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SHORT COMMUNICATION

Mineralization of organic matter from vinasse using physicochemical treatment coupled with Fe^{2+}-activated persulfate and peroxymonosulfate oxidation

M. A. Fagier[1] · E. A. Ali[1] · K. S. Tay[2] · M. R. B. Abas[2]

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Abstract Application of advanced oxidation process for wastewater treatment has gained more attention recently. In this study, the efficiency of coagulation–flocculation pretreatment coupled with sulfate radical-based advanced oxidation process (SR-AOP) in the removal and mineralization of organic matter of sugarcane vinasse was evaluated. For coagulation–flocculation, jar-test experiment was carried out with ferric chloride as coagulant and the removal of TOC, color and UV_{254} was determined. The results revealed that by using 15 g/L of coagulant, 70 % of TOC removal and nearly 100 % of UV_{254} and color removal were achieved. The pretreated vinasse was then subjected to SR-AOP. In this study, sulfate radical was generated using persulfate (PS) and peroxymonosulfate (PMS) activated by Fe(II). The effect of reaction time, oxidants to Fe(II) ratio and pH on the TOC removal efficiency were investigated. For the effect of reaction time, the TOC removal was found to increase significantly for the first 5 min. TOC removal was found to increase with increasing concentration of Fe(II) for PMS. However, for Fe(II)/PS, the TOC removal efficiency was decreased with increasing Fe(II) concentration. Both Fe(II)/PMS and Fe(II)/PS showed the highest TOC removal efficiency when the oxidation was carried out at pH 7. By using the selected optimum condition, nearly 70 and 49 % of TOC removal were achieved for PMS/Fe(II) and PS/Fe(II), respectively. Therefore, it can be concluded that SR-AOP can be a promising alternative method for TOC removal from sugarcane vinasse.

Keywords Waste treatment · Radical · Total organic carbon · Wastewater · Coagulation–flocculation

Introduction

Ethanol production has increased significantly all over the world, due to its application as alternative fuel (Pejin et al. 2015). The massive production of ethanol from sugarcane has produced vinasse as by-product. Vinasse is acidic (pH 3.5–5) dark brown slurry (Satyawali and Balakrishnan 2008) with high organic content. The COD (chemical oxygen demand) and BOD (biological oxygen demand) concentrations of vinasses can range from 90 to 210 and 45 to 100 g/L, respectively (Mane et al. 2006). Direct disposal of vinasse into the aquatic environments tends to increase the organic content of water and consequently causes the proliferation of bacteria that depleted the dissolved oxygen and water quality (Mohana et al. 2009).

So far, the treatment of vinasse has been focused on physicochemical and biological treatments (Campos et al. 2014). However, some of the recalcitrant organic compounds in vinasse are resistant against conventional biological treatments (Siqueira et al. 2013). Furthermore, common chemical oxidation methods such as ozonation showed no significant removal in the organic content of vinasse (Pena et al. 2003). In recent years, advanced oxidation processes (AOPs) have emerged as an important water treatment method. Among various AOPs, Fenton reaction that involved $^{\cdot}$OH as oxidant has been frequently studied for the treatment of vinasse (Mosteo et al. 2007; Tünay et al. 2010). However, the efficiency of COD removal by using Fenton reaction was relatively low (5–47 %)

✉ K. S. Tay
khengsoo@um.edu.my

[1] Department of Chemistry, Faculty of Science, Sudan University of Science and Technology, PO Box 407, Khartoum, Sudan

[2] Environmental Research Group, Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

(Robles-González et al. 2012). In this study, sulfate radical (SR, $SO_4^{\cdot-}$) was selected for the treatment of sugarcane vinasse. SR has been frequently reported as an alternative oxidant for pollutant treatment (Lutze et al. 2014). Its efficiency in the treatment of various types of wastewater has been frequently evaluated (Zhang et al. 2014; Zhao et al. 2014). Recently, sulfate radical-based advanced oxidation process (SR-AOP) has been showed to be one of the most effective chemical oxidation methods for the removal of various organic pollutants (Chen et al. 2015). SR reacts with organic compounds with the rate of 10^6–10^9 $M^{-1}s^{-1}$ (Neta et al. 1977). As compared with hydroxyl radical ($^{\cdot}OH$), SR reacts with organic matter through more selective pathway. It reacts with organic compounds mainly through electron transfer reactions (Anipsitakis et al. 2006). SR-AOP has been employed for the treatment of soil and groundwater (Tsitonaki et al. 2010), but the efficiency of this method in the treatment of vinasse has not been reported. The main objective of this study was to evaluate the efficiency of coagulation–flocculation pretreatment coupled with SR-based advanced oxidation process (SR-AOP) in the removal of total organic carbon (TOC) of vinasse. For SR-AOP, the effects of the main operating parameters, such as oxidant dosage, pH and time, were examined.

