



Research Article

Removal of chemical oxygen demand from agro effluent by ZnO photocatalysis and photo-Fenton

Devagi Kanakaraju¹  · Marvis Sakai Yahya¹ · Soon-Pang Wong¹

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Abstract

The direct discharge of improperly treated effluent from sago industry poses a great threat to water bodies due to the high amount of organic matter. This work investigated ZnO photocatalytic degradation under aerated and non-aerated conditions, and photo-Fenton aiming to reduce the chemical oxygen demand in sago effluent. Photolysis of sago effluent in the presence of ultraviolet irradiation and aeration resulted in 68% of the chemical oxygen demand removal. The results indicate high chemical oxygen demand reductions for different concentrations of sago effluent at 1:10, 1:100, and 1:1000 diluted with distilled water following the ZnO photocatalytic treatment under the aerated conditions. The chemical oxygen demand reductions of 90–95% and 85% were obtained using 3 g/L of ZnO, after 2 h of aerated and non-aerated photocatalytic treatments, respectively, for the sago effluent ratio of 1:1000. On the other hand, the combination of the most concentrated sago effluent at 1:10 and non-aerated ZnO photocatalytic treatment resulted in no appreciable chemical oxygen demand reduction at only 8%. The concentrations of Fe^{2+} (10–60 mM) and H_2O_2 (50–150 mM) greatly influenced the degradation rates of chemical oxygen demand. The optimum parameters of 10 mM of Fe^{2+} and 50 mM of H_2O_2 were able to reduce 97% of the chemical oxygen demand of the 1:1000 sago effluent under the photo-Fenton treatment with 2 h of ultraviolet irradiation. Thus, both ZnO photocatalysis and photo-Fenton can be applied as the possible treatment methods to reduce the chemical oxygen demand in effluent from sago processing.

Keywords Advanced oxidation process · Degradation · Organic matter · Wastewater treatment

1 Introduction

Advanced oxidation processes (AOPs), such as photocatalysis, ozonation, Fenton, and photo-Fenton are regarded as appropriate to degrade organic pollutants. All AOPs are characterised by a common chemical feature, known as reactive oxygen species (ROS) that can react with non-biodegradable or recalcitrant compounds in water [28]. Of the various ROS, the hydroxyl, $\cdot\text{OH}$ radicals have attracted the most attention. The efficiency of AOPs in treating wastewater depends on the (i) composition and concentration of wastewater; and (ii) pollutant load, as the heavier the pollutant load, the stronger the treatment conditions must be applied [32]. Photocatalytic oxidations using titanium

dioxide (TiO_2) and zinc oxide (ZnO) and photo-Fenton are more distinctive compared with the other AOPs for the removal of organic pollutants from wastewater. The photo-Fenton process which uses Fenton reagents, H_2O_2 and Fe^{2+} in the presence of light to produce $\cdot\text{OH}$ radicals has shown to be a cost-efficient process as solar energy can be utilised for its activation [36]. Photo-Fenton oxidation has been reported to be efficient in treating different types of wastewaters [21, 22, 48]. ZnO with a band gap energy of 3.2 eV (similar to TiO_2) can serve as an alternative photocatalyst in organic pollutants degradation due to its high quantum efficiency, high chemical stability, high photosensitivity, low cost, and ability to absorb larger fraction of solar spectrum than that of TiO_2 [30, 34]. Several studies

✉ Devagi Kanakaraju, kdevagi@unimas.my | ¹ Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia.



have concluded that ZnO performs as a better photocatalyst than TiO_2 in the environmental photocatalytic applications [10, 23].

In Malaysia, sago palms (*Metroxylon sagu*) are commercially grown for the production of sago starch, which is considered as the highest starch-producing crop at 25 tonnes per hectare per year [11, 46]. Sago mills that produce sago starch are voracious water consumers. Wastewater or effluent, which is produced from sago mills during sago debarking and processing of sago bark, is generally discharged into rivers [4]. Typically, a sago mill processes about 1000 logs per day. This produces a minimum of 400 tons of sago effluent containing about 5% of solids (20 tons) [3]. Hence, water treatment has become one of the main concerns for this industry. A direct release of sago effluent that contains high levels of organic materials, total suspended solids (TSS), chemical oxygen demand (COD), and biochemical oxygen demand (BOD) into water courses will lead to significant environmental problems [25]. According to previous studies, activated sludge process or biological treatment are preferred to treat sago wastewater. For example, a hybrid upflow anaerobic sludge blanket in the presence of microorganisms was used to reduce the levels of COD and TSS in sago wastewater [6]. In another study, Doraisamy et al. [17] revealed that an anaerobic hybrid reactor can successfully reduce the influent of organic load content with an optimum hydraulic retention time of 10–20 h. Rashid et al. [41] investigated the effect of extended aeration time for the removal of BOD, COD, and TSS from sago wastewater, which was collected from a sago mill in Mukah, Sarawak. In the study, the extended aeration period was able to reduce BOD, COD, and TSS levels to 84%, 88%, and 73%, respectively. An electrochemical treatment using Ti/PbO_2 electrodes has also been investigated as a potential treatment technique for the COD removal [45]. A recent study investigated the removal of COD using a novel mixture, TiO_2 and modified sago bark [29]. A combination 0.10 g of 0.2 g/L TiO_2 and 1% of modified sago bark resulted in 52.83% of the COD removal. On that basis, more studies on the potential of AOPs are necessary to determine the best operating parameters to serve as a baseline data for pilot-scale studies in the future. To the best of our knowledge, no studies are available on the application of ZnO photocatalysis on sago effluent. Our research group have published findings pertaining to the performance of photo-Fenton on sago effluent degradation by using response surface methodology approach [29].

