

# Combination of Persulfate /Peroxymonosulfate Activated By Ion (II) with Hydrogen Peroxide for Mineralization and Valorization of Vinasse

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**Abstract:** Recently, there is an increasing demand for water due to rapid industrialization and a growing human population. There is a too shortage of available water sources; thus, one option for increasing existing resources is the treatment and reuse of wastewaters. Vinasse poses a long-term risk to public health because of its toxic nature and a huge amount. This study investigates a new prospect of a combination of persulfate (PS)/ peroxymonosulfate (PMS) (activated by Ion (II)) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for reducing total organic carbon (TOC) from vinasse and reuse of treated vinasse as well. Behaviors of PS/Fe(II)/ H<sub>2</sub>O<sub>2</sub> and PMS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> on total organic carbon (TOC) removal are explored by evaluating various effects, including H<sub>2</sub>O<sub>2</sub> dosage, Fe (II) dosage, pH and reaction time. Hydrogen peroxide was used as an oxidation agent to improve the degradation of the organic matter of vinasse. The addition of H<sub>2</sub>O<sub>2</sub> to PS/ Fe (II) or PMS/ Fe (II) generates highly oxidizing radicals, which enhanced, significantly, the removal of TOC. Both of PS/ Fe (II)/ H<sub>2</sub>O<sub>2</sub> and PMS/ Fe (II)/ H<sub>2</sub>O<sub>2</sub> systems favored neutral pH in removing the organic matter, and they were very active in the first 5 minutes. At the optimum conditions, about 86 % and 83% of TOC removal were achieved by PS/ Fe (II)/ H<sub>2</sub>O<sub>2</sub> and PMS/ Fe (II)/ H<sub>2</sub>O<sub>2</sub>, respectively. Therefore, a combination of PS/PMS activated by Fe (II) with H<sub>2</sub>O<sub>2</sub> can be considered as a capable technique for sugarcane vinasse treatment and allowing to reuse the effluents in many applications.

**Keywords:** Sugarcane vinasse; Sulfate radical; Hydrogen peroxide; Hydroxyl radical; Total organic carbon

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## 1. Introduction

Ethanol distillery wastewater is rated as one of the 17 most polluting industries [1], among them vinasse is considered to be the most hazardous distilleries due to its acidic nature, dark brown liquid with high biological oxygen demand (BOD), and chemical oxygen demand (COD). A considerable amount of vinasse is produced during ethanol manufacturing. Discharging of such large quantities of pollutants affects the environment in a harmful manner [2].

Recently, PS and PMS gained more attention and have been broadly applied to the degradation of organic compounds [3-5]. PS and PMS can be activated by heat, transition metal, electrolysis (EC) and UV to generate sulfate radical (SO<sub>4</sub>•-) [6-8]. Sulfate radical is a

strong oxidative character with a redox potential of (2.5–3.1 V), and it has high efficiency of mineralization of organic pollutants [9].

A combination of PS / PMS with other substances in order to enhance the removal of contaminants has been reported several times. For example, using activated carbon as a persulfate/ peroxymonosulfate activator was reported by [10-12]. A combination of ozone with persulfate has been used to enhance the biodegradability of stabilized leachate [13].

Hydrogen peroxide has been used to reduce COD and BOD in a wide variety of industrial and domestic wastewater for many years [14]. Due to oxidation potential ( $E_0$ ) of 1.76 V,  $H_2O_2$  is capable of oxidizing different organic contaminants and producing environmentally safe products, such as  $H_2O$ ,  $O_2$ , and  $OH^-$  [15]. Generation of hydroxyl radical ( $HO^\bullet$ ) from  $H_2O_2$  in water and wastewater treatment systems can be achieved by using various activation techniques such as Fenton's reaction and UV, [16, 17]. Although the  $H_2O_2$  reagent can act as a direct oxidant, its performance in the degradation of high organic content is limited [18]. According to many reports, persulfate oxidation in combination with  $H_2O_2$  is more efficient for remediation of organic contaminants [19, 20]. Some of the studies have proposed that  $H_2O_2$  may act as an activator of persulfate. [19]. So far, the role of  $H_2O_2$  in persulfate activation is still vague and poorly demonstrated. In a specific manner, it is not well proved whether  $H_2O_2$  certainly activate persulfate or indirectly involve in degradation reactions, such as Fenton-like reaction and consequently improve the degradation efficiency of organic contaminants.