Materials and methods

Chemicals and reagents

$FeCl_3$, sand and H_2SO_4 (98 %) were obtained from Merck (Germany). Potassium persulfate (PS) (99 %), potassium peroxymonosulfate (PMS) and $FeSO_4 \cdot 7H_2O$ (99.5 %) were purchased from Acros Organics (USA). Sodium hydroxide was obtained from Fluka (Germany). Ultrapure water was used for the preparation of all aqueous solutions.

Vinasse and its main chemical characteristics

The vinasse used in this work was obtained from an ethanol distillery located at White Nile State (Sudan). Vinasse was collected immediately after the distillation. Table 1 shows the main chemical characteristics of the vinasse that determined according to Clesceri et al. (1998).

Coagulation–flocculation pretreatment

Coagulation–flocculation treatment of vinasse was performed as described by Satterfield (2005). All experiments were carried out in batch mode at room temperature; 10 mL of raw vinasse was first diluted to 1000 mL. Then, $FeCl_3$ (as coagulant) was added to the diluted vinasse. The mixture was stirred at 120 rpm for 1 min and followed by 30 rpm for 30 min. After stirring, the floc was allowed to settle for 1.5 h. The pretreatment of vinasse was carried out using different amounts of coagulant and at different pH conditions. The pH of the solution was adjusted using NaOH and/or H_2SO_4 solution. After coagulation–flocculation, the treated vinasse was passed through a rapid gravity sand filter. Then, the pretreated vinasse was subjected to SR-AOP.

Table 1 The main chemical characteristics of selected vinasse

Parameter	Raw vinasse	Parameter	Raw vinasse
pH	3.5	TN	8.31 mg/L
COD	126 g/L	TS	111 mg/L
BOD	69.0 g/L	TDS	63.8 mg/L
TOC	48,000 mg/L	K	121 mg/L
TC	48,500 mg/L	Na	121 mg/L
IC	408 mg/L	Ca	73.8 mg/L

Sulfate radical-based advanced oxidation process

All experiments were performed in batch mode. Experiments were conducted at room temperature in 30-mL glass vials. Oxidation was initiated by the addition of PS or PMS solution to the vial that containing pretreated vinasse and $FeSO_4$ as activator. Vials were shook at 150 rpm by using an orbital shaker. After the reaction, the reaction mixture was filtered through a syringe filter with the pore size of 0.45 µm before TOC analysis. All experiments were conducted in triplicate.

Instrumentation

TOC concentration of all samples was measured by TOC analyzer (Shimadzu TOC-L). All samples were analyzed immediately without quenching. Color and UV_{254} were measured using UV–Vis spectrophotometer (Thermo Scientific, Genesys 10S) at 475 and 254 nm, respectively.

Results and discussion

In this study, mineralization of organic matter was evaluated using the concentration of TOC. TOC analysis is a direct measurement of the concentration of organically bound carbon, and it therefore provides the information on the amount of organic compounds that containing in vinasse. In this work, the treatment of vinasse was carried out in two stages which involved coagulation–flocculation as physicochemical pretreatment followed by SR-AOP.

The efficiency of coagulation–flocculation pretreatment

In this experiment, TOC, UV_{254} and color were used to monitor the efficiency of coagulation–flocculation in the pretreatment of vinasse. Absorbance at 475 nm was used to measure the intensity of color (Chauhan and Dikshit 2012). UV_{254} is used to estimate the amount of aromatic organic compounds such as humic substances in wastewater (Tang et al. 2014). The results indicated that the efficiency of this pretreatment method was pH and coagulant dosage dependent. In general, the results showed that TOC, color and UV_{254} of vinasse were significantly reduced after coagulation–flocculation (Fig. 1a). By increasing the coagulant dosage from 5 to 15 g/L, the percentage of TOC removal was found to increase from 55.8 to 69.7 %. This result might due to the favorable precipitation of ferric hydroxide at high coagulant dosage, and it can physically sweep the organic compounds from the vinasse (Ayguna and Yilmazb 2010). On the other hand, removal of UV_{254} and color was approaching 100 % with coagulant dosage of 5 g/L. This result indicated that the aromatic organic compounds that contributed to the color and UV_{254} can be effectively removed.