Hence, this study aimed to investigate the efficiency of two types of AOP, ZnO photocatalysis and photo-Fenton to reduce an organic matter indicator, COD in sago effluent. COD measurement which indicates the amount of organic matter in water sample via chemical oxidation is

applied in wastewater industry [26]. ZnO photocatalysis was performed under aerated and non-aerated conditions to study their effects on the COD reduction.

2 Materials and methods

2.1 Sampling

Sago palm is a species of palm in the genus of *Metroxylon* which belongs to the *Palmae* family. At present, this species of sago palm is grown commercially in Malaysia, Papua New Guinea, the Philippines, and Indonesia. More than 90% of all sago planting areas are found in the state of Sarawak in Malaysia. Sago wastewater effluent was collected at the Herdson Sago Industries, which is located in Pusa, Sarawak, Malaysia. Raw sago samples were collected from the cooling pond, and were filled into polyethylene bottles. Each bottle was carefully labelled before being refrigerated at 4 °C prior to further analysis.

2.2 Reagents

ZnO, AgSO_4 , and HgSO_4 were supplied by Bendosen Laboratory Chemicals. The characterisations of the used ZnO can be referred to our previously published work [27]. The Brunauer–Emmett–Teller specific surface area (S_{BET}) of ZnO is 25 m^2/g with high crystallinity as proven by the X-ray diffraction pattern [27]. Ammonium iron(II) sulfate, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, were supplied by R & M Chemical. Sodium hydroxide, (NaOH) was purchased from Merck, while hydrogen peroxide (H_2O_2 , 35%) was purchased from Bendosen. Ferroin indicator solution and sulfuric acid (H_2SO_4 , 95–97%) were supplied by Fluka Analytical and Merck, respectively. All chemicals were used without further purification.

2.3 Characterisations of sago effluent

Sago wastewater was characterised for pH, biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solid (TSS), and dissolved oxygen (DO). The analysis for water quality parameters was carried out according to the Standard Method of Water and Wastewater [1]. All parameters were analysed in triplicates, and mean data was used for data analysis.

2.4 ZnO photocatalysis

An 8 W ultraviolet (UV) lamp ($\lambda = 254 \text{ nm}$, Philips TUV) was used as the irradiation source in ZnO photocatalytic treatment. Filtered sago effluents were subjected to aerated and non-aerated conditions under UV irradiation with

different ZnO concentrations. An air diffuser was placed at the bottom of the beaker to continuously supply aeration during the treatment. Approximately 150 mL of sago effluent and different concentrations of ZnO of 0.5, 1, 2, and 3 g/L were added into 250 mL beakers. The specific concentration of ZnO was chosen based on preliminary studies. All the experiments were conducted under continuous magnetic-stirring with 2 h of exposure to UV irradiation. However, during the first 30 min of the treatment, filtered sago effluent and reagents were stirred under dark conditions to establish equilibrium prior to turning on the UV light. Filtered and diluted sago effluents were used because light was unable to penetrate into raw sago effluent. Sago effluent normally contains a large amount of fine fibres, known as roughage or *hampas*, which may also reduce the performance of the ZnO and Fenton reagents used in this study. About 10 mL of sample (t_0) was collected after 30 min of equilibrium time prior to UV irradiation. Likewise, 10 mL of samples were collected at pre-determined intervals during the 2 h irradiation period, and were later analysed for COD level. The efficiency of ZnO photocatalytic treatment was determined on the basis of the percentage of COD reduction. COD analysis was performed based on the Standard Methods for Water and Wastewater Treatment [1]. Another series of experiments were conducted to study the effect of diluted sago effluent using distilled water at 1:10, 1:100, and 1:1000, under aerated and non-aerated conditions, on COD reduction using the optimum ZnO concentration. The photolysis experiment (without ZnO) was also performed to determine the contribution of photolysis in reducing the level of COD. All the experiments were performed in triplicates.

2.5 Photo-Fenton treatment

The photo-Fenton treatment of 150 mL sago effluent was conducted using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 , as the reagents in the photo-Fenton and Fenton reactions. The experiments were performed by varying the concentrations of Fe^{2+} and H_2O_2 , as tabulated in Table 1. Experiments T1–T3 were performed by keeping Fe^{2+} concentration constant, and varying the concentration of H_2O_2 , while for experiments T4–T6, these parameters were reversed. Preliminary experiments were conducted prior to fixing the appropriate concentrations of Fe^{2+} and H_2O_2 .

