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Evaluation of peroxymonosulfate/O_3/UV process on a real polluted water with landfill leachate: Feasibility and comparative study

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Abstract−Landfill leachate is classified as special wastewater because it contains a large amount of hazardous materials that can lead to the pollution of surface water, generating polluted water with landfill leachate (PWLL) with high organic load. This study investigated the treatment of PWLL by peroxymonosulfate (PMS)/O_3/UV process. The effects of several operating parameters such as pH, reaction time, O_3 and PMS dosage were investigated in detail. The results showed that PMS/O_3/UV removed total organic carbon (TOC) (74%), color (98%), ammonia (93%), chemical oxygen demand (COD) (81%), and biochemical oxygen demand (BOD) (69%) in 75 min at optimal conditions (pH=7, PMS=5 mM, O_3=1.7 mg/min). According to the results, O_3 and UV can well activate PMS and promote the ability of the process to remove TOC from PWLL. Adding ferrous ion to PMS/O_3/UV increased the TOC removal efficiency (77%), but cobalt ions had no significant effect on the TOC removal. The elimination of TOC by the PMS/O_3/UV process follows pseudo-first-order kinetic model with the reaction rate constant of 0.0203 min^{-1}. Compared to peroxone/UV, PMS/O_3/UV showed high yield in TOC, COD, color and ammonia removal. Thus the PMS/O_3/UV process can be a new approach for treatment of polluted water in low volume.

Keywords: Peroxymonosulfate, Landfill Leachate, Water Pollution, Ozone, UV Irradiation, Peroxone

INTRODUCTION

Municipal solid waste (MSW) management is one of the major environmental problems in metropolitan cities. Sanitary landfilling is a common method for final disposal of municipal solid waste (MSW) considering its economic advantages. However, landfill leachate, which may percolate through soil and reach water resources, is considered one of the major agents of groundwater and surface water pollution. This necessitates its appropriate collection, treatment, and safe disposal of landfill leachate [1]. World Health Organization (WHO) reported that about 80% of infectious diseases in society are caused by polluted water [2]. Considering seepage of leachate, landfilling is an important source of soil, groundwater, and surface water contamination. The pollutants are fixed in soil or transported to surface water after leaching of toxic organic species from the waste [3]. Waste disposal leads to the production of large amounts of leachate, which contains high concentrations of organic, inorganic, and complex pollutants, that poses adverse impacts on the human health and ecosystem. As a sort of toxic effluent, leachate is classified as special wastewater containing high levels of hazardous pollutants like other industrial wastewaters [4,5]. The concentration of COD (chemical oxygen demand) in young leachate is >10,000 mg/L, while in mature leachate is <3,000 mg/L [6]. Incorrectly collected and treated, landfill leachate can lead to surface and groundwater contamination [7]. Landfill leachate has an undesirable impact on water quality as well as on living beings, since most landfills do not have proper leachate management [8]. In the case of water pollution by leachate, its side effects remain for a long time, which makes the surface water unsuitable for any application and thus it needs to be treated [8]. Various methods have been suggested for treatment of contaminated water, including biological processes, electrochemical oxidation [9], microwave irradiation-activated chemical oxidants [4], ozonation [10], persulfate-based process [11] and other advanced oxidation processes (AOPs) [5]. Among which, AOPs have been recognized as one of the most effective methods for removing contaminants by creating free rad-

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icals such as hydroxyl radicals ($HO^{\bullet}$) [11]. Hydroxyl radical is a non-selective oxidant that can destroy and mineralize organic compounds [12]. Among the precursors of hydroxyl radical generation, ozone (O_3) is a particularly strong oxidizer which is widely used in wastewater treatment due to its high reactivity and selectivity against non-degradable contaminants [10]. Sulfate radical-based AOPs (SR-AOPs) have been expanding for two decades. To produce sulfate radicals, peroxymonosulfate (PMS) and peroxydisulfate (PDS) anions are used as precursors. In the last decade, PMS has been introduced as new oxidant with production potential of sulfate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals [13]. PMS can be activated by different methods, including transition metals [14], carbon-catalysts [15] and high energy inputs [16,17]. Ultraviolet (UV) radiation is one of the common forms of energy to activate various oxidants and produces free radicals [18].

Furthermore, the performance of sole O_3 is low in wastewater treatment, and the use of catalysts and enhancers such as ultrasound and UV improves its effectiveness [10,19]. So far, various studies have been conducted on the use of AOPs for water remediation. Salem et al. declared that using O_3/persulfate for COD removal was more effective than using them alone [7]. Previously our study showed that the combination of PMS and ozone can be an effective method for the treatment of industrial wastewater [16]. Indeed, PMS and ozone lead to the simultaneous formation of sulfate radicals and hydroxyl radicals in the solution (Eqs. (1)-(10)).

$$HSO_5^{-}+UV\rightarrow SO_4^{\bullet-}+OH^{\bullet} \quad (1)$$

$$O_3+H_2O+UV\rightarrow O_2+2OH^{\bullet} \quad (2)$$

$$HSO_5^{-}\rightarrow H^{+}+SO_5^{2-} \quad (3)$$

$$SO_5^{2-}+O_3\rightarrow SO_5^{2-}O_3 \quad (4)$$

$$SO_5^{2-}O_3\rightarrow SO_5^{\bullet-}+O_3^{\bullet-} \quad (5)$$

$$SO_5^{\bullet-}+O_3\rightarrow SO_4^{\bullet-}+2O_2 \quad k=1.6\times10^{5}\ M^{-1}s^{-1} \quad (6)$$

$$2SO_5^{\bullet-}\rightarrow 2SO_4^{\bullet-}+O_2 \quad k=2.1\times10^{8}\ M^{-1}s^{-1} \quad (7)$$

$$2SO_5^{\bullet-}\rightarrow S_2O_8^{2-}+O_2 \quad k=2.2\times10^{8}\ M^{-1}s^{-1} \quad (8)$$

$$O_3^{\bullet-}\rightleftarrows O^{\bullet-}+O_2 \quad k=1.4\times10^{3}\ s^{-1} \quad k_{-}=3.6\times10^{9}\ M^{-1}s^{-1} \quad (9)$$

$$O^{\bullet-}+H_2O\rightarrow HO^{\bullet}+HO^{-} \quad k=1.8\times10^{6}\ M^{-1}s^{-1} \quad (10)$$

Abadan city (Iran) is one of the most important cities in Iran thanks to the presence of petrochemical and refinery industries. The groundwater level in Abadan city is high in which distance between surface water and groundwater is relatively slight. Therefore, landfill leachate site easily contaminates water bodies. In fact, incorrect selection of landfill site results in extensive contamination of surface waters in Abadan city. Since surface waters are used as sources of drinking water for Abadan city, treatment of these polluted waters by leachate is an essential effort for the communication. On the other hand, effective removal or diminishing water pollution is needed for growth and sustainability of each region.

