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Removal of Chemical Oxygen Demand, Colorants and Non-Biodegradable from Leachate Using $KMnO_4$

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Abstract

Leachate is known to have complicated compositions hard to be treated effectively. However, the result presented in this paper shows that large proportions of chemical oxygen demand (COD), colorants and some non-biodegradable groups could be reduced significantly at the preliminary stage of oxidation process using a strong oxidizing agent such as potassium permanganate ($KMnO_4$). At the initial pH of 7.5, the concentrations of 10,800 mg/L COD, 5,926 color (Pt-Co), 133 - 1,034 ppb polycyclic aromatic hydrocarbon (PAH), 7.49 - 712 ppb organochlorine compounds (OCS) and 21.54 - 2,560 ppb organophosphorous compounds (OPS) were investigated. Within 2 hours of treatment with the initial $KMnO_4$ concentration of approximate 1 g/L and air flow rate of 5 L/minute, the removals of COD, color, groups of PAH, OCS and OPS from leachate were found to be 57%, 93% and over 90%, respectively. These results show that this oxidation process is more effective compared to the coagulation processes with iron or aluminum salts and this technique can be a help to improve the leachate treatment efficiency.

Keywords: COD removal, color degradation, leachate treatment.

1. Introduction

Till now, in Vietnam and many other countries of the "third world", landfill is still the most popular technique for treating solid wastes generated from various sources such as industry, household, hospital etc., due to the simplicity and the low cost in operation. However, the leachate generated from the degradation of wastes in the landfill is a serious pollution source to environment and human health. The leachate not only contains a high concentration of chemical oxygen demand (COD) (500-60,000 mg/L) [1], NH_4^+ (39-2,090 mg/L) [2], chloride (119-5,856 mg/L) [2], but also contains many heavy metal ions such as Hg (0.5-1.7 mg/L) [2], As (0.005-1.6 mg/L) [3], Cd (0.01- 0.126 mg/L) [2], Pb (3.45 mg/L) [4] or even non-biodegradable organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (13-1,986 ng/L), the aromatic compounds benzene, toluene and xylene (BTX) (0.04-8.2 µg/L), polychlorinated biphenyls (PCBs) (16-68.1 ng/L) [5].

Leachate treatment methods including many processes such as surface ponds, biological, chemical processess are inefficient and expensive. The selection of treatment processes depend strongly on the age of the landfill and the composition of the leachate [9]. For example, new leachate often contain high organic matters displayed by high biochemical oxygen demand/chemical oxygen demand (BOD_5/COD) ratios which parameter indicated that the biological treatment processes can be feasible and reliable [10-11]. For older leachate, the ratio of BOD_5/COD is often lower than 0.5, therefore, chemical treatment processes such as oxidation method should be considered to alternative for the low biodegradability and refractory toxics [12-13].

In the wastewater treatment systems, preliminary treatment plays an important role as this step helps to remove suspended solid (SS) as well as reduce concentrations of pollutants effectively. However, the chemical agents used for coagulation such as $FeSO_4$, $Al_2(SO_4)_3$, poly aluminium chloride (PAC) etc., can only remove SS and not effect on both the degradable and non-biodegradable organic compounds (PAHs, organochlorine compounds (OCS), organophosphate (OPS) etc.,) because these salts are not oxidizing agents.

Oxidation method processes involve using oxidants such as $KMnO_4$, ozone, hydrogen peroxide, and UV irradiation through the chemical, electrochemical, or photochemical reactions. Oxidants react with the target pollutant or release the free reactive radicals, mainly the hydroxyl radical which reacts with the target pollutant. Contaminants will reduce depending on the reaction time, dosage of oxidants and mixing process.

Potassium permanganate with oxidation potentials of 1.7 V is capable of oxidizing organic

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compounds containing aldehyde groups, carbon-carbon double bonds and hydroxyl groups [14]. Permanganate ion as an electrophile is easily attracted to the electrons in carbon-carbon double bonds found in chlorinated alkenes. Potassium permanganate exposes the advantages of easy handling and highly effective in wastewater treatment [14].

Aiming to enhance the leachate treatment efficiency, direct oxidation of the leachate using $KMnO_4$, applied in preliminary stage of treatment process was carried out. The effect of different dosages of $KMnO_4$, pH, reation time, air flow rate and decomposition of several organic compounds in leachate were study.