The effect of pH on TOC, color and UV_{254} removal was examined at constant dosage of coagulant of 10 g/L. The removal of TOC, color and UV_{254} was relatively higher when the pretreatment was performed under acidic conditions. The efficiency of coagulation–flocculation pretreatment decreased significantly after pH 7 (Fig. 1b). Most of the vinasses are acidic; therefore, this result suggested that this pretreatment method can be applied to remove a large portion of organic content of vinasse without pH adjustment.

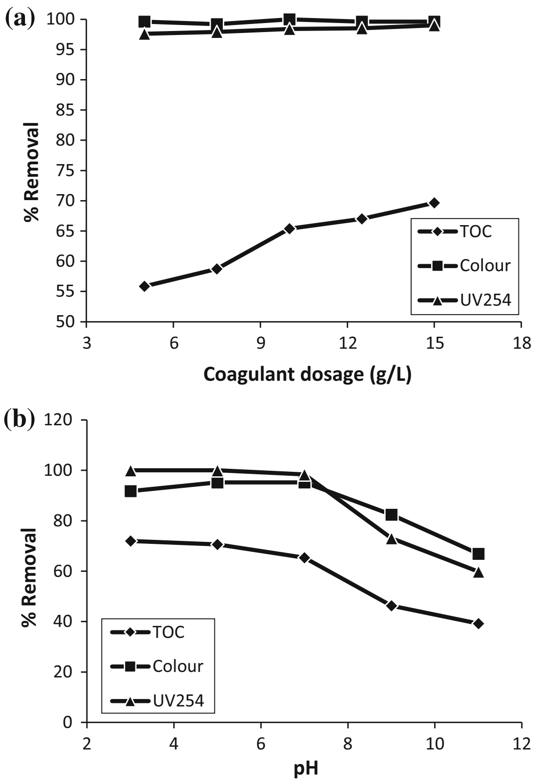

Fig. 1 Effect of **a** coagulant dosage (pH = 7; room temperature) and **b** pH (coagulant dosage = 10 g/L; room temperature)

The efficiency of SR-AOP

SR was generated using PS ($S_2O_8{}^{2-}$) and PMS ($HSO_5{}^{-}$) activated by Fe(II) as indicated by the following equations (Zou et al. 2013; Ayoub and Ghauch 2014):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\cdot -} + Fe^{3+} + SO_4^{2-} \quad k = 2.0 \times 10\ M^{-1}s^{-1} \tag{1}$$

$$HSO_5^{-} + Fe^{2+} \rightarrow SO_4^{\cdot -} + Fe^{3+} + OH^{-} \quad k = 3.0 \times 10^4\ M^{-1}s^{-1} \tag{2}$$

Vinasse contains biodegradable organic compounds as well as recalcitrant organic components such as polyaromatic compounds and polyphenols (e.g., lignins, tannins and humic acid) (Tünay et al. 2010). By using lignin as example, the generated $SO_4^{\cdot -}$ can react with the aromatic ring of lignin to form unstable cyclohexadienyl radical (Intermediate ***I***) (Fig. 2). The reaction between O_2 and Intermediate ***I*** could produce unstable peroxyl radical (Intermediate ***II***). Then, the decomposition of Intermediate ***II*** through the aromatic ring-cleavage mechanism (Anipsitakis et al. 2006) can breakdown the lignin into smaller fragments.

In SR-AOP, the influence of pH, reaction time, amount of Fe(II) and the type of oxidant (PS and PMS) was studied in detail. PS and PMS were selected because these oxidants are relatively stable with the changes of the pH (Park et al. 2010). Therefore, it can be used to treat the vinasse which is acidic. Furthermore, PS and PMS showed high water solubility, high stability in water, producing non-threatening end products and relatively low cost (Rastogi et al. 2009).

To evaluate the effect of reaction time on the TOC removal, the SR-AOP was carried out for 0.083, 0.5, 4, 8 and 24 h on the pretreated vinasse (Fig. 3a). The result indicated that the TOC removal increased significantly for the first 5 min for both PS-Fe(II) and PMS-Fe(II) systems. When the reaction times increased from 5 min to 24 h, TOC removal increased slowly from 13.0 to 23.7 and 29.0 to 36.3 % for PS-Fe(II) and PMS-Fe(II), respectively.