Regarding the inherence of water pollution by landfill leachate, AOPs have been proposed to remediate contaminated water. In general, PMS-based processes are still primary steps for application in large scale and their applications are developed on real matrixes. PMS/O$_3$/UV has been seldom employed for the degradation of synthetic pollutants. Cyanide [20] and atenolol [21] solutions were treated PMS/O$_3$/UV while, to the best of our knowledge, no study has been focused on treatment of a real matrix such as polluted water by landfill leachate (PWLL) using PMS/O$_3$/UV. Moreover, the combination of ozone, PMS and UV is the first attempt for application in real matrix. Therefore, this study aimed to investigate the treatment of PWLL by PMS/O$_3$/UV oxidation processes as a new hybrid method. The effect of operating parameters including pH, ozone and PMS dosages were studied on total organic carbon (TOC) removal. Kinetic study was conducted while the effect of cobalt and iron as transition metals was also studied on TOC removal. The performance of PMS/O$_3$/UV process was evaluated on color, ammonia, biochemical oxygen demand (BOD), and COD. Finally, the phytotoxicity of treated effluent was investigated.

MATERIALS AND METHODS

1. PWLL Collection

In the current study, the polluted water by landfill leachate sample was collected from Abadan municipal landfill site (Fig. 1(a)) (latitude: 30°26′2.83″ and longitude 48°21′41.73″) in which surface

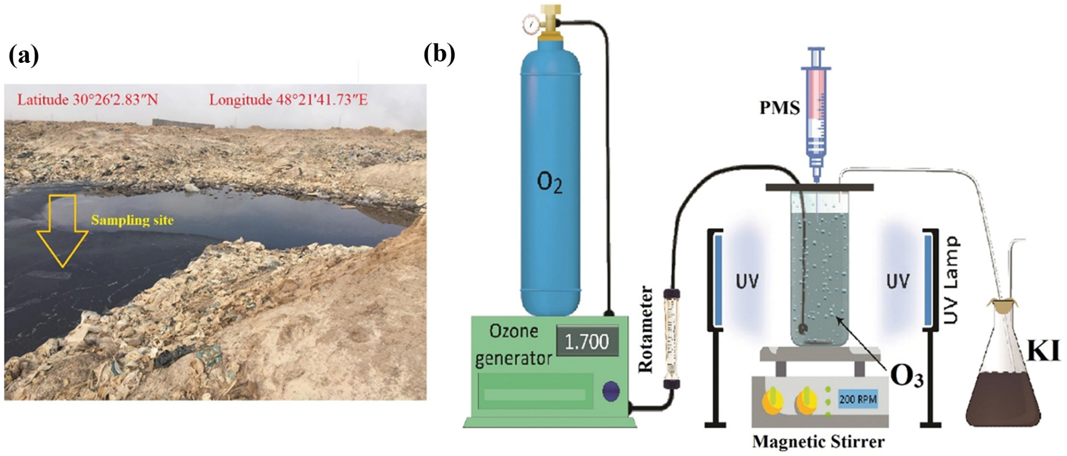

Fig. 1. (a) Sampling site for PWLL and (b) the scheme of PMS/O$_3$/UV process.

Table 1. The characteristics of collected PWLL

Parameter	Unit	Quantity
COD	mg/L	740
BOD_5	mg/L	180
TOC	mg/L	214
TDS (Total Dissolved Solids)	mg/L	1,400
Ammonia	mg/L	120.3
pH	-	7.2
Color	ADMI	1,450
Cl^-	mg/L	348

water is contaminated by landfill leachate. After transferring the sample to the laboratory, it was kept in closed polyethylene containers at 4 °C. To evaluate the efficiency of the PMS/O_3/UV process in leachate treatment, initial quality of samples was carefully monitored. The characterization of the sample is presented in Table 1.

2. Reagents and Materials

The reagents required for the COD test, including potassium dichromate ($K_2Cr_2O_7$, >99%), sulfuric acid (H_2SO_4, >96%), ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, >99%), silver sulfate (Ag_2SO_4, >99%), and mercury sulfate ($HgSO_4$, >99%), were purchased from Samchun Company. Ferrous sulfate ($FeSO_4$, >99%), cobalt chloride ($CoCl_2$, >99%) and Oxone ($KHSO_5 \cdot 0.5KHSO_4 \cdot 0.5K_2SO_4$) (CAS number: 70693-62-8) were purchased from Sigma Aldrich, and other materials were purchased from Merck, Germany. All the required solutions were prepared by deionized water. All the chemicals used were in analytical grade.

3. Experimental Procedures

To evaluate the efficiency of the PMS/O_3/UV process in removing TOC, a quartz reactor with a volume of 500 mL (30.5 cm height and 5 cm diameter) was used. The reaction volume for each experimental run was 350 mL of PWLL. The required O_3 was generated by an ozone generator (COG-40A ARDA, France); with a nominal capacity of 1 g/h using pure dry oxygen as feed. A rotameter was also used to measure and control ozone gas flow. To provide the UV light source, two UVC lamps with a wavelength of 254 nm were placed at a distance of one centimeter from the reactor. The light intensity at the center of the reactor was 2.13 mW/cm^2, and the temperature was kept in the range of 26±2 °C (Fig. 1(b)). A given amount of PMS, as a sulfate radical precursor, in the range of 1-7 mM was added to the solution. 2 mL of the solution was undertaken after each reaction run for TOC analysis. Before TOC analysis, the samples were quenched by sodium thiosulfate. Peroxone/UV system was similar to PMS/O_3/UV process with one difference that H_2O_2 was injected instead of PMS.