2. Materials and Method

2.1. Materials

Leachate was collected from the dumping site at the Nam Son landfill, located in Soc Son district, Hanoi, Vietnam. The characteristics of leachate were analyzed and are presented in Table 1.

Table 1. The chemical compositions of leachate from the Nam Son land fill, Soc Son, Ha Noi, Vietnam

Parameters	Unit	Conc.	Parameters	Unit	Conc.
pH	-	7.5	TP	mg/L	8.383
COD	mg/L	10,800	PO_4^{3-}	mg/L	3.645
BOD_5	mg/L	4,767	Pb	mg/L	1.2
Color	Pt-Co	5,926	As	mg/L	0.022
Cl^-	mg/L	2,130	Cd	mg/L	0.17
TKN	mg/L	700	Hg	mg/L	0.005
NH_4^+	mg/L	131.5	Fe	mg/L	2.3
Triethyl phosphorothioate	ppb	N.D	Disulfoton	ppb	2,560
Thionazin	ppb	127.3	Methyl parathion	ppb	186.79
Sulfotepp	ppb	N.D	Dimethoate	ppb	21.54
Thionazin	ppb	N.D	Parathion	ppb	1,030
Benzo(k) flourathene	ppb	470.33	Flouranthene	ppb	46.24
Naphthalene	ppb	79.53	Pyrene	ppb	48.99
Acenaphthalene	ppb	33.07	Benzo (a) anthracene	ppb	145.92
Acenaphthene	ppb	85.52	Benzo (b) flouranthene	ppb	N.D
Flourene	ppb	49.11	Benzo (a) pyrene	ppb	498.62
Phenanthrene	ppb	8.23	Dibenzo (ah) anthracene	ppb	1,034
Anthracene	ppb	18.44	Benzo (ghi) perylene	ppb	172.49
HCB-alfa	ppb	112.9	Endosulfa I	ppb	0
HCB-beta	ppb	-	DDE	ppb	37.16
HCB-delta	ppb	-	Dieldrin	ppb	51.43
HCB-gama	ppb	-	Endosulfa II	ppb	7.49
Heptachlor	ppb	0	DDD	ppb	18.72
Andrin	ppb	223.26	Endrin aldehyde	ppb	0
Heptachlor epoxide B	ppb	94.38	Endrin	ppb	712.04
Endosunfan	ppb	719.88	DDT	ppb	44.85

2.2. Chemicals

All chemical used in this study ($KMnO_4$, $K_2Cr_2O_7$, Ag_2SO_4, NH_4FeSO_4, $HgSO_4$, H_3NSO_3, H_2SO_4, NaOH, $FeSO_4$, $Al_2(SO_4)_3$, metal ions standard solutions (Cd, As, Hg, Fe, Cr, Al, Ni), PAH, OPS and OCS standard solution, etc were of analytical grade (Merch, Germany).

2.3. Equipments

The experiments were carried out on the pilot shown in Fig. 1. Six columns were made of PVC and have the same volume (60mm x 1500mm). Air was blowed into column through distributer, installed at the bottom of the column by using air blower. The air flow rate into six columns is controlled by vale and flow meter in the pipe. Oxidant, chemicals and leachate were added from the top of columns. After oxidation process, samples were collected from valves at the bottom of columns and analyzed parameters of COD and color. For experiments to evaluate biodegradable organic compounds after of oxidation processes, samples of experiment with optimal conditions were analyzed organic compounds of PAH, OPS and OCS in the leachate before and after treatment by using gas chromatography - mass spectrometry (GC/MS system - Agilent 6890N). The oxidation efficiency of $KMnO_4$ on these compounds are determined. The oxidation efficiency is calculated based on the equation as follows:

$$H(\%) = \frac{C_{initial} - C_{out}}{C_{initial}} . 100\% \quad (1)$$

where:

$C_{initial}$ is initial concentration of COD, BOD, color, PAH, OPS, OCS

C_{out} is concentration of COD, BOD, color, PAH, OPS, OCS in leachate after oxidizing process.