Vinasse contains recalcitrant organic components, such as melanoidins and phenolic compounds [2]. A combination of PS/  $H_2O_2$ /Fe (II) or PMS/  $H_2O_2$ /Fe (II) is expecting to generate high amounts of  $SO_4^{\cdot-}$  and  $OH^\bullet$ . The resulting high amounts of free radicals are expected to exhibit relatively high reactivity and became capable of degrading recalcitrant organic compounds.

In past years, countries and international organizations have designed strategies or laws in order to regulate the reuse of treated wastewaters. These laws or guidelines establish the maximum concentrations of contaminants permitted, taking into account the type of water reuse [21]. Among these countries, Sudan established standard characteristics of the reused treated wastewaters. The reuse of treated wastewater depends on the type of wastewater, the characterization of treated wastewater, and the purposes of using. The treated wastewater can be reused for many purposes such as forestry, ornamental, garden, other green spaces, and cleaning of equipment in agricultural or industrial.

Our previous study [22] has demonstrated that only 49% and 70% of TOC were removed from vinasse using PS/ Fe (II) and PMS/ Fe (II), respectively. However, the TOC removal extent was inconvenient, suggesting that proper activation of PS and PMS is still required. Therefore, the objective of this study is to propose a new approach of treatment of vinasse by a combination of PS/PMS (activated by ferrous ion) with  $H_2O_2$  and reuse the treated vinasse according to Sudanese legislation for wastewater reuse.

## 2. Materials and Methods

### 2.1. Chemicals and reagents.

Hydrogen peroxide  $H_2O_2$  (30%) was obtained from Suprasolv (Germany). Potassium iodide (99%),  $H_2SO_4$  (98 %), and  $FeCl_3$  were obtained from Merck (Germany).  $FeSO_4 \cdot 7H_2O$  (99.5 %), Potassium persulfate (PS) (99 %), and potassium peroxymonosulfate (PMS) were

purchased from Acros Organics (USA). Sodium hydroxide was obtained from Fluka (Germany). Ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> • 4H<sub>2</sub>O] was obtained from Sigma-Aldrich (USA). Soluble starch was purchased from Sigma-Aldrich (USA). Sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> • 5H<sub>2</sub>O) was purchased from Sigma-Aldrich (Germany). All reagents were of analytical grade, and only deionized water was used. Ultrapure water was used for the preparation of all aqueous solutions.

### 2.2. Characterization of Vinasse.

The vinasse used in this study was obtained from an ethanol distillery located at White Nile State (Sudan). Vinasse was collected directly after the distillation. Vinasse was, initially, treated by the coagulation-flocculation process at the optimum condition and then treated by PS- Fe (II) or PMS- Fe (II) system as described previously by [22]. The characteristic parameters of raw vinasse and pretreated vinasse are shown in Table 1. The main physicochemical parameters of vinasse were determined according to [23]. The concentrations of H<sub>2</sub>O<sub>2</sub> were determined according to the method described by Solvay Chemicals [24].

### 2.3. Experimental procedures.

All experiments were performed in a batch mode. All tests were carried out at room temperature in the oxidation reactor. All chemicals and reagents used in the experiments were of analytical grade. Aqueous solutions were prepared in the deionized water (Elga, USA). In order to determine the optimum conditions, we carried out four-stage of experiments as follow:

- a) Optimum dosage of PS/Fe (II) or PMS/Fe (II) [22] and different dosages of H<sub>2</sub>O<sub>2</sub> were added into the oxidation reactor(50-mL glass vials) which contained raw vinasse before the run. The H<sub>2</sub>O<sub>2</sub> reagent was added gradually to achieve the optimum dosage for the treatment of vinasse.
- b) Optimum dosage of PS/Fe (II) or PMS/Fe (II) and H<sub>2</sub>O<sub>2</sub> (obtained from previous oxidation step) were added to the reactor. Then, the immediately different dosage of Fe (II) was added to the mixture to achieve the optimum molar ratio of H<sub>2</sub>O<sub>2</sub>/Fe (II).
- c) Under optimum conditions of three previous oxidation steps, pH values of 3, 5, 7, and 9 were examined and assessed. The pH value of vinasse was adjusted gradually using sulfuric acid and sodium hydroxide. All runs in steps 1, 2, and 3 were performed for 4 hr. of oxidation.
- d) The reaction time was studied from 0.083 hr. to 24 hr. at pH 7.