4. Analytical Methods

The concentrations of COD and BOD were determined according to the standard methods. COD values were determined using colorimetric method by a spectrophotometer (Hach, DR 5000). ADMI (American Dye Manufacturers Institute) method was employed to determine the color value in the initial and final samples. Ammonia was measured based on the Nessler method using Hach reagents. pH was measured by pH meter and the solution pH was adjusted by sodium hydroxide and sulfuric acid. The TOC analyzer (Shimadzu, Japan) was used to determine the TOC of the samples. The removal efficiency of each parameter was found by using the following equation:

$$\text{Removal Efficiency (\%)}=[(C_0-C_t)/C_0]\times 100 \qquad (11)$$

In this equation, C_0 and C_t are concentrations of each parameter before and after the reaction time, respectively.

RESULTS AND DISCUSSION

1. Effect of Initial pH on TOC Removal in PMS/O_3/UV

The performance of AOPs depends on pH solution, which is due to its effect on the form of substrate, oxidant ionization, formation of reactive oxygen species, redox potential and the treatment efficacy [22]. Moreover, the activity and solubility of the oxidant and active species increase since the production rate of the radicals ($SO_4^{\bullet-}$ and $HO^{\bullet}$) is controlled by solution pH, so pH is an important parameter for AOPs. Therefore, to investigate the effect of initial pH on the performance of the PMS/O_3/UV process, different pH values (3, 5, 7, and 9) were examined. The effect of pH on TOC removal efficiency at different reaction times is shown in Fig. 2(a).

According to Fig. 2(a), the TOC removal efficiency dropped at

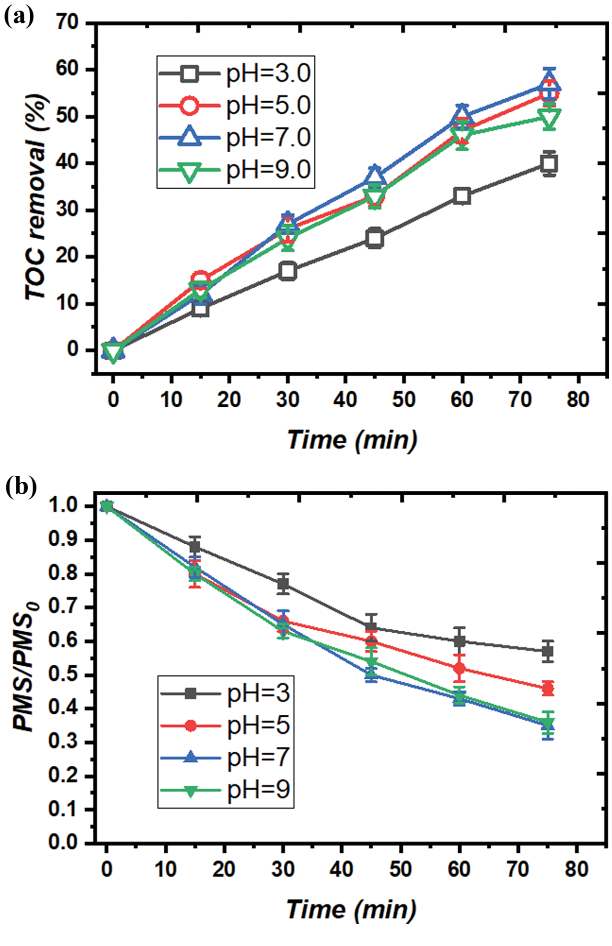

Fig. 2. (a) The effect of pH on TOC removal by PMS/O_3/UV process (b) PMS decomposition is different pHs (PMS=3 mM and O_3=1.2 mg/min).

alkaline and acidic conditions, while the highest removal efficiency of TOC was reached at the neutral pH value. The TOC removal was at its lowest value in acidic conditions. Fig. 2(a) confirms the highest function at pH of 7. This can be justified by saying that sulfate radicals can perform in wide range of pH especially at neutral conditions [23]. Furthermore, at the acidic condition, high concentrations of protons have a detrimental effect on generated free radicals. In fact, sulfate radicals and hydroxyl radicals are converted to ineffective and neutral species of HSO_4^- and H_2O in acidic media (Eqs. (12)-(13)) [14]. Accordingly, the degradation rate may be limited in the acidic condition (pH≤5).

$$HO^{\bullet}+H^{+}+e^{-}\rightarrow H_2O \tag{12}$$

$$SO_4^{\bullet-}+H^{+}+e^{-}\rightarrow HSO_4^{-} \tag{13}$$

At alkaline solution pH, hydroxyl radical can be generated through the reaction of sulfate radicals with HO^- based on electron transfer mechanism (14). Consequently, the sulfate radical proportion is reduced in higher pH values [24].

$$SO_4^{\bullet-}+HO^{-}\rightarrow SO_4^{2-}+HO^{\bullet} \quad k=2.1\times10^{8}\ M^{-1}s^{-1} \tag{14}$$

Moreover, it has been reported that PMS may be decomposed into sulfate ions and water at high alkaline conditions (Eq. (15)) [25]. Hence, PMS as the precursor of sulfate and hydroxyl radicals is eliminated from the reaction chains of generating free radicals.

$$HSO_5^{-}+SO_5^{2-}+OH^{-}\rightarrow 2SO_4^{2-}+O_2+H_2O \tag{15}$$

The concentration of PMS was monitored during 75 min reaction time at different pH values (Fig. 2(b)). As can be seen, increase of pH enhanced PMS decomposition in which PMS decays was 43.2%, 54.2%, 65% and 64.7% for pH values of 3, 5, 7 and 9, respectively. There was no difference between PMS decay in pH=7 and pH=9. Although the increase of pH enhances molar absorption coefficient (ε_{PMS}) [26], the presence of several organics in real matrix may reduce the absorption of UV by PMS. In fact, the composition of real polluted water compared to synthetic solution is totally difference.