The pH of the solution mixture was kept in the range of 2–3 by adding H_2SO_4 accordingly. The solution was continuously stirred with a magnetic stirrer under UV light for 2 h to ensure homogeneity. About 20 mL of sample was withdrawn from the beaker at 30 min intervals during the 2 h treatment, for COD analysis. Upon sampling, the pH of the sample was adjusted to between 11 and 12 by adding NaOH pellets to quench the reaction. Then,

Table 1 Photo-Fenton treatment with different amounts and concentrations of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2

Experiment code	Concentration of Fe^{2+} (mM)	Weight of Fe^{2+} (g)	Concentration of H_2O_2 (mM)	Volume of H_2O_2 (mL)
T1	10	0.41703	50	0.729
T2	10	0.41703	100	1.458
T3	10	0.41703	150	2.187
T4	20	0.83406	80	1.1664
T5	40	1.66812	80	1.1664
T6	60	2.50218	80	1.1664

the collected samples were left overnight to ensure the complete decomposition of H_2O_2 and Fe^{2+} ions. At this pH, Fe^{2+} will react with OH^- ion to form the insoluble ferrous hydroxide, $\text{Fe}(\text{OH})_2$, while H_2O_2 will decompose into water and oxygen [47]. After overnight, the samples were filtered to remove Fe^{2+} and followed by COD analysis. Dark Fenton treatments, which also served as blanks were conducted under the T1 and T4 experimental conditions. This step was conducted to compare the effectiveness between photocatalysis and photo-Fenton in reducing the COD. The beaker used for the dark Fenton treatment was wrapped with aluminium foil to prevent any form of light from getting into the reaction mixture.

2.6 Statistical analysis

The one-way analysis of variance (ANOVA) was carried out for comparison of maximum COD reduction percentage between the treatments. SPSS programme (Version 15.0) was also used to analyse the data.

3 Results and discussion

3.1 Characteristics of sago effluent

Table 2 shows the physicochemical parameters of the analysed sago effluent. Raw sago wastewater demonstrated a pale brownish colour, which consisted of water and fine insoluble fibres or better known as *hampas* or roughage. The pH of the effluent was acidic in nature. This could be due to the production of residual effluents after the extraction process, which often contains a small amount of starch and proteins, and the presence of hydrogen cyanide [7]. The results show that the BOD (2733.33 mg/L), COD (26,953 mg/L), and TSS (6326.67 mg/L) values for this study were higher—with the exception for TSS—compared with the values reported by Rashid et al. [41], which were 910–1300 mg/L, 780–5130 mg/L, and 19–20,000 mg/L for BOD, COD, and TSS, respectively. Overall, the values

Table 2 Physicochemical parameters of sago effluent [15]

Parameters	Values	Parameters limits of effluent (standard B)*
Odour	Light pungent-ashy smell	Not available
pH	5.89±0.01	5.50–9.00
Colour	Brownish	Not available
TSS	6326.67±2076	100.00
BOD ₅ , 25 °C	2733.33±473	50.00
COD	26,953±2004	200.00

All parameters are in mg/L except for odour, colour, and pH

* Department of Environment [15]

obtained from the characterisations of sago effluent showed that its water quality did not meet the requirements of the Department of Environment [15]. Hence, a proper pre-treatment must be applied to improve the discharge quality of the sago effluent.

3.2 ZnO photocatalysis for COD reduction

3.2.1 Effect of ZnO concentration

The diluted sago effluent (1:1000) was aerated to investigate the effect of aeration on the COD reduction. A non-aerated sample was also analysed. The photocatalytic experiments under aerated and non-aerated conditions were conducted simultaneously by varying the ZnO concentration from 0.5 to 3 g/L. Figure 1a, b show the reduction of COD in the sago effluent under aerated and non-aerated conditions, respectively, in the presence of different concentrations of ZnO. The degradation rates of COD in sago effluent under aerated and non-aerated conditions followed the pseudo-first-order kinetics. The rate constant (*k*) and coefficient of determination (*R*²) were obtained from the plot of ln (*C*/*C*₀) versus time (Table 3).

Under UV irradiation and aeration, 68% of the COD reduction was observed in sago effluent without ZnO photocatalyst (*k*=0.0101/min) (Fig. 1a), while only 39% of reduction occurred when no aeration was supplied into the treatment system (*k*=0.0051/min) (Fig. 1b). Photolysis and the presence of oxygen had offered noticeable contributions in reducing the level of COD. A study by Rashid et al. [41] also indicated that the lab-scale extended aeration aided in the reduction of COD in sago effluent sampled from Mukah, Sarawak. Nevertheless, the reduction of COD was enhanced in the presence of ZnO, although differences can be observed between both conditions, as shown in Fig. 1 and by the pseudo-first-order kinetics data (Table 3). In general, the COD reduction at 2 h of treatment time increased with the increasing ZnO concentration.