**Table 1.** Characteristics of raw and pretreated vinasse.

Parameters	Raw vinasse	Pretreated vinasse
pH	3.5	-
Color	Dark brown	Colorless
TS	111mg/L	-
TDS	63.8mg/L	-
COD	126g/L	-
BOD	69.0g/L	-
TOC	48.000mg/L	134.5mg/L
TN	8.31mg/L	-

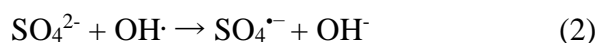
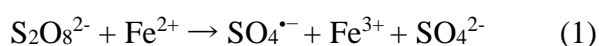
The orbital shaker was used at 150 rpm in all experiments runs. All samples were filtered through a syringe filter with a pore size of 0.45 μm prior to analysis. The extent of

organic matter in vinasse was evaluated by TOC analyses. TOC analyzer (Shimadzu TOC-L) was used to measure TOC concentration in order to monitor the degradation efficiency of organic matter. All samples were immediately analyzed without quenching. The effect of H<sub>2</sub>O<sub>2</sub> dosage, amount of Fe (II), pH, and reaction time was studied in detail. All experiments were conducted in triplicates.

### 3. Results and Discussion

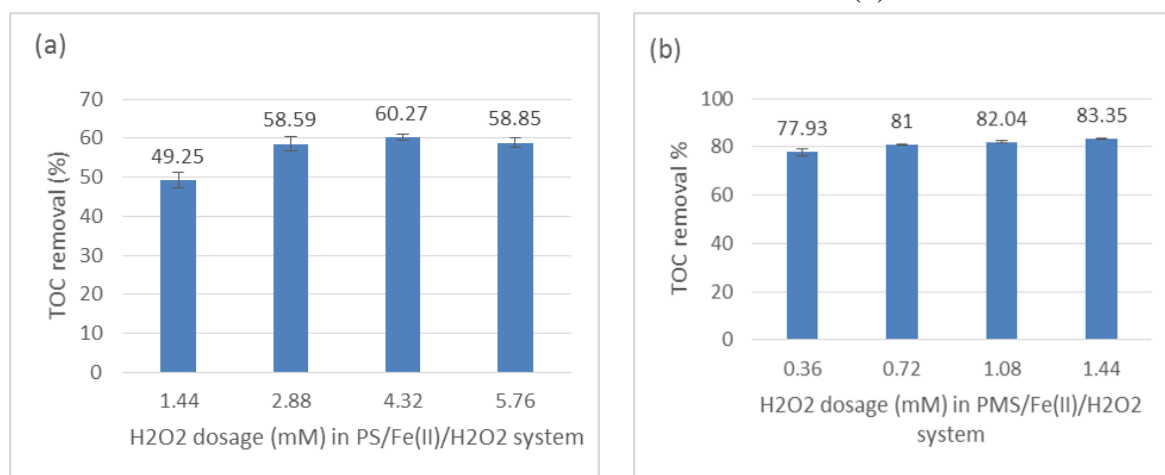
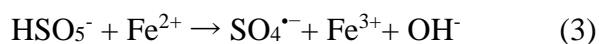
#### 3.1. Effect of H<sub>2</sub>O<sub>2</sub> concentration.

To reveal the performance of H<sub>2</sub>O<sub>2</sub> in enhancing TOC removal from vinasse, the concentration of H<sub>2</sub>O<sub>2</sub> was varied from 1.44 mM to 5.76 mM and from 0.36 mM to 1.44 mM in PS/Fe (II) and PMS/ Fe(II) systems respectively. As shown in figure 1(a and b), the addition of H<sub>2</sub>O<sub>2</sub> to the PS/ Fe (II) or PMS/ Fe (II) system improved the organic degradation. In PS/ Fe (II), the addition of 1.44 mM of H<sub>2</sub>O<sub>2</sub> removed 49% of TOC. Increasing the dosage of H<sub>2</sub>O<sub>2</sub> up to 4.32 mM, provides the greatest active sites to produce higher amounts of sulfate radicals, and consequently gives better degradation efficiency (60.27%). Equations (1) and (2) demonstrate that sulfate radicals were generated in ferrous ion activated systems, and hydroxyl radicals which are produced from the decomposition of H<sub>2</sub>O<sub>2</sub> increases the concentration of sulfate radicals [25], and accordingly enhancement of TOC removal.