In the UV/ozone/PMS process, sulfate radical and hydroxyl radical can be concurrently present in the solution [24]. It has been shown that the proportion of $SO_4^{\bullet-}$ and $HO^{\bullet}$ is a pH dependent process. Indeed, the reduction or increase of initial pH value would dominate sulfate radicals or hydroxyl radicals in which at pH<9, sulfate radicals are the predominant radicals while at pH>11, hydroxyl radicals dominate as reactive radicals [27].

2. Effect of PMS Concentration on TOC Removal in PMS/O_3/UV

As PMS is the main precursor of the sulfate radicals in TOC removal in PMS/O_3/UV process, the various concentrations of PMS (1, 3, 5, and 7 mM) were evaluated. Fig. 3 illustrates the results of TOC removal efficiency at different PMS concentrations. According to Fig. 3, an increasing trend was observed for TOC removal rate by increase of PMS concentration. This can be justified by the fact that oxidation is caused by increased steady-state concentration of reactive radical species ($SO_4^{\bullet-}$ and $HO^{\bullet}$). Regarding the PMS/UV/ozone process, increase of the initial PMS concentration from 1 to 5 mM raised the TOC removal rate. Thus, increasing PMS concentration up to 7 mM reduced the degradation rate of TOC. In concentrations of 7 mM PMS, a slight decrease was observed in TOC removal rate. This phenomenon is due to the scavenging effect of the excessive oxidant concentrations on $SO_4^{\bullet-}$ and $HO^{\bullet}$ and formation of less reactive species like $SO_5^{\bullet-}$, which has been reported in the literature [28]. In fact, $SO_5^{\bullet-}$ (peroxymonosulfate radical) with low reactivity (E^0=1.1 V) is not able to mineralize organic compounds in PWLL. The respective PMS scavenging reaction are represented in Eqs. (16)-(18) [29-31]. Based on the results, Fig. 3 shows that the optimum PMS dosage was 5 mM.

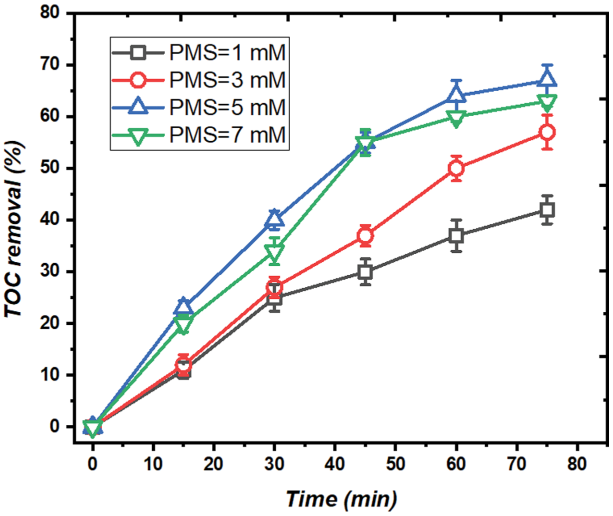

Fig. 3. The effect of PMS concentration on TOC removal efficiency by PMS/O_3/UV process (pH=7, O_3=1.2 mg/min).

$$HSO_5^{-}+SO_4^{\bullet-}\rightarrow SO_5^{\bullet-}+SO_4^{2-}+H^{+} \quad k<1\times10^{5}\ M^{-1}s^{-1} \tag{16}$$

$$HSO_5^{-}+HO^{\bullet}\rightarrow SO_5^{\bullet-}+H_2O \quad k=1.7\times10^{7}\ M^{-1}s^{-1} \tag{17}$$

$$SO_5^{2-}+HO^{\bullet}\rightarrow SO_5^{\bullet-}+HO^{-} \quad k=2.1\times10^{9}\ M^{-1}s^{-1} \tag{18}$$

3. Effect of O_3 Dosage on TOC Removal in PMS/O_3/UV

Finally, the effect of ozone dosage was investigated as one of the

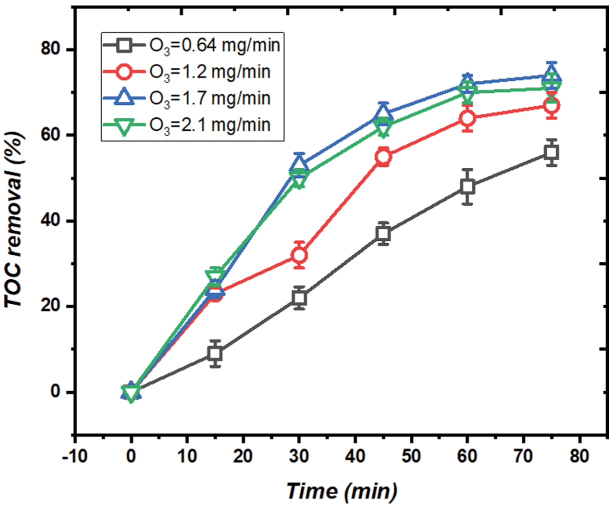

Fig. 4. The effect of PMS concentration on TOC removal efficiency by PMS/O_3/UV process (pH=7 and PMS=5 mM).

operating parameters in PMS/ozone/UV process. To get this objective, varying ozone dosages (0.64, 1.2, 1.7, and 2.4 mg/min) were investigated. As can be seen in Fig. 4, the highest TOC removal efficiency (74%) was obtained for PMS/O_3/UV oxidation after 75 min of treatment. During the sole ozone process, only 23% of the TOC removal was achieved. Therefore, increase of ozone dosage improved TOC removal, saying that concentration of the hydroxyl radicals increases with an increase in the ozone dosage. As a result, more free radicals can be generated after ozone contact with PMS in the solution. The efficiency improved significantly up to ozone dosage of 1.7 mg/min in which the removal efficiency reached 74%. However, the high ozone dosage of the gas in a high ozone dosage of 2.1 mg/min may affect the amount of effective free radicals and act as scavenger based on Eqs. (19)-(20) [32].