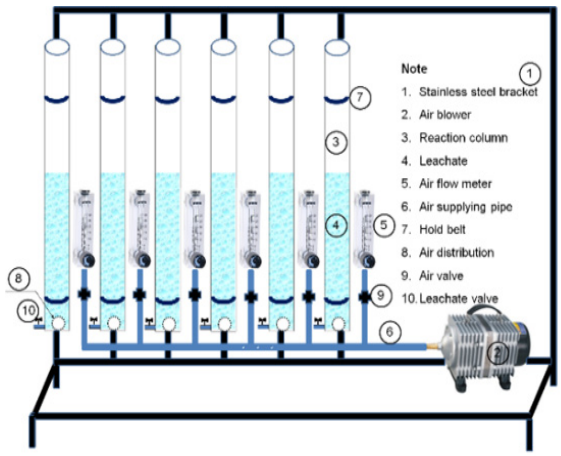


Fig. 1. Experimental pilot

2.4. Analyticals Methods

All parameters analyzed in this study following the current national standards or standard methods for examination of water and wastewater, issued by Ministry of Natural Resources & Environment and the Environmental Protection Agency of America. pH, COD, BOD_5, color Cl^-, TKN, NH_4^+, TP, PO_4^{3-}, Pb, As, Cd, Hg, Fe were analyzed at laboratory of Research and Development of School of Environmental Science and Technology, Hanoi University of Science and Technology.

Leachate samples were also sent to the laboratory in Quality Assurance and Testing Center No. 1. Organic compounds of PAH, OPS and OCS in samples were analyzed by using gas chromatography - mass spectrometry (GC/MS system - Agilent 6890N - Agilent Technologies, Santa Clara, CA, USA). Agilent 6890N is equipped with an Agilent 7683B Injector a 30 m, 0.25 mm i.d. HP-5MS capillary column and an Agilent 5975 mass selective detector (MSD) were used to separate and quantify the PAH, OPS and OCS compounds. Helium was used as a carrier gas at a constant flow rate of 1 mL/min.

3. Results and Discussion

3.1. Effect of Initial pH

The effect of initial pH on the removed efficiency of COD and colorants by $KMnO_4$ is presented in Fig. 2. The results show that the removed efficiency of CODs increases slightly from 44% at pH 2 and reaches to the highest removal efficiency of 45% at pH 7 and changes slightly at pH 8 and pH 9. While the removal efficency of colorants decreases slightly from 98% at pH 2 to 85% at pH 7 and changes slightly at pH 8 and pH 9.

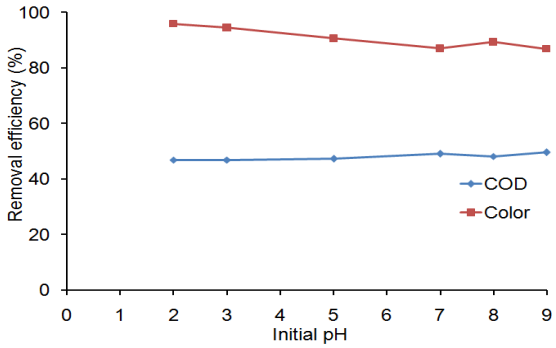
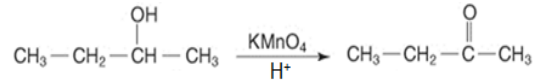


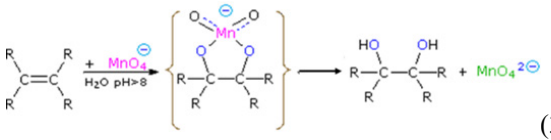
Fig. 2. Effect of initial pH on COD and colorants removal ($KMnO_4$ concentration 1g/L, air flow rate 5L/min, treating time 4h, temperature 25°C)

The results presented in Fig. 2 also pointed that the COD removal and colorants degradation were not similar. It's because of two processes happened at the same time. The first process is the complete oxidation, during which some simple organic compounds such as alcohol, acid, etc (Carbon number less than 4) to CO_2, H_2O, cause of COD and color reduction. The second process is the incomplete oxidation of large moclecules and non-biodegradable such as PAH, OCS, OPS, etc. into intermediate product. This process did

not reduce COD effectively but is excellent with color reduction. That is the reason why colorants degradation was found to over 90% but COD removal efficiency was about 50% only. The pathway may be as the followings:



(2)



(3)

