furthermore, ACH was used to remove different pharmaceuticals such as Amoxicillin (AMO), Colistin (COL), Diclofenac (DIC), Ethynylestradiol (EE), Erythromycin (ERY), and Fluoxetine (FLX) and Total Organic Carbon (TOC) from various river water samples in Poland. The removal efficiencies of AMO,

COL, DIC, EE, ERY, FLX, and TOC achieved 29.0%, 25.5%, 30.4%, 35.4%, 36.4%, 24.7%, and 88.7%, respectively. Additionally, 96.2%, 98.0%, and 97.8% of turbidity, color, and TSS were removed from these samples, respectively. These were reached under pH 6.5, 0.35 mL/L of ACH dose and 30 min operating time [17]. In the study conducted by Teguh *et al.*, 12 mg/L of ACH led to a decrease in turbidity in the river water from 45 NTU to 0.73 NTU under pH approximately equal to 7.0 [18]. By using ACH to treat brewery wastewater, turbidity and COD were reduced by 54% and 34%, respectively [19]. Nevertheless, organic PolyDADMAC also presents efficiency in water and wastewater remediation. This was affirmed by Lopez-Maldonado *et al.* in treating semiconductor wastewater reducing the COD content from 1432 mg/L to 122 mg/L [20]. Zahrim *et al.* also achieved 48% color removal using 1000 mg/L of PolyDADMAC to treat palm oil mill biogas plant wastewater (POMBPW) [21]. In the remediation of a biologically treated yeast processing effluent, PolyDADMAC coagulation resulted into 68.25%, 63.63%, and 88.51% color, COD, and turbidity removal, respectively, under pH 6.0 [22]. These display the potential of ACH and PolyDADMAC coagulants to treat different types of water and wastewater streams.

The utilization of dual coagulants (inorganic coagulant and polymer-based coagulant) has advantages compared with the use of sole inorganic or polymer coagulants. These include inorganic coagulant dosage reduction and the production of denser, larger, and stronger flocs [23]. The use of dual coagulants ( $\text{FeCl}_3$  + PolyDADMAC) led to the enhancement of the coagulation-flocculation process (80% color removal) compared to the usage of sole  $\text{FeCl}_3$  coagulant which only led to 60.1% color removal [24]. The efficiency of dual coagulation was also affirmed by Ariffin *et al.* using polyacrylamide-PolyDADMAC coagulant which led to 80%, 96.8%, and 98% turbidity, TSS, and COD removal efficiencies, respectively [25]. The addition of polyamine to ACH also improved its efficiency in terms of turbidity and COD removal by about 30% in the treatment of brewery wastewater [19].

Olive mill wastewater was treated by single PolyDADMAC coagulation followed by Fenton oxidation reducing the COD content by 45% which is higher than single coagulation achieving only 12.5% COD removal [26]. This shows that sequential coagulation and Fenton oxidation is effective in wastewater remediation.

## III. MATERIALS AND METHODS

### A. Distillery Wastewater Sampling

The DWW used in this study was obtained from Absolut Distillery Inc., a sugarcane mill and ethanol distillery located in Barangay Malaruhatan, Lian, Batangas, Philippines. The initial characteristics of the DWW are shown in Table 1.

Table 1. Initial distillery wastewater characteristics

Parameter	Units	Values
COD	mg/L	130,000
TSS	mg/L	15,000
Turbidity	NTU	121
Color	-	Dark Brown
pH	-	4-5

## B. Dual Coagulation

### 1) Effect of dual coagulant dosage

The inorganic coagulant used in this study is Aluminum Chlorohydrate, while the organic coagulant is Polydiallyldimethylammonium Chloride, both having a concentration of 23% w/v. The inorganic and organic coagulant concentrations were optimized in five batches. A jar test apparatus will perform the dual coagulation and flocculation process. Five 250-mL beakers for each batch will be prepared. Each beaker contained 200 mL of DWW with a concentration of 10 ppm. 5 M NaOH was used to adjust the pH of the sample to a pH of 8 [27]. Different dual coagulant concentrations were prepared based on the following %w/v ACH: %w/v PolyDADMAC ratios: 95:5, 90:10, 80:20, 70:30, and 60:40. The different dual coagulant concentrations were added to their corresponding beakers. Each beaker with the different coagulant concentrations was then subjected to rapid stirring (150 rpm) for 5 mins and slow stirring (60 rpm) for 15 mins [28]. After the coagulation and flocculation, the mixture was allowed to settle for 4 h. Supernatants of the settled DWW were obtained to determine turbidity and color removal of the mixtures. The color removal quantified the absorbance of the sample solution by scanning the different wavelengths of the sample solution and determining the peak absorbance.