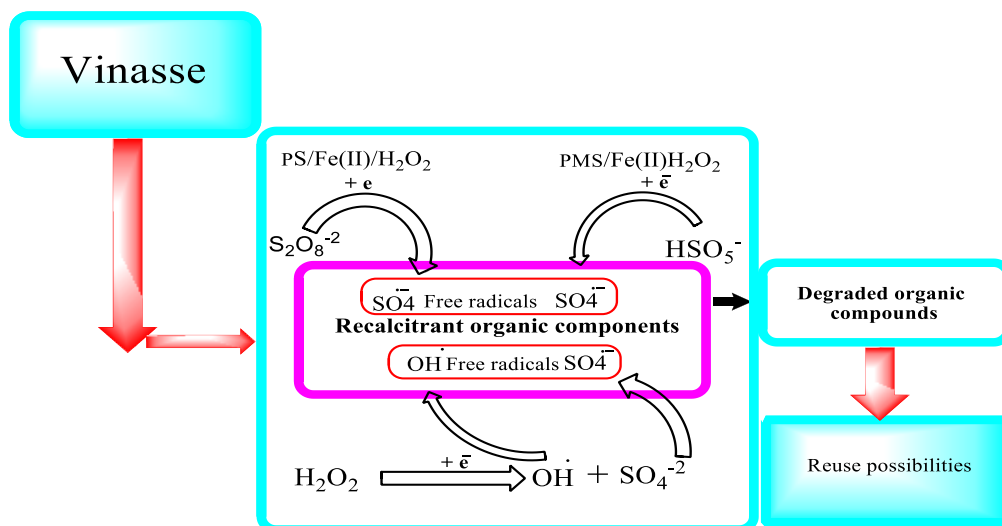
Crimi and Taylor, [26] described the mechanism of the cooperative reaction between PS and H<sub>2</sub>O<sub>2</sub>, which is the decomposition of H<sub>2</sub>O<sub>2</sub> to form OH<sup>·</sup>, followed by the activation of the PS to produce SO<sub>4</sub><sup>·-</sup>. In addition, many studies demonstrated that the addition of H<sub>2</sub>O<sub>2</sub> to the PS, can improve the pollutant removal efficiency [27, 28].

In PMS/ Fe (II) system, TOC removal was significantly increased by addition (0.36 mM) of H<sub>2</sub>O<sub>2</sub> Figure 1b. The increased degradation efficiency is attributed to the producing sulfate radical equation (3). As well as hydroxyl radical, which is formed via decomposition of H<sub>2</sub>O<sub>2</sub>.



**Figure 1.** Effect of a: H<sub>2</sub>O<sub>2</sub> dosage in PS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system: concentration of PS = 1.44 mM; concentration of Fe (II) = 0.72 mM; pH = 7; reaction time= 4 h b: H<sub>2</sub>O<sub>2</sub> dosage in PMS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system: concentration of PMS = 0.36 mM; concentration of Fe(II) = 0.9 mM; pH = 7; reaction time= 4 h.

Moreover, both sulfate and hydroxyl radicals may have played an important role in enhancing TOC removal. Further addition of H<sub>2</sub>O<sub>2</sub> demonstrated slight enhancement of TOC removal, from 77.93 to 83.35%. This may be attributed to the very strong and rapid reactions caused by the high oxidant dosages, which may inhibit the generation of hydroxyl radicals and consequently slow down the rate of pollutant degradation. Based on the results and the literature, the mechanism of PS/Fe (II)/ H<sub>2</sub>O<sub>2</sub> and PMS/Fe(II)/ H<sub>2</sub>O<sub>2</sub> processes were illustrated in Figure 2.



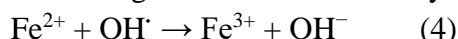
**Figure 2.** Proposed mechanism of PS/Fe (II)/ H<sub>2</sub>O<sub>2</sub> and PMS/Fe (II)/ H<sub>2</sub>O<sub>2</sub> processes.