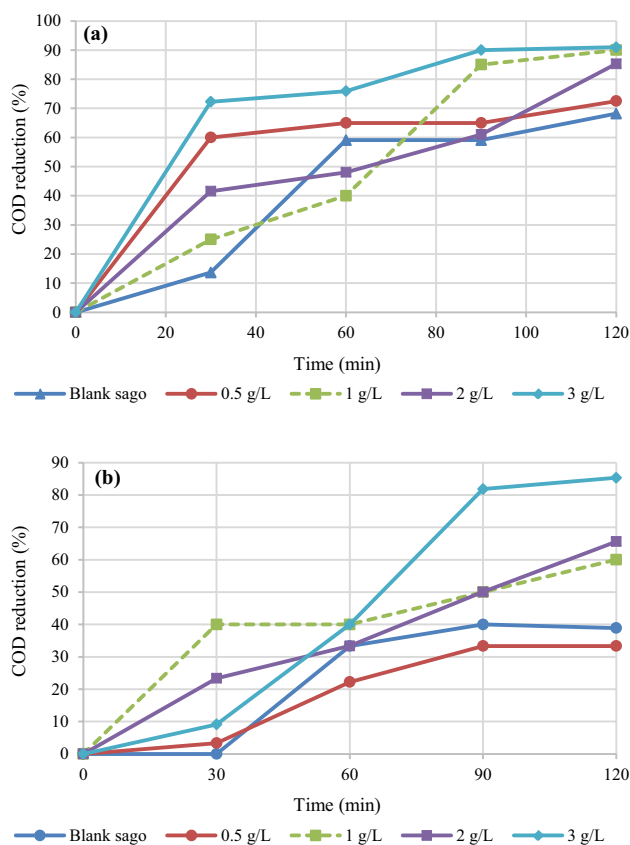


Fig. 1 COD reduction in sago effluent under **a** aerated condition and **b** non-aerated condition in the presence of different ZnO concentrations (UV irradiation: 2 h; sample volume: 150 mL; dilution ratio: 1:1000)

Similar trend was also reported by a study which investigated the potential of ZnO on the removal of COD (and BOD) from sewage wastewater [40]. As seen in Fig. 1a, 0.5 g/L of ZnO was not as efficient as the other concentrations in reducing COD under aerated photocatalysis. The COD reduction became almost constant after 30 min of irradiation up until 90 min at 60–65%, and slightly increased to 73% at the end of the treatment. In fact, the COD reduction percentage in the presence of 0.5 g/L ZnO under aeration was slightly higher than that of sago effluent only (68%). Nevertheless, a rapid increase during the initial phase of 60 min resulted in slightly higher kinetic value for sago only compared to photocatalytic treatment using 0.5 g/L ZnO under aeration (Table 3). Meanwhile, the efficiency of 1 g/L of ZnO was comparable to that of 3 g/L of ZnO. However, the curve for 3 g/L of ZnO was steeper, indicating a rapid COD reduction. The reduction efficiencies for 1 and 3 g/L of ZnO at the end of the treatments were almost similar at 90% and 91%, respectively. On the other hand, although the COD reduction was slightly lower for 2 g/L of ZnO during the first 60 min compared with that for 0.5 g/L of ZnO (the lowest concentration used in

Table 3 Pseudo-first-order kinetic parameters of aerated and non-aerated ZnO photocatalysis of sago effluent using different ZnO concentrations

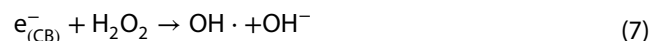
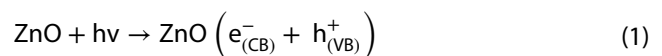
ZnO (g/L)	Aerated			Non-aerated		
	Reduction (%)	k (min)	R ²	Reduction (%)	k (min)	R ²
0.5	73	0.0091	0.80	33	0.0039	0.92
1.0	90	0.0253	0.90	60	0.0067	0.89
2.0	85	0.0196	0.80	66	0.0087	0.97
3.0	90	0.0289	0.93	85	0.0184	0.90
Sago only	68	0.0101	0.89	39	0.0051	0.84

(i) The treatment was performed for 2 h, (ii) $\ln(C/C_0)$ was plotted based on COD values (mg/L), (iii) C = COD value at time t, and C₀ = initial COD

this study), its COD reduction efficiency increased to 85% after the 2 h treatment. Therefore, the concentration of ZnO greatly affected the reduction of COD in sago effluent under aerated photocatalytic treatment. The non-aerated ZnO photocatalysis using the lowest concentration of ZnO (0.5 g/L) exhibited the lowest efficiency in reducing the COD. The removal reached almost a constant value of 33% at 90 min of treatment (Fig. 1b). The active sites on the ZnO surface could have been saturated by the adsorbed pollutant molecules resulting no vacant sites and competitive adsorption between molecules for adsorption onto ZnO surface [30, 40]. The treatment using 1 g/L of ZnO outperformed the higher concentrations of 2 and 3 g/L during the initial 60 min of the treatment. However, as the reaction time continued, the latter demonstrated a higher efficiency to reduce the COD. The highest COD reduction of 85% was attained using 3 g/L of ZnO, while 1 and 2 g/L of ZnO accomplished 60% and 66% reductions, respectively, after 2 h of treatment time under non-aerated photocatalytic condition (Fig. 1b).