### 2) Effect of settling time

The sample that provided the highest turbidity and color removal efficiency was used to determine the settling time effect. Similarly, five 250-mL beakers containing 200-mL of DWW were prepared for each run, and the optimum dual coagulation dosage was added. The five beakers containing the mixture were performed simultaneously and were subjected to rapid stirring (150 rpm) for 5 minutes, followed by slow stirring (60 rpm) for 15 minutes [28]. After the coagulation and flocculation process, the different mixtures were allowed to settle from 60 to 300 minutes. For every 60 minutes, the turbidity and color were determined. In addition to turbidity, the pH, COD, and TSS were also determined for the sample that provided the best results.

## C. Photo-Fenton Oxidation

The optimum dual coagulant concentration was used for the next stage of the hybrid treatment process, which is the photo-Fenton oxidation process. This process combines two AOPs: Fenton oxidation reaction and photocatalysis using UV light irradiation. The reagents used were 30% w/v lab-grade Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ , Fluka) and Iron (III) Chloride Hexahydrate ( $(\text{FeCl}_3 \cdot 6\text{H}_2\text{O})$ ), which acts as a catalyst to promote the oxidation of organic contaminants. The optimal Fenton reagent and exposure time were used to create a control sample. Fig. 1 shows the experimental setup of the UV Photo-Fenton reaction. The samples were placed directly below the 150 W UV lamp and were constantly stirred at 100 rpm using a hotplate and a magnetic stirrer.

### 1) Effect of $\text{H}_2\text{O}_2$ concentration

Varying  $\text{H}_2\text{O}_2$  concentration at constant  $\text{Fe}^{3+}$  concentration was made to determine the optimum  $\text{H}_2\text{O}_2$  concentration. The time of exposure and the intensity of UV radiation were held constant. Five batches of treated DWW by dual coagulation

were first prepared. After settling the initial treated DWW samples, the different  $\text{H}_2\text{O}_2$  concentrations were added to each batch, respectively. The  $\text{H}_2\text{O}_2$  concentrations varied from  $49 \times 10^{-3}$  mol/L to  $245 \times 10^{-3}$  mol/L. The beakers containing the mixture with Fenton reagents were exposed to UV radiation for 80 minutes at a UV intensity of 150W with constant stirring at 100 rpm. The COD and color removal efficiencies for each batch were determined. Furthermore, the TSS and turbidity for the sample that provided the highest COD and color removal efficiencies were then determined.

### 2) Effect of UV-C light irradiation

The optimum  $\text{H}_2\text{O}_2$  concentration was used to determine the optimum UV-C exposure time. Likewise, five batches of treated DWW using the optimum dual coagulants and settling time were first prepared. After the dual coagulation treatment, the Fenton reagents were then added. The UV-C intensity and stirring speed follow the same conditions as stated previously. The UV-C exposure time was varied from 60 to 300 mins. For every 60 mins, the turbidity and color removal were determined. The TSS and COD of the sample that provided the best results were then determined.

## D. Chemical Analysis

### 1) Turbidity determination procedure

For turbidity determination, Eutech ECTN100IR was used to quantify the initial conditions and changes in the turbidity of the sample after treatment. The turbidity meter was first calibrated using the calibration standards available with the equipment, which are 800 NTU, 100 NTU, 20 NTU, and 0.2 NTU. The sample vial was rinsed using the sample of interest, inverted several times, and discarded. The vial was then filled with the sample until it reached the indicated markings on the vial. The vial containing the sample was placed in the turbidity meter testing. Afterward, the sample vial was cleaned and wiped. This process was repeated until all the samples of interest are tested.

### 2) Color removal determination procedure

The color removal data were quantified by scanning for the peak absorbance of the sample with a concentration of 0.25% v/v; it was then compared to the change in absorbance of the treated samples. PerkinElmer Lambda 35 UV-Vis Spectrophotometer was used for data collection. In the PerkElemer UV Winlab tab found on the desktop, the wavelength-quant method was selected. Autozero was then performed by filling two cuvettes with distilled water and scanning it at wavelengths ranging from 200–900 nm. One cuvette was then removed and refilled with the prepared DWW sample to determine the wavelength at peak absorbance. The peak absorbance value was 2.77 measured at the maximum wavelength of 280 nm. This wavelength was then used to determine the absorbance of the samples in all runs. From the obtained peak absorbance data and the absorbance of each sample, the color removal efficiency was determined using Eq. (1).

$$\text{Color Removal (\%)} = \left(1 - \frac{\text{Abs}^M}{\text{Abs}_0^M}\right) \times 100 \quad (1)$$

where  $\text{Abs}^M$  The treated samples' average absorbance value

at the maximum absorbance wavelength.  $Abs_o^M$  and  $Abs^M$  are the absorbance values measured before and after the treatment, respectively.