### 3.2. Effect of H<sub>2</sub>O<sub>2</sub>/Fe (II) molar ratio.

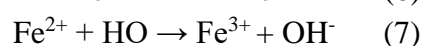
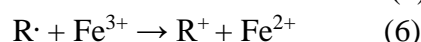
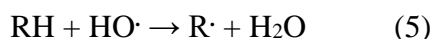
To assess the effect of Fe(II) concentration, fixed concentrations of H<sub>2</sub>O<sub>2</sub> (2.88 mM and 0.72 mM) were added to PS/H<sub>2</sub>O<sub>2</sub> and PMS/H<sub>2</sub>O<sub>2</sub> systems respectively, whereas, the concentration of Fe (II) was varied from 2.88 to 8.64 mM and 0.72 to 2.16 mM for PS/H<sub>2</sub>O<sub>2</sub> and PMS/H<sub>2</sub>O<sub>2</sub> respectively. Figure 3a presents TOC removal versus H<sub>2</sub>O<sub>2</sub>/Fe (II) molar ratio in PS/ H<sub>2</sub>O<sub>2</sub> or PMS/H<sub>2</sub>O<sub>2</sub> systems. Increasing Fe (II) in PS/H<sub>2</sub>O<sub>2</sub> system leads to increase TOC removal, most likely, the added of favorable concentration of Fe (II), resulting in producing a high amount of HO• radical. It may play a significant role in producing more SO<sub>4</sub>•<sup>-</sup> as well [25]. On the other hand, both HO• and SO<sub>4</sub>•<sup>-</sup> might concurrently react with organic pollutants and enhanced the degradation performance.

Our result is in good agreement with Lin *et al.*, [29], who proved that both sulfate and hydroxide radicals could work simultaneously for pollutant removal. However, this phenomenon needs further studies to clarify it.

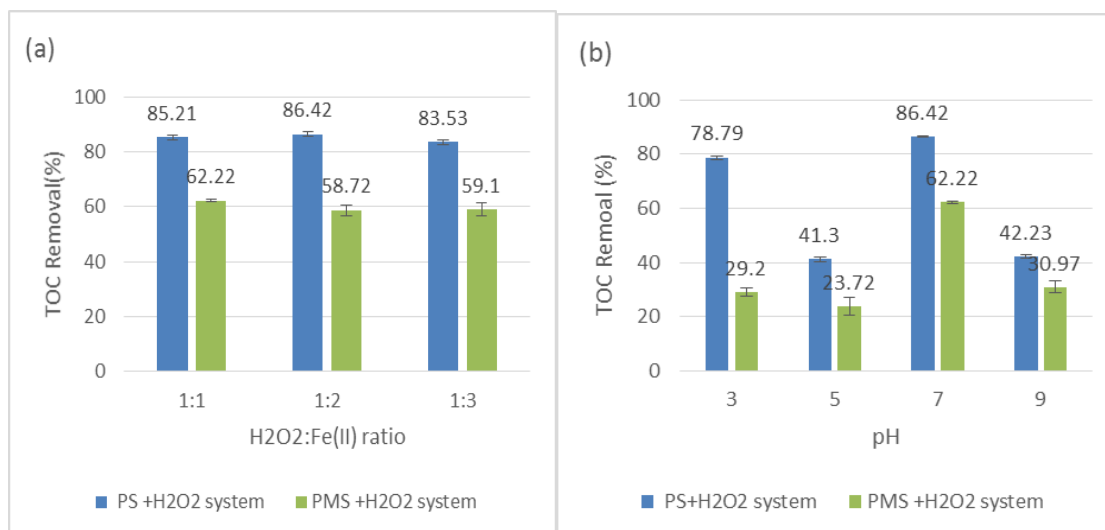
The performance of TOC removal is slightly decreased at a further increase of Fe (II) dosage. This could be ascribed to an excessive amount of Fe<sup>2+</sup>, which acts as an intrinsic scavenger of radicals due to the forming of Fe<sup>3+</sup> as indicated by equation 4 [30].



While in PMS/H<sub>2</sub>O<sub>2</sub> system, the addition of Fe (II) leads to a decrease of TOC removal. This reduction is properly due to the form of some representative reactions expected during the oxidation are as following equations 4, 5, and 6 [31].