The another reason why COD removal efficiency was 50% only might be due to the presence of inorganic ions, which can react with such as Fe^{2+}, Cl^-. Especially, Cl^- with very high concentration (2,000 mg/L) can be considered as one of the main causes of low COD removal efficiency. The reaction between MnO_4^- and Cl^- is as follow:

$$MnO_4^- + 2Cl^- + 8H^+ + 5e^- \rightarrow 2Mn^{2+} Cl_2 + 4H_2O \quad (4)$$

As a common knowledge, pH is always one of the most important impacting on the removal efficiency for any wastewaters. Especially, in the oxidation process, pH effects directly on the oxidative capacity of any oxidizing reagent. Although Mn is a multiple oxidation state reagent, which has 6 different oxidation numbers under various forms existing in both acid (MnO_4^-, $HMnO_4^-$, H_3MnO_4, MnO_2, Mn^{3+}, Mn^{2+}) and base media (MnO_2, Mn^{2+}) with the different potential (Fig. 3) [6], pH seems impact slightly on the removed efficiency of COD and colorant. Since the initial pH of leachate is 7.5, the pH 7.5 was selected as the value for next experiments.

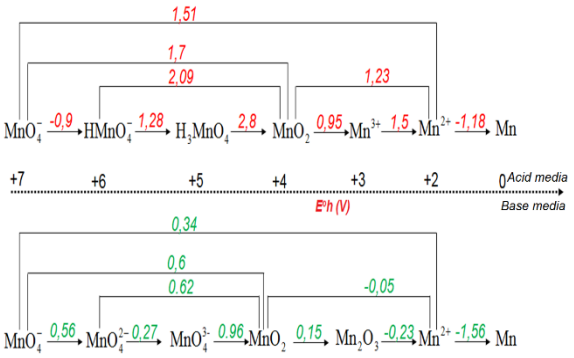


Fig. 3. Standard potential oxidation of Mn

3.2. Effect of Air Flow Rate

The results of the effect of air flow rate in ranging from 0 to 20 litter per minute on the removal efficiency are presented in Fig. 4.

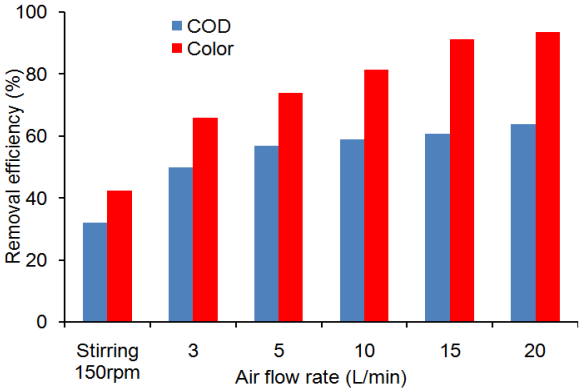


Fig. 4. Effect of air flow rate on COD and color removal (initial pH 7.5, $KMnO_4$, concentration 1g/L, temperature 25 ºC, treating time 4 h)

Both the removal efficiency of COD and colorant increase with the increase of air flow rate. The removal efficiency of COD increase quickly from 33% with no air blow to 55% at air flow rate of 5l/min and increase slightly to 63% at air flow rate of 20 l/min. The removal efficiency of colorant were 43%, 65%, 78%, 80%, 88% and 90% at the air flow rate of 0, 3, 5, 10, 15, 20 l/m, respectively. Since the optimum of COD removal efficiency (60%, respectively) corresponding to the flow rate of 5l/min were observed, therefore the air flowrate of 5l/min was selected for next experiments.

The results show that air supplied by air blower were more effective than stirring. As seen in Fig. 4, the air flow rate enhanced the removal of COD and colorant. It is becaused of presentation of oxygen made changing the potential redox of leachate [8]. Although oxygen did not react directly with any components in the oxidation process, it still plays an important role as providing from 1 to 5 electron "e-" source for oxidative reaction happened.

$$MnO_4^- + 8H^- + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad (5)$$

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad (6)$$

$$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^- \quad (7)$$

$$MnO_4^- + e^- \rightarrow MnO_4^{2-} \quad (8)$$

3.3. Effect of $KMnO_4$ Concentration

The results of the effect of $KMnO_4$ concentration on oxidation process are showed in Fig. 5. The removal efficiency of COD in $KMnO_4$ concentration of 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2 g/L were 36%, 52%, 57%, 56%, 55%, 5%, respectively. The removal efficiency of colorant in $KMnO_4$ concentration of 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2 g/L were 73%, 74%, 81%, 74%, 73%, 73%, 72%, respectively.