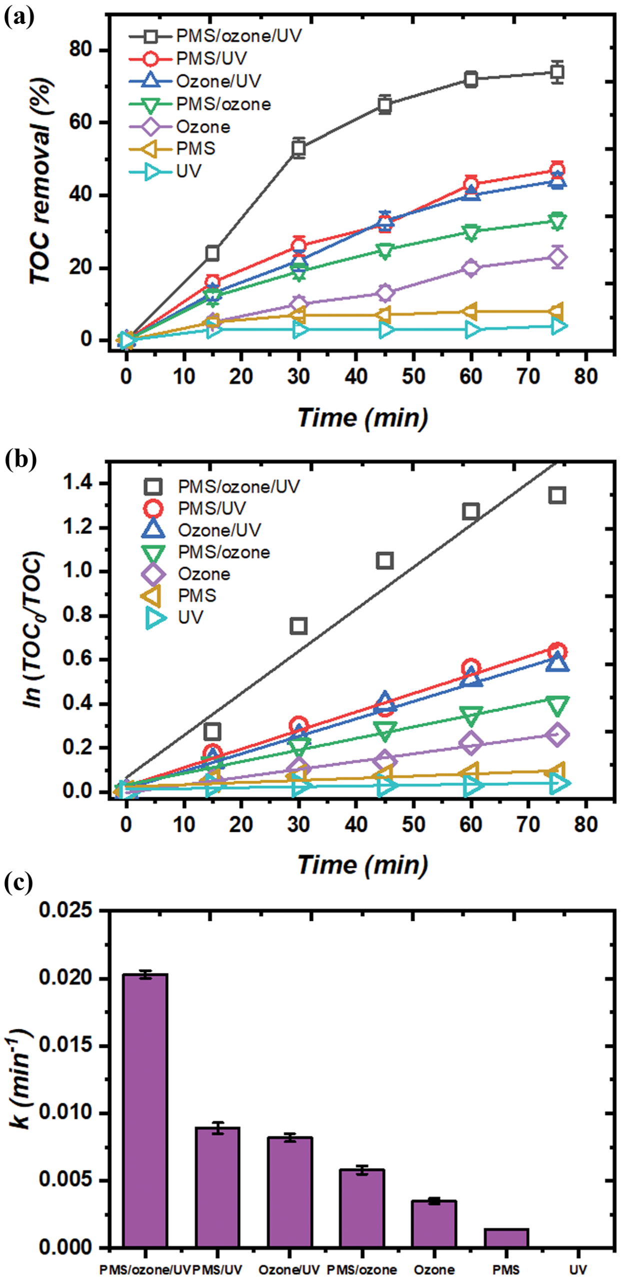

Fig. 5. (a) TOC removal efficiency with different processes in optimal conditions, (b) the plot of t *vs* ln (TOC_0/TOC_t) for pseudo-first order, (c) the rate constants obtained for different processes (pH=7, PMS=5 mM, O_3=1.7 mg/min).

$$O_3+HO^{\bullet}\rightarrow HO_2^{\bullet}+O_2 \quad k=3\times10^{9}\ M^{-1}s^{-1} \tag{19}$$

$$O_3+SO_4^{\bullet-}\rightarrow SO_5^{\bullet-}+O_2 \tag{20}$$

4. Comparison of Different Processes for TOC Removal from PWLL

Experiments were executed with UV, O_3, PMS, O_3/UV, PMS/UV, O_3/UV, and PMS/O_3/UV at the same conditions (pH=7, PMS=5 mM, and O_3=1.7 mg/min) to investigate the influence of each constituent on the TOC removal rate. The removal efficiency of TOC for all treatment processes is shown in Fig. 5(a).

The removal efficiency of direct UV-C radiation and sole PMS was negligible, which is in accordance with other studies [16,33]. It has been frequently reported that the UV is far less effective than UV/oxidant processes, such as UV/O_3 [34], UV/PDS [35] and UV/Cl_2 [36]. In the current study, O_3 was more effective at reducing TOC than UV and PMS. It can be a result of direct ozonation in which some organic compounds are oxidized by ozone. This is related to the fact that the redox potential of ozone is more than that of PMS (2.01 V vs. 1.82 V) and so, ozone can degrade some organic compounds [37]. Previous study has also shown that the combination of PMS with ultraviolet radiation increased synergistically removal efficiency [18]. This increase was because of enhanced generation of sulfate and hydroxyl radicals to degrade organic pollutants [38]. The decrease in TOC by PMS/UV was 47% after 75 min, while the UV/O_3 removed 44% of TOC, and the PMS/O_3 had a lower efficiency for TOC removal than two other processes (33%). This clearly demonstrated that UV irradiation can significantly enhance TOC removal.

By adding O_3 to the PMS/UV process, TOC removal efficiency increased from 47 to 74% in a way that removal efficiency has been improved by around 27%. This development is related to the further activation of PMS by O_3, which leads to the production of more free radicals. The mechanism of degrading organic compounds by the PMS/O_3/UV process can be explained by formation of several radical and non-radical reactions [1,38]. Activation of PMS by UV radiation was recognized as one of the most effective methods in the formation of active radicals and can produce hydroxyl and sulfate radicals (Eq. (1)). Also, the activation of O_3 by UV radiation induces the formation of hydroxyl radicals (Eq. (2)) as oxidative agents [37]. Therefore, the existing contaminants in polluted water are eliminated by indirect and direct O_3 oxidation [39]. O_3 is not only an oxidant but also plays an important role in the PMS activation process. In this way, dianion of PMS (SO_5^{2-}) reacts with ozone and produces an adduct ($OOSO_3^{2-}O_3$) (Eq. (4)) in which it is decomposed to ozonide radical and peroxymonosulfate radicals ($SO_5^{\bullet-}$) (Eq. (5)). Sulfate radicals can be generated through combination of ozone and $SO_5^{\bullet-}$ based on Eq. (6). Note that recombination of $SO_5^{\bullet-}$ results in the formation of two moles of sulfate radicals or peroxydisulfate (Eqs. (7) and (8)). On the other hand, $OOSO_3^{2-}O_3$ may be decomposed to hydroxyl radicals and sulfate radicals via UV irradiation according to Eq. (21).

$$O_3SO_5^{2-}+2H_2O+UV\rightarrow SO_4^{\bullet-}+3HO^{\bullet}+O_2+OH^- \tag{21}$$

Our previous study demonstrated that high energy input such ultrasound can decompose this adduct into free radicals [16]. On the other hand, ozonide radical is consequently decomposed to hydroxyl radicals (Eqs. (9)-(10)). This reactions chain accelerates the degradation of organic pollutants in the contaminated water. Several active radicals including $SO_5^{\bullet-}$, $SO_4^{\bullet-}$, ozonide radicals and ${}^{\bullet}OH$ can be produced during the oxidation process by PMS, among which $SO_4^{\bullet-}$ and ${}^{\bullet}OH$ are the predominant active species for the decomposition of organic pollutants from aquatic environments [40].