The effect of PS and PMS concentration on TOC removal was examined using Fe(II) concentration of 0.36 mM. The reaction time was set at 4 h. All degradation experiments were conducted without pH adjustment. For Fe(II)-PS, TOC removal increased from 9.4 to 15.5 % as PS concentration was increased from 0.18 to 1.44 mM (Fig. 3b). Further increased in PS concentration does not show any significant enhancement in TOC removal. This might due to the limited availability of Fe(II) for SR generation. Fe(II)-PMS was more reactive by showing higher TOC removal efficiency.

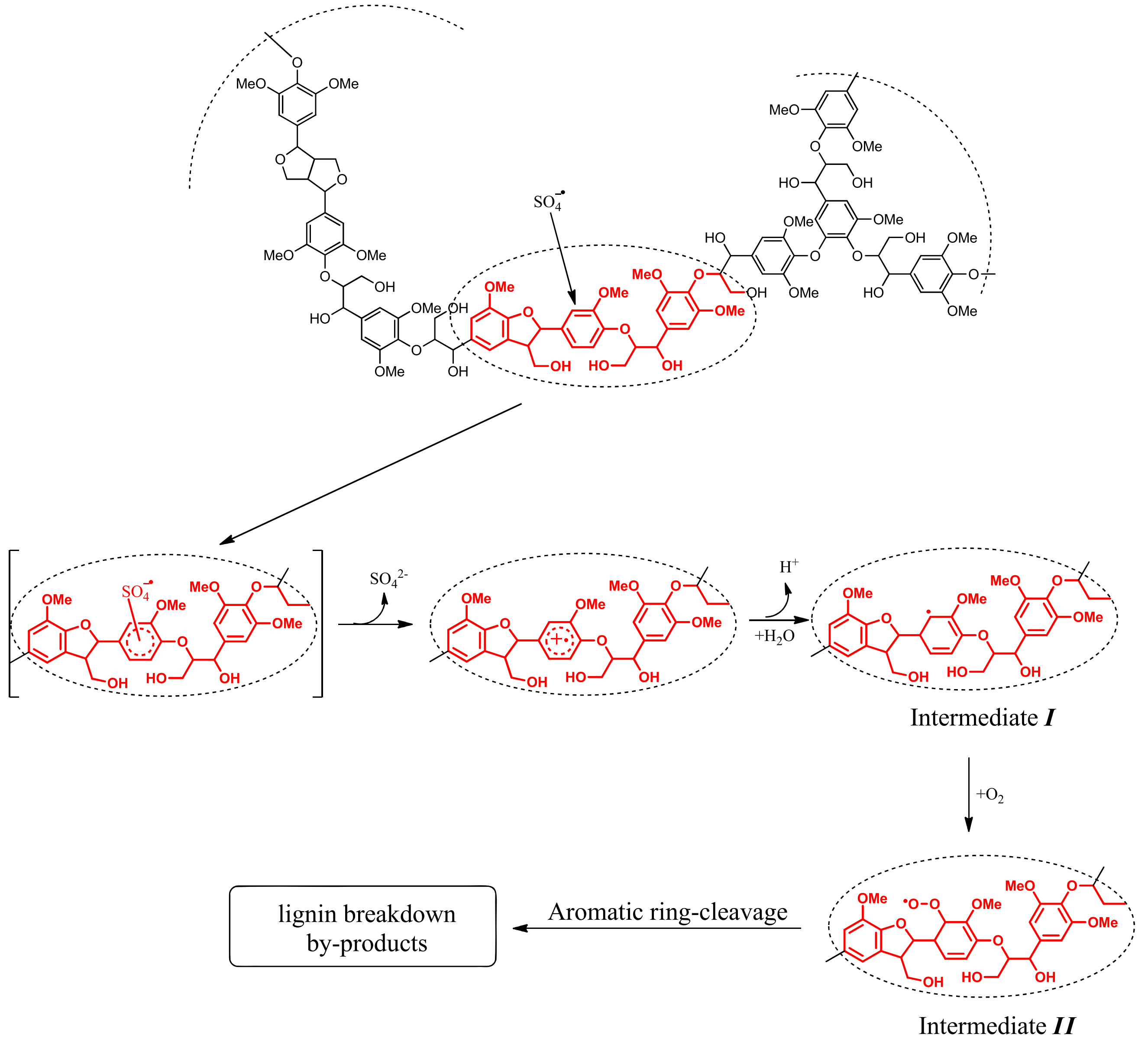

Fig. 2 Proposed mechanism for the degradation of lignin containing in vinasse [partial structure of lignin is obtained from Vanholme et al. (2010)]