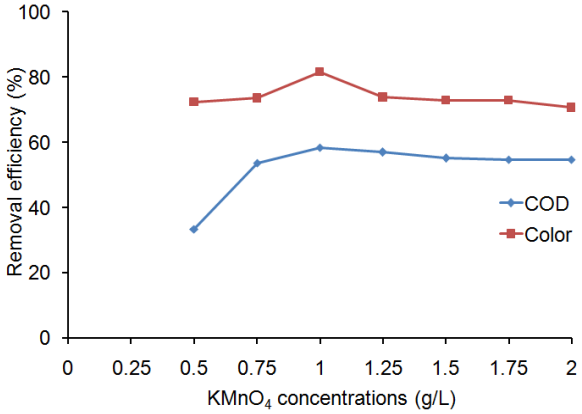


Fig. 5. Effect of $KMnO_4$ concentration on COD and color removal (initial pH 7.5, air flow rate 5 L/min, temperature 25 °C, treating time 4h)

The results show that the COD remval efficiency increase quickly with the increase of concentration of $KMnO_4$ from 0.5 g/L to 1.0 g/L and then are nearly constant with the dose of $KMnO_4$ of 1.25 or 2.0 g/L, while the removal efficiency of colorant changes slightly in variation of $KMnO_4$ concentration. This results can be explained by the amount of electron "e-" provided by diffused oxygen (5L/min) enough for 1 g/L of $KMnO_4$ only. Therefore, when $KMnO_4$ concentration increased to higher than 1 g/L, the COD removal and colorants degradation efficiency were not found to increase, too.

3.4. Effect of Treating Time

The results of time variations are show in Fig.6. As was anticipated and can be seen in Fig 6., the reaction time increase favoured the removal efficiency of COD and colorant. The COD removal efficiency in reaction times of 15, 30, 45, 60, 75, 90, 120, 135, 150 minutes were 19%, 25%, 32%, 34%, 40%, 50%, 51%, 52%, respectively. The colorant removal efficiency in reaction times of 15, 30, 45, 60, 75, 90, 120, 135, 150 minutes were 64%, 66%, 67%, 68%, 69%, 86%, 87%, 89%, respectively.

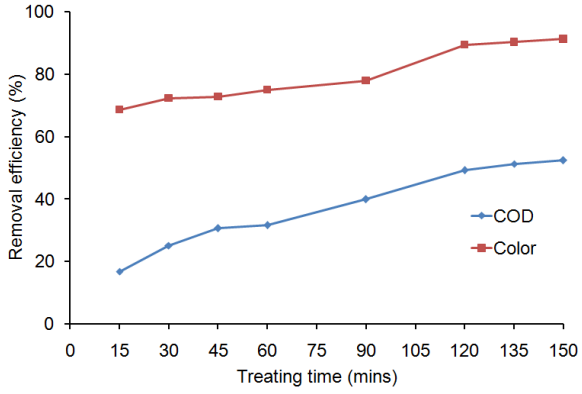


Fig. 6. Effect of treating time on COD and color removal (initial pH 7.5, air flow rate 5 L/min, temperature 25 °C).

Within the first 120 minutes, the oxidation efficiency increased gradually and reached balance as increasing time. Since the concentration of $KMnO_4$ in the first 120 minutes remained at the high value, leading to the quickly oxidation reaction. After 120 minutes, almost of $KMnO_4$ was consumed for oxidizing pollutants in leachate. Thus, the removal efficiency of COD and colorant changed slightly after 120 minutes of reaction.

3.5. Comparison with Coagulation Method

In order to compare with coagulation method, experiments with several popular coagulants such as PAC, $FeSO_4$, $Al_2(SO_4)_3$ were carried out. The results of these experiments are presented in Fig. 7 and Fig. 8. The COD removal efficiency by $KMnO_4$, $FeSO_4$, $Al_2(SO_4)_3$, PAC were 52%, 28%, 20%, 28%, respectively. The colorant removal efficiency by $KMnO_4$, $FeSO_4$, $Al_2(SO_4)_3$, PAC were 90%, 60%, 52%, 59%, respectively. As seen in Fig. 7, the best results of removal efficiency occurred by using $KMnO_4$, therefore preliminary treatment of leachate by using $KMnO_4$ was more effective than that using PAC, $FeSO_4$, $Al_2(SO_4)_3$. $KMnO_4$ not only shows the good ability of treatment both COD and color but also improves BOD/COD ratio up to 0.53 which is good ratio for microorganism treatment process.