### 3) Chemical Oxygen Demand Determination Procedure

Treated chemical oxygen demand data samples were determined using the Hach COD mid-range digestion vials. The instruments used in this procedure are the Lovibond ET-108 COD reactor and Lovibond PC CheckIT photometer. The COD reactor was turned on and set to 120 °C, and a blank sample was prepared using deionized water. Since the DWW samples are extremely dark in color, the photometer won't be able to read them. Hence, the samples were diluted. 2-mL of the diluted samples were then pipetted to the digestion vials. The vials were then placed in the COD reactor for 2 h at 120 °C. After 2 h, the vials were cooled for 20 mins until it reached room temperature. After cooling the vials, the blank sample was first placed in the photometer for calibration, followed by the vials with the diluted DWW samples. The values obtained on the photometer were then recorded, and the COD removal efficiency was calculated using Eq. (2).

$$COD\ Removal\ (\%) = \left(1 - \frac{COD_t}{COD_o}\right) \times 100 \quad (2)$$

where  $COD_o$  and  $COD_t$  corresponds to the chemical oxygen demand in ppm, before and after the treatment, respectively.

### E. TSS Determination Procedure

Total suspended solids were examined to ensure the concentration of sludge or waste that may generate due to the wastewater treatment process. The materials needed are a 250-mL suction flask, desiccator, filter paper, vacuum pump, and filter holder. First, the sample volume was measured, after which the suction flask was attached to the vacuum pump. The filter holder with the filter paper was placed on top of the suction flask; then, the vacuum pump was attached and opened, allowing the sample to drain completely. After filtration, the filter paper was placed in an oven and heated to 104 °C for an hour. Afterward, it was placed in a desiccator until wholly cooled. Finally, the dried filter paper was weighed, and the TSS was calculated using Eq. (3).

$$TSS, ppm = \left(\frac{W_f - W_i}{V_s}\right) \times 1,000,000 \quad (3)$$

where  $W_f$  and  $W_i$  are the final and initial weight of the filter in grams, respectively while  $V_s$  is the sample volume measured in mL.

## IV. RESULT AND DISCUSSION

### A. Dual Coagulation Analysis

Initial adjustment of the pH was conducted before the application of the dual coagulation compositions.

The measurement of the data shown below is gathered after the allotted settling time of 4 h for the varying composition, while every subsequent hour for the measure of the best settling time using the best arrangement for dual coagulation.

The implication of the varying compositions used in Fig. 1(a) provides the best possible removal efficiency while minimizing the cost of the coagulants. In this section, 10 ppm

was used to treat the distillery wastewater. The pH of the raw DWW was adjusted to pH 8 for optimum reaction conditions. The data gathered shows that the 70:30 composition provides the best results. However, given that organic coagulants are more costly than inorganic ones, a one-way ANOVA was conducted, and it is here that it was determined that there was no significant difference between the compositions. As such, the 90:10 was chosen given that the composition had a higher removal efficiency while low use of organic coagulants. In addition, based on the current prices of the coagulants used, it was observed that the 90:10 composition is estimated to be 81.60% lower than the 70:30 composition, which is \$0.017/(L-yr) and \$0.088/(L-yr), respectively. From this, the settling time is then examined, which resulted in the 5 h settling time being the best result which has color, COD, and turbidity removal to be 47.75%, 30.05%, and 92.56%, respectively, which supports the claim of previous pieces of literature [29]. However, further analysis showed that there were no significant differences between the settling times. It indicates that there only be a minimal increase in effectively increasing the settling time. Upon testing of the TSS (20,897 ppm), it was found that it became higher than the initial parameters of the sample. It is due to the re-stabilization of the particles for the coagulants to destabilize the particles within the sample, while flocculation is the agglomeration of these particles [30]. Because of this, the coagulation-flocculation process was hampered. Hence, it could be claimed that overdosing may have affected the turbidity removal of the sample such that it could be higher. In addition, the cost of this coagulation treatment could be lower while providing lower than or similar to the results presented here. Lowering the concentration used for the sample will be more cost-efficient and prevent this effect from occurring during the treatment process.

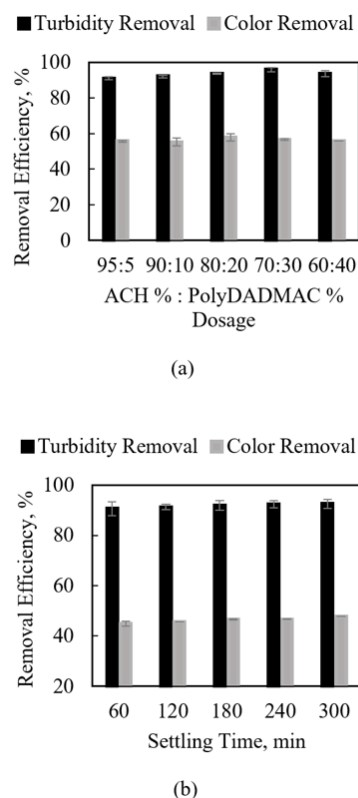


Fig. 1. Effect of (a) different coagulant concentrations and (b) effect of settling time on turbidity and color removal efficiencies.