To determine the degradation of organic compounds in PMS/O_3/UV process, TOC removal was investigated during 75 min reaction time. The pseudo-first-order kinetics was applied to determine the rate constant of TOC removal according to following equation [35];

$$\ln\left(\frac{TOC_0}{TOC_t}\right)=kt \tag{22}$$

where TOC_0 and TOC_t are initial and final TOC concentration, respectively, k and t are first-order rate constant (min^{-1}) and reaction time (min), respectively. To obtain the rate constant, t (reaction time) *vs* ln (TOC_0/TOC_t) is plotted and the obtained slope of the line is considered as the rate constant. The obtained plots for all processes are presented in Fig. 5(b). As can be seen, the pseudo first-order model was well fitted for TOC removal with R-squared 0.98.

The rate constants of TOC removal by different processes are presented in Fig. 5(c). According to the kinetic model, the reaction rate constant (k) for TOC removal by PMS/ozone/UV was obtained as 0.0203 min^{-1}. According to the rate constants of pseudo-first-order shown in Fig. 5(c), the order of the investigated processes follows: PMS/ozone/UV>PMS/UV>ozone/UV>PMS/ozone>ozone>PMS>UV.

5. Removal Efficiency of PMS/O_3/UV Process in Combination with Transition Metals

To increase the efficiency of TOC removal, Fe(II) and Co(II) were selected as transition metals for activation of O_3 and PMS, and production of more active radicals in the presence of UV radiation. Fe(II) and Co(II) are among the best catalysts for activating PMS and O_3 [41]. Fe(II) and Co(II) have demonstrated high catalytic activity for both ozone and PMS. The results of TOC removal efficiency by the PMS/O_3/UV process in the absence and presence of the mentioned metal ions are shown in Fig. 6(a).

The results showed that PMS/O_3/UV/Fe(II) process was more efficient than PMS/O_3/UV/Co(II) process. Accordingly, the removal efficiency in the presence of transition metal ions was higher than the PMS/O_3/UV process. Co(II) is well recognized as the best catalyst for PMS activation based on Eq. (23). In addition, Co(II) can activate ozone to generate hydroxyl radicals based on Eq. (24). However, this reaction is very slow; therefore, the role of cobalt ions was probably slight in progress of the degradation rate [42].

$$Co(II)+HSO_5^-\rightarrow Co(III)+SO_4^{\bullet-}+OH^- \tag{23}$$

$$Co(II)+O_3+H_2O\rightarrow Co(OH)^{2+}+HO^{\bullet}+O_2 \tag{24}$$

On the other hand, Fe(II) is similar to Co(II) in the case of PMS activation (Eq. (25)) while Fe(II) has a different behavior in which Fe(IV) is produced through an O-transfer mechanism when ozone reacts with ferrous ion (Eq. (26)) [43].

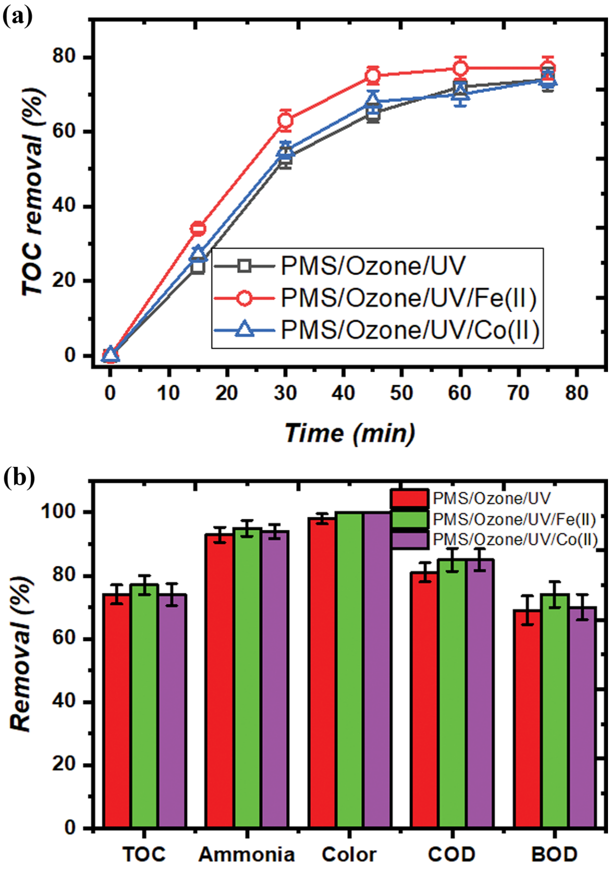

Fig. 6. Effect of transition metal ions on (a) TOC removal (b) ammonia, color, TOC, COD and BOD removals (pH=7, PMS=5 mM, O_3=1.7 mg/min, Fe^{2+}, Co^{2+}=1 mM and time=75 min).

$$Fe(II)+HSO_5^-\rightarrow Fe(III)+SO_4^{\bullet-}+OH^- \quad k=3\times10^4\ M^{-1}s^{-1} \tag{25}$$

$$Fe(II)+O_3\rightarrow FeO^{2+}+O_2 \quad k=8.2\times10^5\ M^{-1}s^{-1} \tag{26}$$

Fe(IV) is a strong oxidant for degradation of organic pollutants. In fact, in the presence of iron, another oxidative agent (Fe(IV)) is added to accelerate the degradation of organic compounds. Note that UV irradiation facilitates reduction of Fe(III) to Fe(II) through decomposition of formed iron complexes and generate hydroxyl radicals consequently as stated in Eqs. (27)-(28) [44].

$$Fe(OH)^{2+}+UV\rightarrow Fe^{2+}+HO^{\bullet} \tag{27}$$

$$Fe^{3+}+H_2O+UV\rightarrow Fe^{2+}+HO^{\bullet}+H^+ \tag{28}$$

This increase could be due to the production of more free radicals through the activation of PMS and O_3 by Fe(II) as abovementioned. Indeed, iron enhances the generation of free radicals and also forms a reactive species (Fe(IV)) to further degradation of organic compounds in PWLL. Although iron enhances the performance of PMS/O_3/UV process, iron residual may produce a sludge that its recovery and separation is costly.