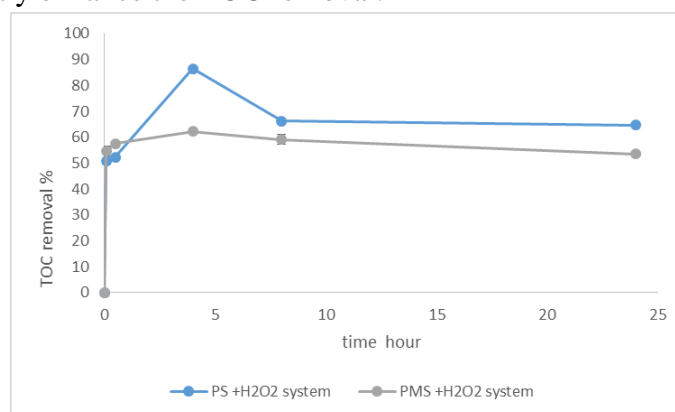
Where RH = organic compound



**Figure 3.** Effect of a; Fe (II) concentration in PS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system, conditions: concentration of H<sub>2</sub>O<sub>2</sub>= 2.88 mM, pH =7 and reaction time =4 h; PMS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system: concentration of H<sub>2</sub>O<sub>2</sub>= 0.72 mM, pH =7 and reaction time =4 h; b; pH in PS/Fe(II)/ H<sub>2</sub>O<sub>2</sub> system, concentration of H<sub>2</sub>O<sub>2</sub>=2.88 mM, Fe(II) = mM 5.76 and reaction time =4h, in PMS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system conditions: concentration of H<sub>2</sub>O<sub>2</sub>= 0.72 mM, Fe(II)= 0.72 and reaction time =4h.

### 3.3. The effect of pH.

The effect of pH on TOC removal was examined in both acidic and basic ranges over 4 hours. Therefore, values of 3, 5, 7, and 9 were taken. The ratios of the H<sub>2</sub>O<sub>2</sub> to Fe (II) ratio were fixed in 1:2 and 1:1 for PS/ H<sub>2</sub>O<sub>2</sub> and PMS/ H<sub>2</sub>O<sub>2</sub> systems, respectively. As shown in figure 3b, maximum removal of TOC 86.4% for PS/ H<sub>2</sub>O<sub>2</sub> and 62.2% for PMS/ H<sub>2</sub>O<sub>2</sub> were achieved at pH 7. Most researchers reported that the PS, PMS, and H<sub>2</sub>O<sub>2</sub> achieve the highest efficiency of organic pollutants degradation at low pH, due to the formation of SO<sub>4</sub><sup>-</sup> and HO· radicals through acid-catalysis reaction [27,32]. In contrast to these reports, the improvement of TOC removal in a neutral medium may be explained by the formation of some complexes due to some reactions between Fe (II) and soluble compounds in the vinasse, such as polyaromatic and polyphenols [33]. These complexes prevent the oxidation of Fe (II) to Fe (III) and consequently enhance the TOC removal.



**Figure 4.** The effect of reaction time in PS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system, concentration of H<sub>2</sub>O<sub>2</sub>= 2.88, Fe(II) = 5.76 and pH =7, in PMS/ Fe(II)/ H<sub>2</sub>O<sub>2</sub> system conditions: concentration of H<sub>2</sub>O<sub>2</sub>= 0.72mM,Fe(II)= 1.44mM 0.72 and pH =7.

### 3.4. The effect of reaction time.

To observe the effect of reaction time, the oxidation experiments were carried out for 0.083, 0.5, 4, 8, and 24 hours on the pretreated vinasse. The results indicated that the TOC

removal increased significantly for the first 5 min for both PS/Fe (II)/H<sub>2</sub>O<sub>2</sub> and PMS/ Fe (II)/H<sub>2</sub>O<sub>2</sub> systems, as indicated in figure 4. When the reaction times increased from 5 min to 4 h TOC removal increased significantly, from 50 to 86.42% and 54.6 to 62.2 % for PS/ Fe (II)/H<sub>2</sub>O<sub>2</sub> and PMS/ Fe (II)/H<sub>2</sub>O<sub>2</sub> systems respectively. After 24 h of reaction time, the TOC removal decrease to 64.7 and 53.53% in both systems, respectively. This might be due to the reforming of some of the organic compounds.

#### 4. Conclusions

This study has focused on the degradation of the organic matter from vinasse through a combination of PS/PMS mediated activation Fe (II) with H<sub>2</sub>O<sub>2</sub> and reused the treated vinasse for the first time. The effects of H<sub>2</sub>O<sub>2</sub>, a further dosage of Fe (II), pH, and reaction time were studied. At higher H<sub>2</sub>O<sub>2</sub> dosage, a significant amount of radicals were produced, leading to a removal of 83.35% of TOC in PMS/ Fe (II)/ H<sub>2</sub>O<sub>2</sub> system. In PS/ Fe (II)/ H<sub>2</sub>O<sub>2</sub> system, at optimum experimental conditions of H<sub>2</sub>O<sub>2</sub> and Fe (II), 86% of TOC removal was achieved. Summing up the results, it can be concluded that PS/H<sub>2</sub>O<sub>2</sub>/Fe (II) and PMS/H<sub>2</sub>O<sub>2</sub>/Fe (II) were capable of mineralizing the recalcitrant organic compounds in vinasse and allowing reuse the effluents in irrigation of plenteous trees and green areas, side of roads outside cities according to Sudanese legislation for wastewater reuse.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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