According to Table 3, the highest degradation rates under the aerated ($k = 0.0289/\text{min}$) and non-aerated ($k = 0.0184/\text{min}$) conditions were achieved with 3 g/L of ZnO. As such, the optimum concentration of ZnO was fixed at 3 g/L for both conditions. It is known that removal enhancement is resulted by the increased amount of pollutant molecules adsorbed on the ZnO photocatalysts and density of particles on the radiation exposed surface [16]. This study shows that ZnO photocatalytic treatment performed better under aerated condition compared with that under non-aerated condition. The presence of oxygen may have enhanced the COD reduction in sago effluent, judging from the pseudo-first-order kinetics data (Table 3) and the reduction profiles (Fig. 1). Aeration was reported to positively affect the degradation of wastewater by means of photocatalysis using ZnO or TiO₂ in various related studies [2, 42]. The role of oxygen in photocatalysis includes being an electron acceptor, getting involved in the formation of other oxidative species (e.g., hydroxyl radical, superoxide radical, or hydrogen peroxide), as well as to prevent reduction reactions [14]. Oxygen can

also act as electron scavenger to prevent the recombination of photogenerated electron-hole pairs, which could reduce the photocatalytic activity of ZnO [14]. When the recombination rate of photogenerated electron-hole pairs is reduced, positive holes can either directly oxidise the organic pollutants or react with OH⁻ anions to form powerful HO· radicals, which could promote the degradation of sago effluent. This would aid the reduction of COD because more organic matter in sago effluent can be oxidised to their simpler forms. Hence, COD levels in sago effluent can be reduced by supplying oxygen via aeration, which is an economical way to enhance the ZnO photocatalytic treatment of sago effluent. When pilot-scale treatments are considered, operating costs can be potentially reduced if air is used instead of pure oxygen [29]. Overall, the ZnO-mediated photocatalytic treatment of sago effluent can be postulated due to the formation of HO· radicals on the surface of the photocatalyst as shown in the following equations (Eqs. 1–7): [16, 30, 37].



The powerful HO· radicals can attack sago effluent adsorbed on the surface of ZnO leading to the formation of intermediate compounds and eventually complete mineralization [37].

3.2.2 Effect of dilution on COD reduction

High turbidity and the presence of high amount of fibres or *hampas* may hinder the photocatalytic activity of ZnO due to opacity, where light might not be able to reach the suspension to photo-activate ZnO. Hence, three different ratios of diluted sago wastewater effluents at 1:10, 1:100, and 1:1000 were subjected to aerated and non-aerated conditions to investigate the effect of dilution on COD reduction. Figure 2a, b show the percentages of COD reduction for various dilution ratios under aerated and non-aerated conditions, respectively. For ZnO photocatalytic treatment under aerated condition, the COD reduction increased when the dilution ratio was increased from 1:10 to 1:1000, although the COD reduction for the 1:10 diluted sample was much lower, and levelled off after 60 min of irradiation (Fig. 2a). When the dilution ratio was increased from 1:10 to 1:1000, the COD reduction significantly increased from 19 to 95% at the end of the 2 h irradiation under aerated condition (Fig. 2a). On the other hand, the non-aerated condition showed that the dilution

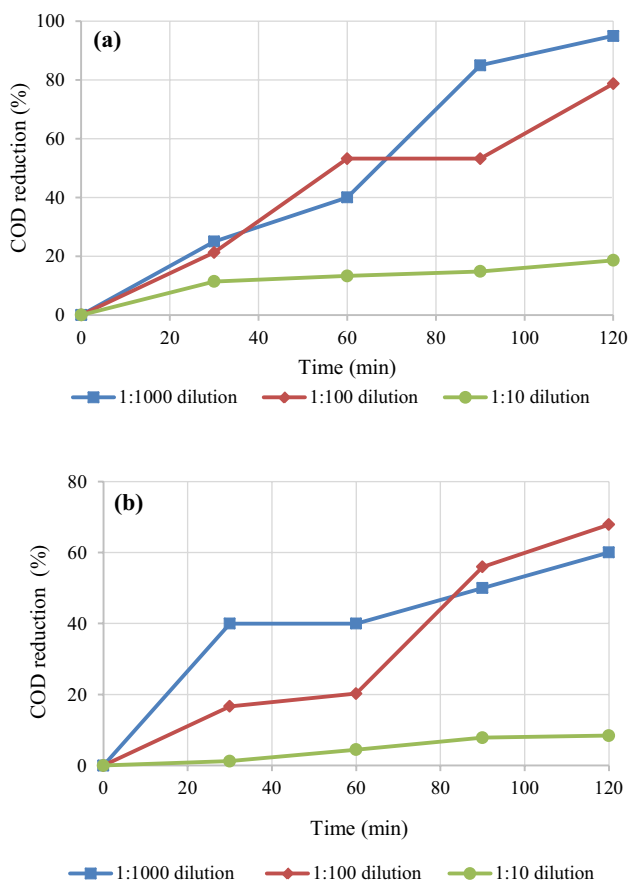


Fig. 2 COD reductions in sago effluent under **a** aerated condition and **b** non-aerated condition using different dilution ratios of sago effluent