Similarly, the settling time was also examined by ANOVA. It was then found that there was no significant difference, but 5 h was still chosen for this study. Thus, it can be claimed that 1 h of settling time with a lower concentration with a 90:10 composition may be able to neutralize the surface charge and will be able to reduce the contaminants, and may be able to filter or remove them after treatment [31]. At the best-set conditions, the dual coagulation process obtained high turbidity removal but was scarce in color and COD removal. In contrast, one study using a standalone photo-Fenton process technology for vinasse treatment reported a 73% COD removal achieved at pH 5.5 [32]. Hence, a post-treatment using the photo-Fenton process of the treated DWW by dual coagulation was done to improve or reach better removal efficiencies.

### B. Photo-Fenton Analysis

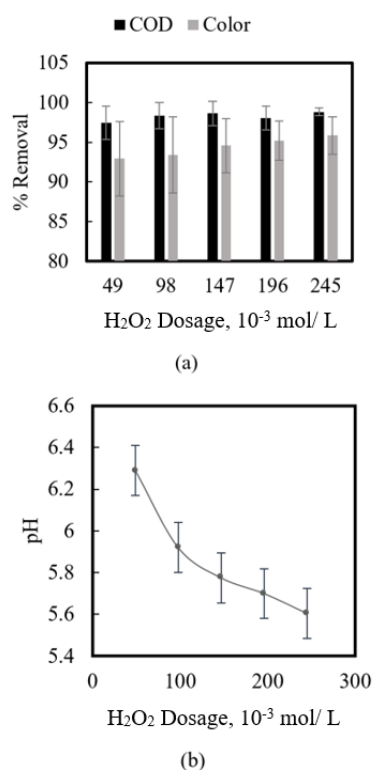


Fig. 2. (a) Effect of H<sub>2</sub>O<sub>2</sub> concentration on COD and color removal and (b) pH change on H<sub>2</sub>O<sub>2</sub> concentration.

In the photo-Fenton oxidation process, the H<sub>2</sub>O<sub>2</sub> concentration is critical for the generation of ·OH radicals which are responsible for the degradation of recalcitrant organic compounds found in DWW [33]. By applying this process to the treated DWW using dual coagulation, higher COD and color removal were observed. Fig. 2 investigated the effect of varying H<sub>2</sub>O<sub>2</sub> concentrations ranging from 49 × 10<sup>-3</sup> mol/L to 245 × 10<sup>-3</sup> mol/L on COD and color removal. At this range, it was found that high COD and color removal were observed for all concentrations, with only slight differences between them. The best concentration is 245 × 10<sup>-3</sup> mol/L of H<sub>2</sub>O<sub>2</sub> since it obtained the highest COD and color removal of 98.8% and 95.84%, respectively. The increase in removal efficiencies can be attributed to the increased generation of ·OH radicals as the concentration of H<sub>2</sub>O<sub>2</sub> increase. In addition, high-intensity UV radiation at 150

W and constant stirring at 100 rpm also contribute to the increase of ·OH radical generation, leading to more degradation of recalcitrant compounds. UV radiation makes the dark Fenton process more efficient since it regenerates the Fe<sup>2+</sup> used to react with H<sub>2</sub>O<sub>2</sub> and generate ·OH radicals. Constant stirring of the samples also helps generate more ·OH radicals as it increases the contact between the reactants and catalysts [34].

Despite the high efficiencies mentioned earlier, upon observation of other factors such as TSS and Turbidity, it resulted in higher than the initial parameters of the wastewater since an increase to 918 NTU and 23,333 ppm, respectively, were observed. These changes can be attributed to a side reaction during the photo-Fenton reaction. At a pH of greater than 3.5, Fe<sup>3+</sup> precipitation of FeCl<sub>3</sub>·6H<sub>2</sub>O occurs, forming ferric hydroxide precipitates [35]. This precipitation leads to an increase in turbidity, resulting in less light precipitation. In conjunction with this, a study indicated that the precipitation of these compounds leads to a decrease in the efficiency of the Photo-Fenton process [35].

Further data analysis showed no significant differences in the COD and color removal efficiencies. Despite this, it can be observed that as the pH of the sample decreases, the efficiency increases; therefore, it indicates that the hydroxyl radicals have a higher oxidation potential at lower pH [36]. Hence, 245 × 10<sup>-3</sup> mol/L of H<sub>2</sub>O<sub>2</sub> can achieve high COD and color removal for a lower cost or amount of Fenton reagents. Based on the current pricing of H<sub>2</sub>O<sub>2</sub>, is \$1.81/L.