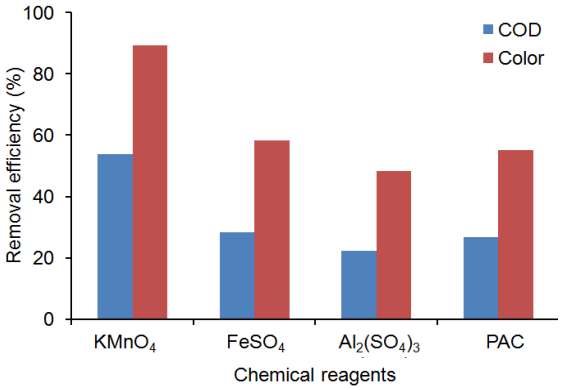


Fig. 7. COD and color removal efficiency by using various chemical reagents

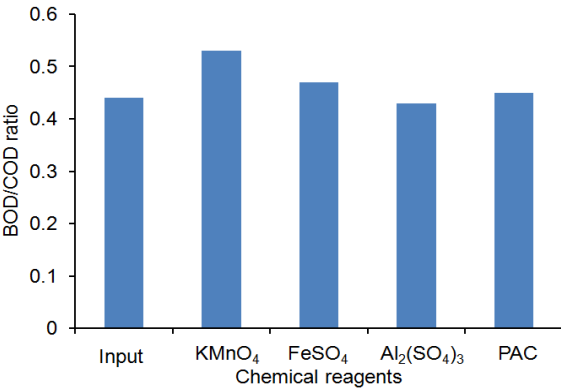


Fig. 8. BOD/COD ratio after treatment by using various chemical reagents

3.6. Evaluation of Biodegradable Organic Compounds after of Oxidation Processes

As seen in Table 1, the chemical compositions of leachate are very complicate. Many organic compounds exist in leachate. In addition, to investigation of COD and color removal efficiency, in this study some groups of non-biodegradable such as PAH, OCS, and OPS were also analyzed. The presentations of these groups are given as Fig. 9, Fig. 10, and Fig. 11.

It is easy to release the different in the number and height of peaks which occurred. As the results presented in Fig. 9, almost peaks, appeared in a) before oxidation, were disappeared in b) after oxidation process. It means that some organic compounds belong to PAHs group have been converted completely to CO_2 and H_2O.

However, the results in Fig. 10 and Fig. 11 show that some peaks were found to be higher as well as new peaks appeared in b) after oxidation process comparing to in a) before oxidation process. It means some organic compounds belong to OCS and OPS groups were not completely oxidized to CO_2 and H_2O and converted to many intermediate organic compounds. The BOD_5/COD ratio of leachate before oxidation is around 0.44 and that after oxidation is around 0.54 (Fig. 8). These results show that new organic compounds after oxidation are easily biodegradable comparing to before oxidation.

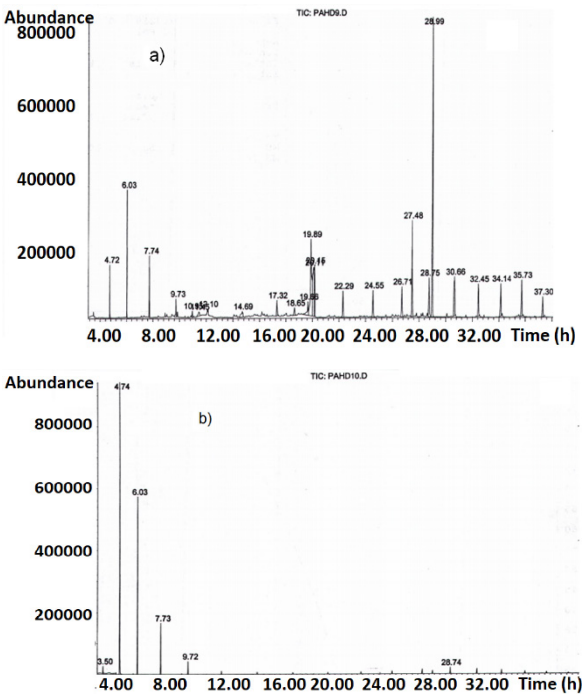


Fig. 9. Chromatography of polycyclic aromatic hydrocarbon (PAHs) in leachate: a) before and b) after oxidation process.