ratio of 1:100 yielded a slightly higher COD reduction at 68% compared with only 60% for the 1:1000 sago effluent. Nevertheless, the COD reduction in the 1:1000 sago sample was higher compared with that in the 1:100 sample during the first 60 min. The percentage of COD reduction became much higher as time progressed. It is likely that photostable intermediates or UV absorbing intermediates had formed during the degradation of the 1:1000 sago sample during the first 60 min of treatment. Their formation could have caused the slow progress of COD reduction (Fig. 2b). Additionally, the absence of aeration could have led to insufficient mixing of the sago effluent and ZnO when compared with the performances observed for aerated ZnO photocatalysis. The dilution ratio of 1:10 resulted in only 8% of COD reduction, which also levelled off after 60 min of irradiation, similar to those observed under the aerated condition (Fig. 2b). This observation implies that the concentrated sago effluent produced no appreciable COD reduction under both conditions, which may be due to the opacity of the suspensions and the oxidation of organic matter became almost impossible. Furthermore, Liu et al. [31] stated that the higher initial concentration of pollutant would lead to higher adsorbed intermediates, which would affect the overall reaction rate. As such, the high concentration of sago effluent could have also hindered the COD reduction because of the higher concentration of the adsorbed intermediates. Thus, the dilution ratio of 1:1000 was concluded to be suitable for ZnO photocatalytic treatment under the experimental conditions of this study. The organic compounds that were present in the 1:1000 aerated sago sample may be completely oxidised during the photocatalytic treatment. The results show that the dilution or concentration of pollutant can greatly affect the COD reduction in sago effluent using ZnO photocatalysis.

In addition, this study shows that aeration can also promote the degradation of organic matters in sago effluent. Numerous studies that dealt with the photocatalytic treatment of wastewater had performed filtration and dilution prior to treatment [13, 47]. Dilution and filtration were performed mainly because in its present form, wastewater, such as palm oil mill effluent, would be impenetrable for the light source, as well as to avoid microbial degradation, which would alter the content of the wastewater [13]. The one-way ANOVA was performed to determine any significant differences between the COD reduction under aerated ZnO photocatalysis and non-aerated ZnO photocatalysis when different dilution ratios of sago effluent were applied. The one-way ANOVA shows that no significant difference between the obtained COD reductions as the *p* value is 0.564 at 95% confidence level.

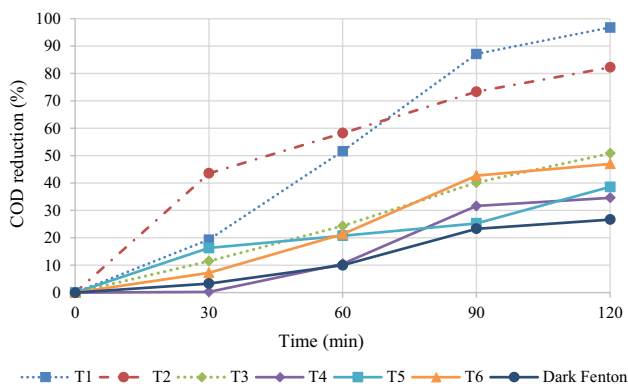


Fig. 3 COD reduction using photo-Fenton for experiments T1–T6

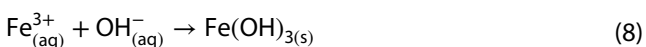
Table 4 Second-order-kinetic analysis for photo-Fenton treatment of sago effluent

Experiment code	Concentration (mM)		Mean COD reduction (%)	k (L/mg/min)	R ²
	Fe ²⁺	H ₂ O ₂			
T1	10	50	97	3.50 × 10 ⁻³	0.91
T2	10	100	82	4.00 × 10 ⁻⁴	0.95
T3	10	150	51	8.90 × 10 ⁻⁵	0.96
T4	20	80	35	3.64 × 10 ⁻⁵	0.89
T5	40	80	39	3.30 × 10 ⁻⁵	0.93
T6	60	80	47	8.30 × 10 ⁻⁵	0.94
Dark Fenton	10	50	27	5.50 × 10 ⁻⁵	0.94

The treatment was performed for 2 h

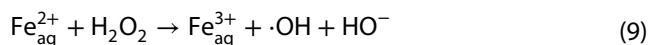
3.3 Photo-Fenton for the reduction of COD