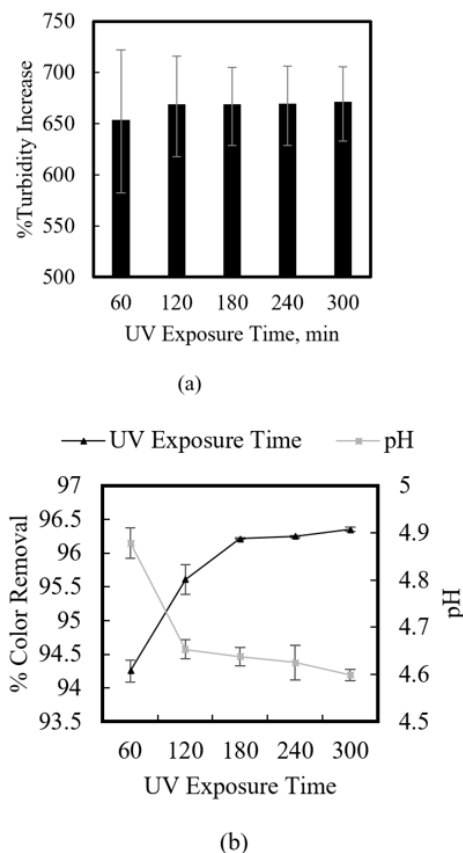


Fig. 3. Effect of UV exposure time on (a) turbidity removal and (b) pH, and color removal.

The effect of the photo-Fenton process under UV-C exposure time on pH, turbidity, and color removal is shown in Figs. 3a and 3b. UV radiation improves the rate of ·OH

radical generation, leading to more degradation of recalcitrant organic compounds. This study determined the effect of UV-C exposure time using the same operating conditions earlier but with the best H<sub>2</sub>O<sub>2</sub> concentration,  $245 \times 10^{-3}$  mol/L. An upward trend in the color removal efficiency and turbidity was observed as the UV-C exposure time increased. The highest color removal was observed at 300 min of exposure: 96.35% color removal and 669.42% turbidity increase. Furthermore, 99.81% COD removal efficiency and a TSS of 112,667 ppm were observed at this time. Only slight differences in color removal and turbidity were observed between exposure times. Using ANOVA, it was determined that there were no significant differences between the parameters. Hence, 60 min of UV-C exposure is preferable to save time while also getting high color removal (94.25%) and lower turbidity (910 NTU).

As discussed previously, the increased turbidity is associated with the formation of ferric hydroxide precipitates at a pH greater than 3.5. Since the pH 7.2 of the dual coagulation treated DWW was not adjusted, ferric hydroxide precipitates were formed during the photo-Fenton process. Consequently, turbidity increases with UV-C exposure time since more ferric hydroxide precipitates are produced. In conjunction with this, the intensity of the UV light may have varied due to the distance that the bulb was placed such that as the distance increases, the intensity of the light decreases, which may have affected the effectivity of the AOP treatment. According to one study, the pH is typically between 2.0 to 4.0 to maximize the generation of ·OH radicals in the photo-Fenton process [37]. Another study reported that pH 2.8 is optimum to prevent the iron catalyst from precipitating [13]. Therefore, adjusting the pH to acidic conditions before the photo-Fenton process is recommended to increase its removal efficiencies and degradation of more organic compounds. Several studies have shown that application of chelating agents can reduce the formation of ferric hydroxide with the use of EDDS, oxalate, EDTA, NTA, and citrate with varying efficiencies with EDDS having the highest to be 95% for EDSS [38]. However, it is important to note that many of these studies have different samples from municipal wastewater, streams with aromatic solutions, and herbicides. In conjunction with this, a study indicated that the precipitation of these compounds leads to a decrease in the efficiency of the Photo-Fenton process [31].

Furthermore, due to this, the Photo-Fenton reaction was able to occur, an example of which is EDDS, which was more efficient than citrate at a neutral pH for treating the municipal wastewater treatment plant containing pharmaceuticals [39]. However, it is essential to note that many of these studies have different samples from municipal wastewater, streams with aromatic solutions, and herbicides, to name a few. For this reason, it is recommended that the optimization of these chelating agents and their effects on the distillery wastewater can be studied to minimize the formation of ferric hydroxide to reduce the cost of pH adjustment during treatment.

### C. Summary and Comparison of Results

In the study conducted by Domingues *et al.* single PolyDADMAC coagulation followed by Fenton oxidation in the treatment of olive mill wastewater achieved a COD removal of 45% [26]. With the addition of ACH in the present

study, the COD removal was improved to 92.56% which is more than a 100% increase. Subsequently, further treatment via UV-C photo-Fenton process increased the COD removal to almost complete removal. Furthermore, only 66% COD removal was reached by Vlotman *et al.* in the remediation of winery wastewater using ACH-PolyDADMAC coagulants [40]. This displays that the sequential dual coagulation and photo-Fenton oxidation utilized in this current work is better in terms of COD removal performance.