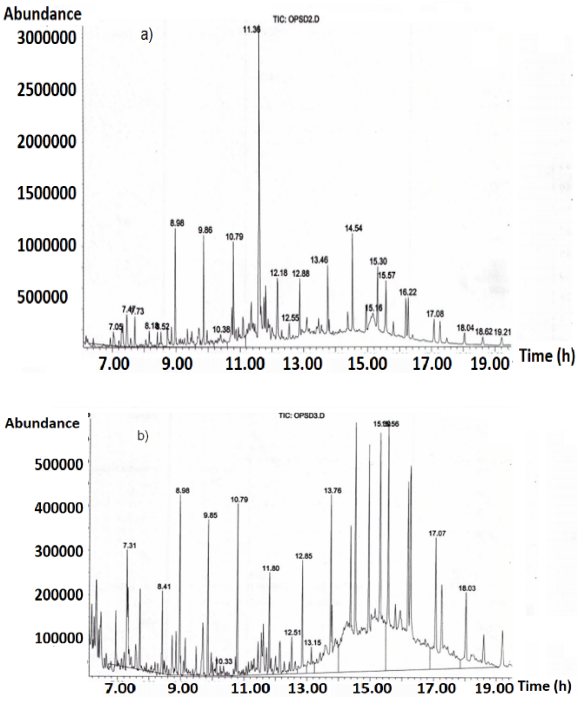


Fig. 10. a) Chromatography of organophosphate (OPS) in leachate before oxidation process. (b) Chromatography of organophosphate (OPS) in leachate after oxidation process

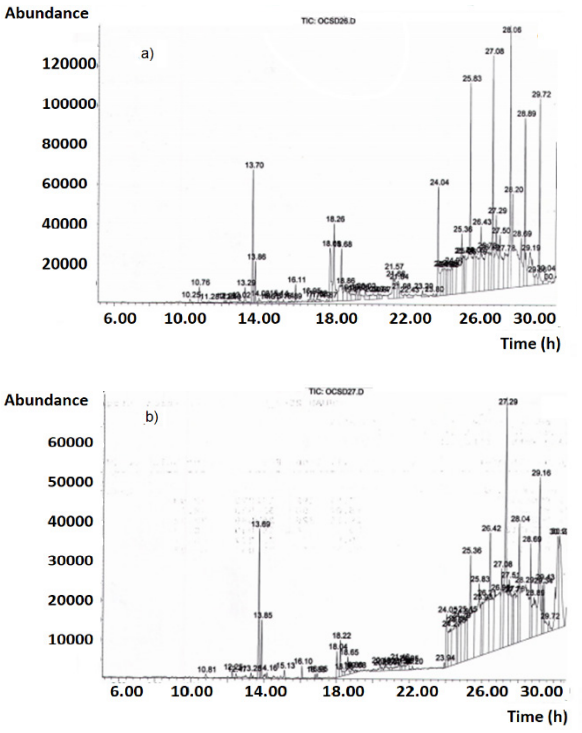


Fig. 11. Chromatography of organochlorine compounds (OCS) in leachate: a) before and b) after oxidation process

4. Conclusion

According to the results, it can be concluded that oxidation by $KMnO_4$ is reliable, feasible and efficient for pre-treatment and also post-treatment of leachate. The obtained data are sumaried below.

- $KMnO_4$ can be used as an effective oxidizing reagent for COD, color and non-biodegradable organic compound removal in preliminary treatment of leachate.
- $KMnO_4$ can oxidize both of biodegradable and non-biodegradable as well as improve the ratio of BOD/COD, which is good index for microorganism treatment process.
- With the initial pH 7.5, COD 10,800 mg/L, color 5960 Pt-Co, PAH 133-1,034 ppb, OCS 7.49 - 712 ppb, OPS 21.54 - 2,560 ppb, $KMnO_4$ concentration 1g/L, air flow rate 5L/min and treating time 2 hours, the COD, colorant, PAH, OCS, OPS treatment efficiency reached 57%, 93%, and over 90%, respectively. BOD/COD ratio increased to 0.53 compared to 0.4 before oxidizing process.

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