However, the TOC removal was found to decrease from 22.5 to 17.9 % as the PMS concentration increased from 0.18 to 1.44 mM (Fig. 3b). This might due to the unfavorable consumption of SR by the excessive PMS which leads to the formation of less reactive $SO_5^{\cdot -}$ and scavenged the SR as shown in the following equation (Lin et al. 2014).

$$HSO_5^- + SO_4^{\cdot -} \rightarrow SO_5^{\cdot -} + SO_4^{2-} + H^+ \qquad (3)$$

To assess the effect of Fe(II) concentration on TOC removal, the concentration of PS and PMS was fixed at 0.72 and 0.36 mM. The concentration of Fe(II) was varied from 0.36 to 1.8 and 0.18 to 0.9 mM for Fe(II)-PS and Fe(II)-PMS, respectively. The results from these experiments were presented as TOC removal versus PS or PMS to Fe(II) ratio (Fig. 3c). For Fe(II)-PS, TOC removal was slightly decreased with increasing concentration of Fe(II). This might be attributed to the consumption of SR by the access amount of Fe(II) (Zou et al. 2014). As indicated by Eqs. 1 and 4, the rate of deactivation of SR through the reaction with Fe(II) is much more higher than the rate of SR production. Therefore, higher amount of Fe(II) would limit the amount of SR for organic compound oxidation.

$$SO_4^{\cdot -} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \quad k = 4.9 \times 10^9\ M^{-1}s^{-1} \qquad (4)$$

In contrast, for PMS-Fe(II), the increasing Fe(II) concentration showed the enhancement of TOC removal efficiency