## V. CONCLUSION

The main purpose of this study was to remove various parameters including COD, TSS, turbidity, and color from bioethanol DWW via sequential dual ACH-PolyDADMAC coagulation and photo-Fenton oxidation under UV-C light irradiation. The optimum coagulant dosage for the dual coagulation process is 90% ACH:10% PolyDADMAC under 5 h of settling time resulting to color and COD removal efficiencies of 47.75% and 92.56%, respectively. Additionally, the optimum H<sub>2</sub>O<sub>2</sub> dosage is  $245 \times 10^{-3}$  mol/L within UV-C exposure time of 5 hours for the photo-Fenton process yielding color and COD removal of 94.25% and 99.81%, respectively. Sequential dual ACH-PolyDADMAC coagulation and photo-Fenton oxidation under UV-C light irradiation was found to be effective in treating real distillery wastewater. In this context, this approach should constitute an interesting option for the full-scale molasses-based DWW treatment.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## AUTHOR CONTRIBUTIONS

I.C.T.A. and C.A.D.V. were involved in the methodology, collecting data, and the preparation of the original draft and was supervised by M.C.A. and K.G.N.Q. All authors are involved in analysis, validation, reviewing, editing, and approving the final version of the manuscript.

## ACKNOWLEDGMENT

The authors would like to thank Ian Carlo T. Abareta and Cyrus Alexander D. Vizon's parents for the untiring support and help to make this work complete and possible. Special thanks to Absolut Distillery, Inc. for providing the real distillery wastewater to proceed with the research.

## REFERENCES

- [1] W. Mikucka and M. Zielińska, "Distillery stillage: Characteristics, treatment, and valorization," *Appl. Biochem. Biotechnol.*, vol. 192, no. 3, pp. 770–793, 2020, doi: 10.1007/s12010-020-03343-5.
- [2] S. Ratna, S. Rastogi, and R. Kumar, "Current trends for distillery wastewater management and its emerging applications for sustainable environment," *J. Environ. Manage.*, vol. 290, no. April, p. 112544, 2021, doi: 10.1016/j.jenvman.2021.112544.
- [3] S. Apollo, M. S. Onyango, and A. Ochieng, "An integrated anaerobic digestion and UV photocatalytic treatment of distillery wastewater," *J. Hazard. Mater.*, vol. 261, pp. 435–442, 2013, doi: 10.1016/j.jhazmat.2013.06.058.
- [4] Y. Kharayat, "Distillery wastewater: bioremediation approaches," *J. Integr. Environ. Sci.*, vol. 9, no. 2, pp. 69–91, 2012, doi: 10.1080/1943815X.2012.688056.
- [5] D. Garcia-Calderon, P. Buffiere, R. Moletta, and S. Elmaleh, "Anaerobic digestion of wine distillery wastewater in down-flow