The photo-Fenton treatment was employed on the diluted sago wastewater sample (1:1000). Dilution is essential for photo-Fenton treatment, especially when dealing with real wastewater sample [5]. NaOH pellet was added into the sample prior to the COD analysis to stop the oxidation reaction at pH 12, which would allow the decomposition of H₂O₂. Colloidal ferric hydroxide was formed when NaOH was added. The formation of Fe(OH)₃ can be expressed in Eq. 8:

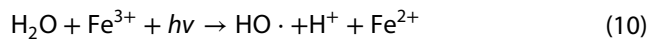


The effect of Fe²⁺ and H₂O₂ dosages on the COD reduction in sago effluent at pH 2.0–3.0 is shown in Fig. 3. The rate of COD removal depends on both H₂O₂ and Fe²⁺ concentrations ($r = k[\text{H}_2\text{O}_2][\text{Fe}^{2+}]$) [8, 9]. The optimum concentrations of H₂O₂ and Fe²⁺ are equally important because they determine the quantitative degradation and reaction kinetics, respectively [39]. Experiments T1–T3 were performed by fixing Fe²⁺ concentration and varying the

concentration of H₂O₂, while the parameters were reversed for experiments T4–T6. As shown in Fig. 3, the percentages of COD reduction and reaction rate, k (Table 4) decreased for experiments T1–T3. As for experiments T4–T6, the final COD percentages and reaction rates fluctuated (Table 4). In experiment T1, which was performed in the presence of 10 mM of Fe²⁺ and 50 mM of H₂O₂, the highest percentage of COD reduction was obtained at 97%, while the lowest percentage of COD reduction was recorded in experiment T4 (20 mM of Fe²⁺ and 80 mM of H₂O₂) at only 35%. A dark Fenton experiment was performed using the same condition in experiment T1, which produced the highest reduction rate ($k = 3.50 \times 10^{-3}$ L/mg/min). The percentage of COD reduction in the dark Fenton experiment was the lowest at 27% ($k = 5.50 \times 10^{-5}$ L/mg/min) compared with those in the photo-Fenton experiments (Table 4). As such, the photo-Fenton treatment was more efficient than the dark Fenton treatment. In the dark Fenton process or classical Fenton, ·OH radicals can be generated via the reaction between Fe²⁺ and H₂O₂, as shown in Eq. 9 [21, 38].



In the absence of light, after the initial conversion of Fe²⁺ to Fe³⁺, COD reduction would decrease, mainly due to the slower reaction of reducing Fe³⁺ back to Fe²⁺ in the presence of another H₂O₂ molecule [33]. Furthermore, the formation of intermediates, such as oxalic acid (H₂C₂O₄) during Fenton reaction (acidic condition) may also contribute to the slower reduction rate of Fe³⁺ back to Fe²⁺, which may subsequently reduce the percentage of COD reduction, because Fe³⁺ can be chelated by the oxalate anion [33]. However, in the photo-Fenton process, Fe³⁺ is converted back to Fe²⁺ and HO· radicals in the presence of UV irradiation as described in Eq. 3. Fe²⁺ can further react with H₂O₂ to produce more HO· radicals [21, 38], which are responsible for the degradation of organic matter via Eq. 10.



3.3.1 Effect of H₂O₂

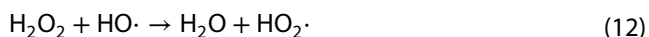
In experiments T1–T3, when the concentration of H₂O₂ was increased from 50 to 100 mM, the efficiency of the photo-Fenton treatment reduced (Fig. 3). When 50 mM of H₂O₂ was used, the percentage of COD reduction was the highest at 97% with $k = 3.50 \times 10^{-3}$ L/mg/min. However, the COD reduction rates significantly decreased to 4.00×10^{-4} and 8.90×10^{-5} L/mg/min when the H₂O₂ concentration was increased to 100 mM and 150 mM, respectively. This could be due to the recombination of the HO· radicals as shown in Eq. 11 [24].

Table 5 Price of reagents and cost estimation

Reagent	Price (USD)/kg	Required amount (kg) (> 90% COD removal)	Total cost (USD)
ZnO ^a	2.2	0.0045	0.00099
(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O (sigma-aldrich)	117	0.41703	48.79
H ₂ O ₂ (30%) ^a	0.35	0.000729	

^aElmolla and Chaudhuri [20]

The excess H₂O₂ may also react with the HO· radicals and compete with the organic pollutant, which can eventually reduce the efficiency of the treatment. According to Miklos et al. [35], excess H₂O₂ could also lead to the reduction of Fe(III) to Fe(II). Besides increasing the cost of treatment for high volume of organic wastewater, an excessive concentration of H₂O₂ also increases the COD level of the effluent [49]. Furthermore, the excessive H₂O₂ concentration may also negatively impact the degradation kinetics. A possible explanation for this is due to the recombination of the ·OH radicals and the auto-decomposition of H₂O₂ into O₂ and H₂O. Furthermore, the excessive amount of H₂O₂ will act as scavengers for the ·OH radicals to produce hydroperoxy radicals (HO₂·) as explained in Eq. 12, which have a lower oxidation capacity compared with that of the ·OH radicals [5].