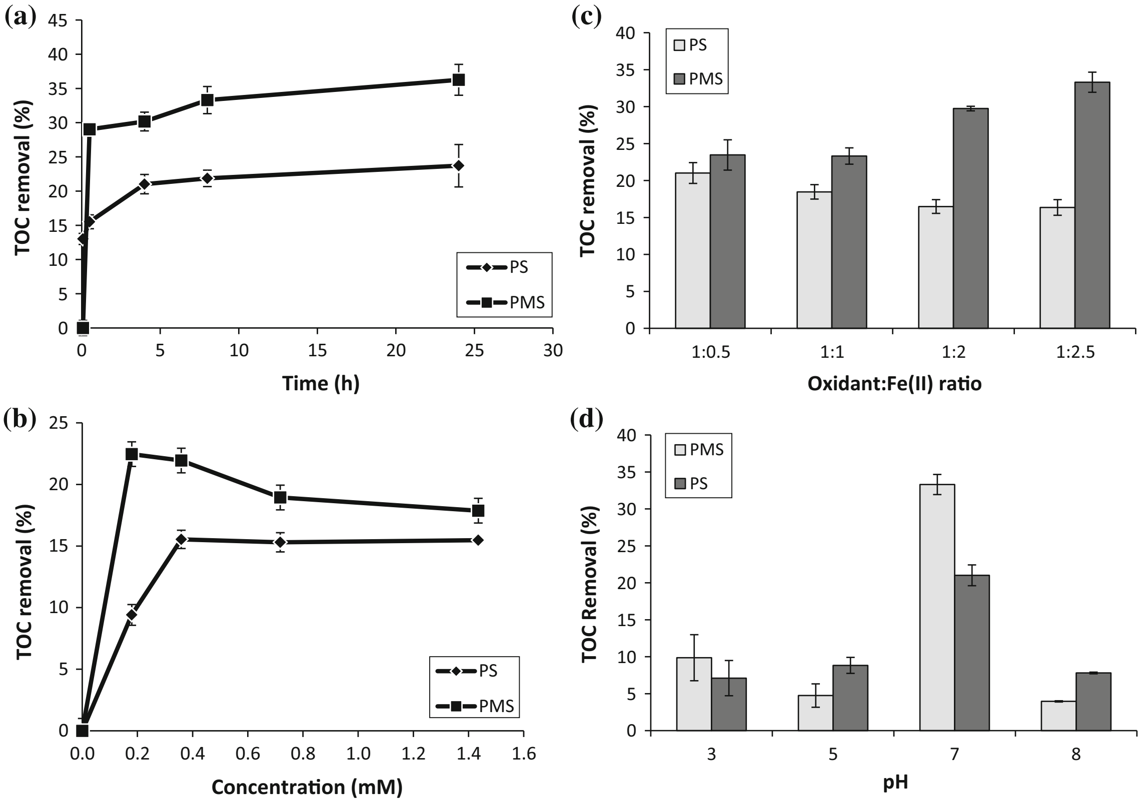

Fig. 3 Effect of **a** reaction time (PS-Fe(II) system: concentration of PS = 0.72 mM; concentration of Fe(II) = 0.36 mM; pH = 7. PMS-Fe(II) system: concentration of PMS = 0.36 mM; concentration of Fe(II) = 0.90 mM; pH = 7), **b** PS and PMS dosage (concentration of Fe(II) = 0.36 mM; reaction time = 4 h; pH = 7), **c** PS and PMS to Fe(II) ratio (concentration of PS = 0.72 mM; concentration of PMS = 0.36 mM, pH = 7; reaction time 4 h) and **d** pH on TOC removal (PS-Fe(II) system: concentration of PS = 0.72 mM; concentration of Fe(II) = 0.36 mM; reaction time = 4 h. PMS-Fe(II) system: concentration of PMS = 0.36 mM; concentration of Fe(II) = 0.90 mM; reaction time = 4 h)

(Fig. 3c). In this case, the efficiency of TOC removal was not influence by the scavenging effect of SR by Fe(II). As indicated by Eqs. 1 and 2, the rate of reaction between PMS and Fe(II) is about 1500 times higher than the reaction between PS and Fe(II). Therefore, higher amount of SR is available in PMS-Fe(II) for the treatment of vinasse and consequently increased the efficiency of TOC removal.

For the effect of pH, the TOC removal was evaluated at pH 3–8. As shown in Fig. 3d, TOC removal achieved the highest efficiency at pH 7. At pH 7, TOC removal was 21.0 and 33.3 % for PS-Fe(II) and PMS-Fe(II), respectively. Most of the SR-AOP studies reported that the degradation of organic pollutants achieved it highest efficiency at acidic conditions due to the formation of SR through acid-catalysis reaction (Zhang et al. 2015). For this study, it was proposed that Fe(II) complexed with soluble organic substances in the vinasse at neutral condition. Complexation can stabilize the Fe(II) from been oxidized to Fe(III) and consequently enhanced the TOC removal. Wu et al. (2014) also reported that the complexation between Fe(II) with organic ligand enhanced the removal of organic pollutants by using SR-AOP. At pH 8, TOC removal was retarded and it was most probably due to the precipitation of Fe(II) for the formation of hydroxide species and it reduced the amount of Fe(II) that available for the activation of PS and PMS.

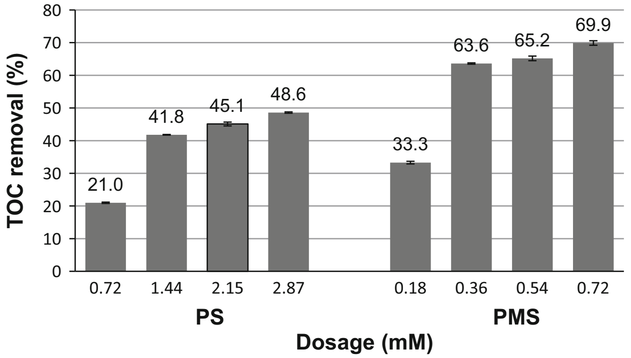

Fig. 4 TOC removal from vinasse by using optimized PS-Fe(II) and PMS-Fe(II) systems with increasing PS, PMS and Fe(II) dosage

Figure 4 shows the results of the TOC removal produced by increasing the dosage of selected oxidant and Fe(II) under the optimum operating condition. For this experiment, the ratio of PS and PMS to Fe(II) was kept at the ratio of 1:0.5 and

1:2.5. The pH of the pretreated vinasse was adjusted to 7, and the reaction time was set at 4 h. TOC removal can be enhanced by increasing the dosage of oxidant–Fe(II). For PS-Fe(II), TOC removal was increased from 21.0 to 48.6 % when the concentration of PS was increased from 0.72 to 2.88 mM. For PMS-Fe(II), TOC removal increased from 33.3 to 69.9 % when PMS concentration increased by four times.

Conclusion

The result of this study demonstrated that the coagulation–flocculation coupled with SR-AOP is an effective method to remove TOC from vinasse. In general, the TOC removal was more favorable when the coagulation–flocculation was performed at acidic conditions. The TOC removal can be enhanced by increasing the amount of $FeCl_3$. For SR-AOP, the results indicated that this method can be an effective oxidation process in the reduction in TOC from the pretreated vinasse. However, the TOC removal efficiency of SR-AOP is influenced by the type of oxidant (PMS and PS), initial pH, amount of Fe(II) and oxidant dosage.

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