- fluidized bed,” *Water Res.*, vol. 32, no. 12, pp. 3593–3600, 1998, doi: 10.1016/S0043-1354(98)00134-1.
- [6] L. F. Romanholo Ferreira *et al.*, “Evaluation of sugar-cane vinasse treated with Pleurotus sajor-caju utilizing aquatic organisms as toxicological indicators,” *Ecotoxicol. Environ. Saf.*, vol. 74, no. 1, pp. 132–137, 2011, doi: 10.1016/j.ecoenv.2010.08.042.
- [7] E. Gašpariková, Š. Kapusta, I. Bodík, J. Derco, and K. Kratochvíl, “Evaluation of anaerobic-aerobic wastewater treatment plant operations,” *Polish J. Environ. Stud.*, vol. 14, no. 1, pp. 29–34, 2005.
- [8] Y. J. Chan, M. F. Chong, C. L. Law, and D. G. Hassell, “A review on anaerobic-aerobic treatment of industrial and municipal wastewater,” *Chem. Eng. J.*, vol. 155, no. 1–2, pp. 1–18, 2009, doi: 10.1016/j.cej.2009.06.041.
- [9] Z. Song, C. J. Williams, and R. G. J. Edyvean, “Coagulation and anaerobic digestion of tannery wastewater,” *Process Saf. Environ. Prot.*, vol. 79, no. 1, pp. 23–28, 2001, doi: 10.1205/095758201531103.
- [10] P. Asaithambi, B. Sajjadi, and A. R. A. Aziz, “Integrated ozone-photo-Fenton process for the removal of pollutant from industrial wastewater,” *Chinese J. Chem. Eng.*, vol. 25, no. 4, pp. 516–522, 2017, doi: 10.1016/j.cjche.2016.10.005.
- [11] Q. Yi, W. Liu, J. Tan, B. Yang, M. Xing, and J. Zhang, “Mo0 and Mo<sup>4+</sup> bimetallic reactive sites accelerating Fe<sup>2+</sup>/Fe<sup>3+</sup> cycling for the activation of peroxymonosulfate with significantly improved remediation of aromatic pollutants,” *Chemosphere*, vol. 244, p. 125539, 2020, doi: 10.1016/j.chemosphere.2019.125539.
- [12] M. Ahmadi, K. Rahmani, A. Rahmani, and H. Rahmani, “Removal of benzotriazole by Photo-Fenton like process using nano zero-valent iron: Response surface methodology with a Box-Behnken design,” *Polish J. Chem. Technol.*, vol. 19, no. 1, pp. 104–112, 2017, doi: 10.1515/pjct-2017-0015.
- [13] P. Gebbie, “A dummy’s guide to coagulants,” in *Proc. 68th Annu. Water Ind. Eng. Oper. Conf.*, 2005, no. 75, pp. 75–83.
- [14] S. Ma *et al.*, “Preparation of a new inorganic-organic composite dual-coagulant and application of oily wastewater treatment,” *Adv. Mater. Res.*, vol. 233–235, pp. 523–527, 2011, doi: 10.4028/www.scientific.net/AMR.233-235.523.
- [15] A. K. Verma, P. Bhunia, and R. R. Dash, “Effectiveness of aluminum chlorohydrate (ACH) for decolorization of silk dyebath effluents,” *Ind. Eng. Chem. Res.*, vol. 51, no. 25, pp. 8646–8651, 2012, doi: 10.1021/ie301201r.
- [16] I. A. Omar and S. Q. Aziz, “Optimization of ACH coagulant, settling time and powdered activated carbon as coagulant aid with economic analysis,” *Glob. Nest J.*, vol. 23, no. 3, pp. 340–350, 2021, doi: 10.30955/gnj.003797.
- [17] J. Kuc *et al.*, “Determination and removal of selected pharmaceuticals and total organic carbon from surface water by aluminum chlorohydrate coagulant,” *Molecules*, vol. 27, no. 17, 2022, doi: 10.3390/molecules27175740.
- [18] D. Teguh, T. E. Agustina, M. Hafiz Ridho, N. Febriyanti, and D. Ermaya, “The effectiveness and cost optimization of Coagulant Aluminum Chlorohydrate (ACH), Aluminum Sulfate (AS), and Poly Aluminium Chloride (PAC) in coagulation process at the PT. Pupuk Sriwijaya (PT. Pusri) Utility Unit,” *Indones. J. Environ. Manag. Sustain.*, vol. 6, no. 1, pp. 189–195, 2022, doi: 10.26554/ijems.2022.6.1.189-195.
- [19] K. P. Shabangu, B. F. Bakare, and J. K. Bwapa, “The treatment effect of chemical coagulation process in South African Brewery wastewater: Comparison of polyamine and aluminum-chlorohydrate coagulants,” *Water (Switzerland)*, vol. 14, no. 16, 2022, doi: 10.3390/w14162495.
- [20] E. A. López-Maldonado, M. T. Oropeza-Guzmán, and A. Ochoa-Terán, “Improving the efficiency of a coagulation-flocculation wastewater treatment of the semiconductor industry through zeta potential measurements,” *Ecol. Technol. Ind. Wastewater Manag. Petrochemicals, Met. Semi-Conductors, Pap. Ind.*, vol. 2014, pp. 167–195, 2015, doi: 10.1201/b18617-17.
- [21] A. Y. Zahrim and Z. D. Dexter, “Decolourisation of palm oil mill biogas plant wastewater using Poly-Diallyldimethyl Ammonium Chloride (polyDADMAC) and other chemical coagulants,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 36, no. 1, 2016, doi: 10.1088/1755-1315/36/1/012025.
- [22] S. Manhokwe and C. Zvidzai, “Post-treatment of yeast processing effluent from a bioreactor using aluminium chlorohydrate polydadmac as a coagulant,” *Sci. African*, vol. 6, pp. 4–11, 2019, doi: 10.1016/j.sciaf.2019.e00125.