To investigate the function of PMS/O_3/UV on the removal efficiency of parameters (ammonia, color, BOD, COD and, TOC) from polluted water, a series of experiments was conducted. Based on the obtained results (Fig. 6(b)), in general, the use of Fe(II) and Co(II) in PMS/O_3/UV had a slight improvement in the treatment of PWLL compared to the main process. PMS/O_3/UV, the PMS/O_3/UV/Fe(II) and PMS/O_3/UV/Co(II) processes could remove ~100% of the polluted water color. Organic compounds (with indices of TOC, COD and BOD) were effectively removed by all processes. Lower efficiency for BOD parameter can be related to the destruction of non-biodegradable compounds into biodegradable compounds increasing residual BOD in the solution.

In the case of ammonia removal, ammonia is destructed by hydroxyl radicals and sulfate radicals while the reaction of ozone with ammonia is very slow ($k=2\,M^{-1}\ s^{-1}$). Further oxidation by reactive oxidative agents resulted in mineralization of ammonium to nitrogen in which to oxidize each mole of ammonia, three moles of sulfate or hydroxyl radicals are required. However, it has been reported that final by-product of further oxidation of ammonia by sulfate radicals is nitrate ions [16].

$$6HO^{\bullet}+2NH_3 \rightarrow N_2+6H_2O \tag{29}$$

$$6SO_4^{\bullet-}+2NH_3 \rightarrow N_2+6HSO_4^{-} \tag{30}$$

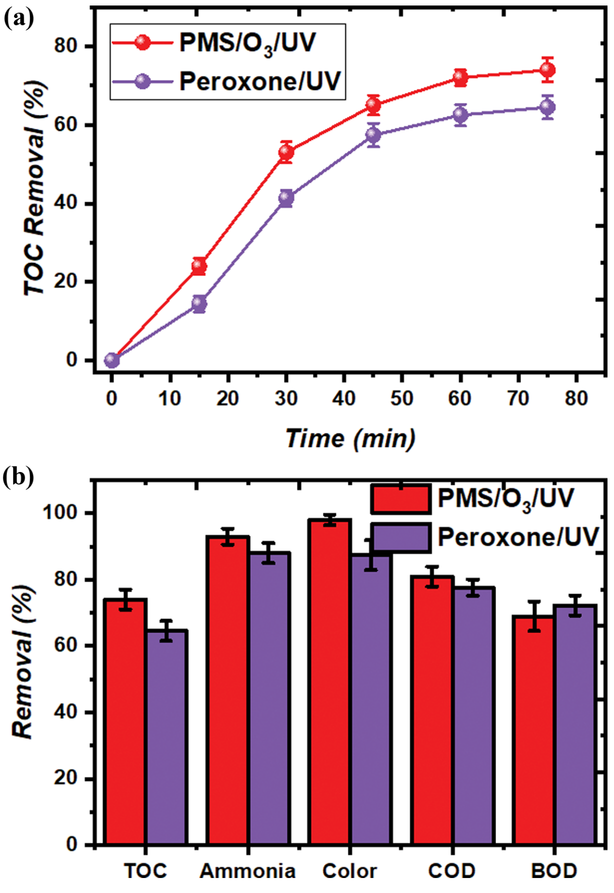

Fig. 7. (a) TOC removal by PMS/O_3/UV and peroxone/UV processes (b) TOC, ammonia, color, COD, BOD removal by PMS/O_3/UV and peroxone/UV processes (pH=7, H_2O_2=PMS=5 mM, O_3=1.7 mg/min).

6. PMS/O_3/UV vs. Peroxone/UV

Peroxone reagent (H_2O_2/O_3) has been widely used for the remediation of various wastewaters. In current study, peroxone/UV was compared with PMS/O_3/UV under the same conditions. Fig. 7(a) demonstrates TOC removal from polluted water using two systems. A supremacy was observed in case of PMS/O_3/UV with 74% TOC removal against 64.5% TOC removal for peroxone/UV after 75 min. PMS/O_3/UV had higher rate constant compared to peroxone/UV (0.0203 vs 0.0147 min^{-1}). This indicates that sulfate radical probably has a significant role for this supremacy in PMS/O_3/UV compared to peroxone/UV. In peroxone/UV process, $HO^{\bullet}$ is the main reactive oxidative species which is produced through the following equation:

$$2O_3+H_2O_2 \rightarrow 2HO^{\bullet}+3O_2 \tag{31}$$

PMS/O_3/UV process benefits the simultaneous application of $SO_4^{\bullet-}$ and $HO^{\bullet}$ for the degradation of organic pollutants while mainly $HO^{\bullet}$ plays the main role in peroxone-based processes. Sulfate radical has lower reaction rate compared to hydroxyl radicals in case of co-existing water constituents such as (bi)carbonate and chloride ions [13]. In fact, sulfate radicals are less under influence of water matrix compared to hydroxyl radicals. Therefore, this difference observed in efficiency for these processes is probably attributable to the presence of sulfate radicals in PMS/O_3/UV.