Hence, considering the previously outlined reasons, 50 mM of H₂O₂ was taken as the optimum dosage under these experimental conditions.

3.3.2 Effect of Fe²⁺

The concentration of Fe²⁺ was varied from 20 to 60 mM for experiments T4–T6 (Fig. 3). The percentage of COD reduction slightly increased with the increased concentration of Fe²⁺ ions. The reaction rate also increased from 3.64×10^{-5} L/mg/min for 20 mM of Fe²⁺ to 8.30×10^{-5} L/mg/min for 60 mM of Fe²⁺ (Table 4). However, when the reaction rates obtained from experiments T4–T6 were compared with those from experiments T1–T3, it was clear that 10 mM of Fe²⁺ produced higher reaction rates. Hence, under the investigated experimental conditions, 10 mM of Fe²⁺ can be considered as the optimum concentration. Having an optimum concentration for Fe²⁺ is crucial to ensure that no excess Fe²⁺ is left unutilised in the reaction because it can contribute to an increased level of total dissolved solid or iron sludge in the treated effluent [5, 24]. Nonetheless, high concentrations of Fe²⁺ ion can only increase the rate of the reaction up to a certain limit.

Exceeding the optimum concentration, the rate of degradation becomes less significant due to the scavenged radicals by Fe²⁺ [43]. In addition, it can also inhibit the degradation process because Fe²⁺ ions may compete with the organic pollutants to react with the ·OH radicals (Eq. 13). A large quantity of Fe³⁺ sludge could also be generated at the end of the wastewater treatment due to the high amount of Fe²⁺ ions [44].



3.3.3 Effect of pH

Both the Fenton and photo-Fenton reactions are strongly pH-dependent as the pH value affects the production of ·OH radicals, and thus, their oxidation efficiency [24]. In this study, the photo-Fenton experiments were carried out at a pH range of 2.0–3.0. This pH range was chosen because pH values of 2.5–3.0 were reported as the optimum pH values for homogeneous Fenton-like processes [49]. A higher COD removal in sago effluent was also reported in acidic condition by electrochemical treatment due to the enhanced formation of the ·OH radicals to facilitate the oxidation of organic matter [45]. At pH > 3, the dissociation and auto-decomposition of H₂O₂ may lead to inefficient reduction of COD. However, the reaction of Fe²⁺ with H₂O₂ was significantly affected at pH < 2.5 [49]. H₂O₂ has been reported to be more stable at low pH values, as a result of the formation of oxonium ions (H₃O⁺), which may subsequently reduce its reactivity with Fe²⁺ ions [18, 19]. This may lead to a reduced ·OH radical production because of the ·OH radical scavenging by H⁺ ions, as shown in Eq. 14 [24].



3.3.4 Cost comparison

A thorough cost estimation can be done based on maintenance, operating cost and capital [12, 20]. Based on the batch studies performed, optimized conditions were chosen for cost estimation purpose. Cost comparison based on reagent price used in ZnO photocatalysis and

photo-Fenton was performed to determine a more cost-effective method to achieve a maximum COD removal (> 90%) (Table 5). Comparatively, ZnO photocatalytic treatment appeared to be more cost effective than photo-Fenton. Nevertheless, solar based-photo Fenton can be considered for future studies to reduce the operation cost.

4 Conclusion

To ensure the efficient degradation of sago effluent, raw effluent needs to be diluted prior to ZnO photocatalysis and photo-Fenton treatment. The findings reveal that the dilution of sago effluent with distilled water at the ratio of 1:1000 resulted in the highest percentage of COD reduction. Additionally, the aerated ZnO photocatalytic treatments performed better than the non-aerated ZnO photocatalytic treatments in reducing COD levels. ZnO loading of 3.0 g/L was the best concentration for sago effluent degradation in this study. Whereas for photo-Fenton, the maximum COD reduction was obtained using a combination of 10 mM of Fe^{2+} and 50 mM of H_2O_2 , which resulted in 97% of COD reduction after 2 h of UV irradiation. First-order- and second-order-kinetics are a good fit for the COD reduction data of ZnO photocatalysis and photo-Fenton treatments, respectively. Both treatment methods, aerated ZnO photocatalysis, in particular, and photo-Fenton in general, were applied for the degradation of sago effluent. This study had shown their potential applications to reduce COD levels, provided that a dilution unit is installed prior to this treatment. Further studies are required to look into the BOD parameter. This is because the BOD_5/COD ratio, which indicates the biodegradability level of wastewater, can be used as an indicator to determine if the wastewater could be degraded using biological treatments. A combination of biological and chemical treatments may offer a more effective treatment to degrade sago effluent.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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