- [23] L. Fan, T. Nguyen, and F. A. Roddick, “Characterisation of the impact of coagulation and anaerobic bio-treatment on the removal of chromophores from molasses wastewater,” *Water Res.*, vol. 45, no. 13, pp. 3933–3940, 2011, doi: 10.1016/j.watres.2011.04.050.
- [24] A. Y. Zahrim, Z. D. Dexter, C. G. Joseph, and N. Hilal, “Effective coagulation-flocculation treatment of highly polluted palm oil mill biogas plant wastewater using dual coagulants: Decolourisation, kinetics and phytotoxicity studies,” *J. Water Process Eng.*, vol. 16, pp. 258–269, 2017, doi: 10.1016/j.jwpe.2017.02.005.
- [25] A. Ariffin, M. A. A. Razali, and Z. Ahmad, “PolyDADMAC and polyacrylamide as a hybrid flocculation system in the treatment of pulp and paper mills waste water,” *Chem. Eng. J.*, vol. 179, pp. 107–111, 2012, doi: 10.1016/j.cej.2011.10.067.
- [26] E. Domingues, E. Fernandes, J. Gomes, S. Castro-Silva, and R. C. Martins, “Olive oil extraction industry wastewater treatment by coagulation and Fenton’s process,” *J. Water Process Eng.*, vol. 39, no. October 2020, 2021, doi: 10.1016/j.jwpe.2020.101818.
- [27] D. T. Moussa, M. H. El-Naas, M. Nasser, and M. J. Al-Marri, “A comprehensive review of electrocoagulation for water treatment: Potentials and challenges,” *J. Environ. Manage.*, vol. 186, pp. 24–41, 2016, doi: 10.1016/j.jenvman.2016.10.032.
- [28] L. W. M. Zailani and N. S. M. Zin, “Application of Electrocoagulation in Various Wastewater and Leachate Treatment-A Review,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 140, no. 1, 2018, doi: 10.1088/1755-1315/140/1/012052.
- [29] R. Krishna Prasad and S. N. Srivastava, “Electrochemical degradation of distillery spent wash using catalytic anode: Factorial design of experiments,” *Chem. Eng. J.*, vol. 146, no. 1, pp. 22–29, 2009, doi: 10.1016/j.cej.2008.05.008.
- [30] T. Tondee, S. Sirianuntapiboon, and S. Ohmomo, “Decolorization of molasses wastewater by yeast strain, *Issatchenkia orientalis* No. SF9-246,” *Bioresour. Technol.*, vol. 99, no. 13, pp. 5511–5519, 2008, doi: 10.1016/j.biortech.2007.10.050.
- [31] R. A. Pandey, S. Malhotra, A. Tankhiwale, S. Pande, P. P. Pathe, and S. N. Kaul, “Treatment of biologically treated distillery effluent – A case study,” *Int. J. Environ. Stud.*, vol. 60, no. 3, pp. 263–275, 2003, doi: 10.1080/00207230290024270.
- [32] P. C. Sangave, P. R. Gogate, and A. B. Pandit, “Combination of ozonation with conventional aerobic oxidation for distillery wastewater treatment,” *Chemosphere*, vol. 68, no. 1, pp. 32–41, 2007, doi: 10.1016/j.chemosphere.2006.12.053.
- [33] Y. Satyawali and M. Balakrishnan, “Performance enhancement with powdered activated carbon (PAC) addition in a membrane bioreactor (MBR) treating distillery effluent,” *J. Hazard. Mater.*, vol. 170, no. 1, pp. 457–465, 2009, doi: 10.1016/j.jhazmat.2009.04.074.
- [34] P. Asaithambi, M. Susree, R. Saravanamithan, and M. Matheswaran, “Ozone assisted electrocoagulation for the treatment of distillery effluent,” *Desalination*, vol. 297, pp. 1–7, 2012, doi: 10.1016/j.desal.2012.04.011.
- [35] T. Zayas, V. Rómero, L. Salgado, M. Meraz, and U. Morales, “Applicability of coagulation/flocculation and electrochemical processes to the purification of biologically treated vinasse effluent,” *Sep. Purif. Technol.*, vol. 57, no. 2, pp. 270–276, 2007, doi: 10.1016/j.seppur.2007.04.019.
- [36] N. A. Oladoja, “Headway on natural polymeric coagulants in water and wastewater treatment operations,” *J. Water Process Eng.*, vol. 6, pp. 174–192, 2015, doi: 10.1016/j.jwpe.2015.04.004.
- [37] A. C. Pradhan, M. K. Sahoo, S. Bellamkonda, K. M. Parida, and G. R. Rao, “Enhanced photodegradation of dyes and mixed dyes by heterogeneous mesoporous Co-Fe/Al<sub>2</sub>O<sub>3</sub>-MCM-41 nanocomposites: Nanoparticles formation, semiconductor behavior and mesoporosity,” *RSC Adv.*, vol. 6, no. 96, pp. 94263–94277, 2016, doi: 10.1039/c6ra19923b.
- [38] A. Nath, A. Mishra, and P. P. Pande, “A review natural polymeric coagulants in wastewater treatment,” *Mater. Today Proc.*, vol. 46, pp. 6113–6117, 2019, doi: 10.1016/j.matpr.2020.03.551.
- [39] N. Shaylinda Mohd Zin and Z. Azraff Zulkapli, “Application of dual coagulant (Alum + Barley) in Removing colour from Leachate,” in *Proc. MATEC Web Conf.*, 2017, vol. 103, pp. 1–6, doi: 10.1051/mateconf/201710306002.
- [40] D. Vlotman, D. Key, B. Cerff, and B. J. Bladergroen, “Wastewater treatment using shear enhanced flotation separation technology: A pilot plant study for winery wastewater processing,” *Separation Processes for Environmental Preservation*, 2024.

Copyright © 2024 by the authors. This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited ([CC BY 4.0](https://creativecommons.org/licenses/by/4.0/)).