Fig. 7(b) shows TOC, COD, BOD, color and ammonia removals from PWLL using two systems. According to Fig. 7(b), PMS/O_3/UV exhibited a higher efficiency in case of all parameters except for BOD. In case of BOD, although there is a scant difference between two systems, it probably indicated that higher residual BOD in PMS/O_3/UV is derived from the conversion of non-biodegradable compounds to biodegradable compounds. As a conclusion, PMS/O_3/UV had better performance compared to H_2O_2/O_3/UV. In a study based on SR-AOPs for landfill leachate treatment, peroxydisulfate (PDS)/heat removed 77% of TOC from landfill leachate with 100 mM PDS and 90 °C during 120 min [45]. Compared to our study, this study suffers from high concentration of PDS, which increases the cost and residual sulfate ions as by-products. In another study, PDS/O_3 eliminated 70% COD from landfill leachate under the conditions of 2,480 mg/L PDS, 30 mg/L ozone and 210 min reaction time [46]. As deduction, PMS/O_3/UV showed high efficiency for treatment of organic content and ammonia from PWLL, but operation and the cost of materials are relatively more than conventional methods since the costs of UV and ozone generation are always concerns of water engineers.

7. Comparison with other Studies with Focus on their Strength and Shortcoming

Regarding the literature, we compared several studies with current work in case of efficiency, strength and shortcoming (Table 2). First, it should be mentioned that, “Well, no treatment method is perfect” (in regard to “Some Like it Hot” (movie, 1959)). Therefore, giving a manifest for the best method is irrational. SR-AOPs have showed high efficiency for ammonia removal while residual sulfate ion derived PDS and PMS activation is a problem for effluent [17,47]. Ozone based process is an efficient process for treatment of polluted water, while the cost of ozone generation is relatively high. On the other hand, Fenton-coagulation based processes such

Table 2. Comparison of different AOPs for the treatment of landfill leachate

Process	Conditions	Removal efficiency	Strengths	Shortcoming	Refs
PDS/heat	PDS/12COD$_0$=2, Temperature=50 °C and pH=4	COD (91%) Ammonia (100%)	Efficient process, Effective for ammonia removal	Residual sulfate ions, High energy consumption	[47]
Peroxi-coagulation	pH=3, Voltage=10 V, inter electrode distance =4 cm, time=90 min	COD (93%)	Efficient, Simultaneous application of coagulation and oxidation	Production of sludge, High energy consumption, Electrode passivation	[50]
Fenton oxidation	pH=2, Fe(II)=12 g/L, H_2O_2/Fe=12 (molar ratio), and Time=55 min	COD (87%)	Efficient, Simple process, Short reaction time	Production of sludge, Need to acidic condition, High concentration of reagent (iron and H_2O_2)	[51]
PDS/heat/Ag(I)	PDS=112.5 g/L, Temperature=80 °C, Ag=0.25 g/L and Time=30 min	COD (20%), Color (65.4%)	Simple operation	High concentration of PDS, Residual sulfate ions, High energy consumption, High cost of catalyst (Ag)	[52]
W-C@TiO$_2$ (Cascade photoreactor)	40 W light intensity, coating surface density= 10.59 g·m^{-2}, flow rate= 1 L/min, and time=40 h	COD (84%)	Efficient, Sustainable process	Long reaction time, Need to UV light	[53]
Electro-Peroxone	O_3 concentration of 157 mg/L, Time=4 h and applied current=350 mA	COD (87%)	Efficient, in situ generation of oxidant	High electrical energy consumption, the cost of O_3 production	[49]
UV-Ultrasound	pH=10, Time=40 min, Ultrasound frequency =60 Hz and UV intensity =30 W	Ammonia (93%)	Efficient, Chemical-less process	Extreme electrical energy consumption, Difficulty in scale up	[54]
PMS/O_3/UV	pH=7, PMS=5 mM, O_3=1.7 mg/min and Time=75 min	TOC (74%), COD (81%), Ammonia (93%)	Efficient for all parameters	High energy consumption, Residual sulfate ions, the cost of O_3 production	Current study
Peroxone/UV	pH=7, H_2O_2=5 mM, O_3=1.7 mg/min and Time=75 min	TOC (64.5%) COD (78.6%), Ammonia (88%)	Efficient for all parameters	High energy consumption, the cost of O_3 production	Current study

as peroxi-coagulation benefits both coagulation and oxidation processes, whereas the production of sludge is the main demerit. In case of photocatalysis processes, they often need more reaction time in real wastewater, thus electrical energy for UV irradiation increases consequently. Moreover, this system may not be suitable for dark wastewater with high suspended solids and color due to impeding transmission of light through solution [48]. However, its performance in the degradation of pollutants is incontrovertible. Electrochemical processes such as electro-peroxone and electro-Fenton, which in situ generate hydrogen peroxide in the reactor continuously, are promising processes to reduce the cost of chemicals and prevent scavenging hydroxyl radical due to high concentration of hydrogen peroxide compared to peroxone and Fenton reagent. However, high energy consumption is the most important disadvantage of electrochemical processes [49]. The use of ultrasound, UVC, vacuum UV(VUV) and their combination has exhibited high efficiency without any chemicals. But these processes require high energy and are often effective in laboratory scale. Current work has the problems of PMS-ozone-UV based processes which are above mentioned. However, the low PMS and ozone dosages with high mineralization are considered as the most important advantage.

CONCLUSIONS

SR-AOPs are developed for application in real wastewater. In this study, the treatment of PWLL was investigated by the PMS/O_3/UV process. This process benefits both hydroxyl and sulfate radicals for the degradation of organic compounds. The optimal reaction conditions were pH=7, PMS=5 mM, O_3=1.7 mg/min, and reaction time of 75 min; under this condition 98% of color 93% of ammonia, 81% of COD, 74% of TOC and 69% of BOD were removed. Addition of ferrous ions enhanced the performance of PMS/O_3/UV process, while no improvement was observed in the case of cobalt ions. The pseudo-first-order kinetic model was fitted to TOC removal with a reaction rate constant of 0.0203 min^{-1}. Compared to peroxone/UV, PMS/O_3/UV had a higher function for the treatment of PWLL. This study showed that hybrid-AOPs can be applied for the treatment of polluted water in neutral condition. Further studies should be conducted on real matrix by SR-AOPs to give a clear scheme of cost and environmental impact.

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