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Investigation on the effect of ozonation process before and after coagulation on reduction in leachate pollutants

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ABSTRACT

One of the main problems of landfills, as the most common disposal method of municipal solid waste, is leachate's adverse effects on the environment. Leachate treatment to acceptable standards is considered as the best solution for pollution reduction. In this study, the effectiveness of ozonation is investigated in reducing the leachate pollution of the Aradkooh disposal center before and after coagulation and flocculation. The efficacy of this method is determined by investigating total suspended solids (TSS), the chemical oxygen demand (COD), pH, and subsequent jar test with two coagulants, that is, ferric chloride and poly aluminum chloride (PACl) with a coagulant-aid, polyelectrolyte. Results showed that ferric chloride with a dosage of 1 g/L at pH = 11 had better efficiency rather than poly aluminum chloride (PACl), removing 49.8% of COD and 55.6% of TSS. Ozonation was performed best at pH = 9 and the optimal dosage of 6.42 g/min for 120 min. Ozonation after coagulation–flocculation of COD and TSS removal efficiency was about 75% and 78% at the optimal pH of 9 with a dosage of 6.42 g/min ozone, respectively. In contrast, this removal efficiency was 71% and 76.7% for COD and TSS in ozonation and then the coagulation–flocculation process. The result indicated that ozonation after the coagulation–flocculation unit had better performances in COD and TSS removal, and the efficiency was more comparable to the combination of ozonation before the coagulation–flocculation process.

Keywords: Leachate; Coagulation–flocculation; Ozonation; Ferric chloride

1. Introduction

Garbage is the primary source of environmental degradation and pollution. If garbage is not buried in principle, given that 60%–70% is organic matter, it will produce greenhouse and destructive environmental gases through the decomposition of the waste by anaerobic microorganisms and fermentation [1]. Various methods are utilized for purifying and controlling the pollution of leachate, one of the waste products. Mature landfills have leachates with a high content of ammonium (NH^{4+}) that are weakly biodegradable (its BOD_5/COD ratio is low), and the fraction of large organic molecules and refractory material like fulvic and humic acids are high in such leachates [2,3]. Biological treatment does not apply to this kind of leachate. Many other treatment methods, including electrochemical oxidation [4], coagulation and flocculation [5,6–8], chemical precipitation and adsorption by activated carbon [9], a combination of chemical oxidation, advanced oxidation [2], ozonation [11–13], combined ozonation, Fenton, and biodegradation, can be used to degrade the organic matter [14]. Since the leachate consists of many different elements, it is hard to assess the impact of each constituent on the environment. Colloidal particles and the organic compounds

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are typically eliminated through coagulation and flocculation processes. Since these two processes consume a high amount of chemicals, they are known to be expensive methods; other disadvantages are their pH sensitivity, sludge production, and the processing and sludge disposal cost. In recent two decades, AOPs have been used for color elimination and organic load reduction; they also can enhance the biodegradation of recalcitrant pollutants of mature leachate [3,15,16]. Many hydroxyl groups (OH^-) and free radicals are produced in these processes. A single oxidant like ozone (O_3) or a mixture of strong oxidants can produce hydroxyl radicals. One of the suggested means of landfill leachate treatment is using ozone [17]; it can be used in any of the three phases of pretreatment, intermediate treatment, and the final treatment [18]. The primary purpose of the pre-ozonation step is to decompose the large organic molecules [19] for improving the subsequent phases, such as biodegradation or activated carbon adsorption [20]. Ozone has other applications in color and odor removal, coagulation [21], and elimination of chemical oxygen demand (COD) of leachates; it also prevents the generation of associated sludges. Ozone ($pH < 6$) acts as a robust oxidizer and can selectively react with organic contaminants like aromatics [22,23]. One of the advanced processes for the oxidation of landfill leachate is using ozone or its combination with other oxidants in alkaline conditions [24,25]. Despite the high effectiveness of AOPs in the elimination of refractory organic pollutants, they might be costly if used as the sole treatment process. A feasible and reliable way of completing the oxidation of refractory compounds is to transform the initial bio-recalcitrant compounds to the intermediates readily biodegradable and then to oxidize them to water and biomass in the next step [26]. This research aims to investigate the ozonation process impact in decreasing the content of pollutants in leachate before and after the coagulation. Some similar researches are: Taghipoor [27] investigated the combined coagulation–ozonation system on new leachate in Tabriz. Consequently, the application of coagulation–flocculation, and ozonation together caused the COD and total suspended solids (TSS) reduction of 68% and 58% with an initial concentration of COD equal to 61,000 mg/L, respectively. Calli et al. [28] examined the ozonation of leachate in Turkey. They concluded that the addition of 510 g/L of ozone at pH = 9 caused COD removal of 85% with initial COD concentration equal to 4,047 mg/L. Monje-Ramirez et al. [12] performed an investigation on leachate treatment by coagulation and ozonation in Mexico. They obtained COD removal of 87% with an initial value of 4,777 mg/L by simultaneous addition of 10×10^{-2} g/L of ozone and 515 g/L of iron sulfate coagulant to leachate at pH = 4–5 [29]. They concluded that the simultaneous use of coagulation and ozone had a greater impact on the removal of organic materials rather than the usage of each one alone [30].

2. Materials and methods

All materials in the research were prepared by Merck, Germany, with a laboratory grade. The leachate was taken from the Kahrizak landfill; the leachate specifications of the study area are presented in Table 1. The instruments of this study included a pH meter of model 20. Basic manufactured by Crison Co., (Germany), six-chamber device manufactured by chemistry Zagros Co., (Iran), Genhardt 6-cell light, COD, Turb 550 IR-turbidity meter manufactured by WTW Co., (Germany), COG-5S ozone generator system manufactured by ARDA Co., (France), producing ozone at a rate of 5 g/h that transforms the entrance oxygen O_2 into ozone, and 3-F7-O_2 generator device manufactured by the Chinese YUYUE Co., (China), generating oxygen at a rate of 2.14–10.7 g/min with a purity of 90%. The samples were collected in a 5-L container and carried to the Environmental Laboratory of Tehran Science and Research Branch. The samples were kept in a refrigerator at 4°C to experiment. To avoid any changes in the quality characteristics of samples before the experiment, they were stirred again. The experiments were performed on leachate under the procedures of Standard Methods for the examination of water and wastewater [31].

Table 1
Qualitative characteristics of Aradkooh city waste leachate

Parameters	Raw leachate
COD, ppm	3,200
BOD, ppm	14,800
TSS, ppm	15,400
Turbidity, NTU	>1,000
pH	7.25
Pb, ppm	1.65
Cd, ppm	<0.1

The coagulating tests were performed on raw leachate samples separately to determine the optimum conditions of coagulation by coagulants (ferric chloride and poly aluminum chloride). Coagulation tests were performed by a jar test instrument. The standard jar test method is one of the best methods to determine the amount of required coagulant and the best pH for optimal performance of that matter to treat the water and wastewater. First, the initial experiments were performed on raw samples. On the next stage, the coagulation and flocculation processes were performed by the two coagulants, ferric chloride and poly aluminum chloride. First, ferric chloride was added to the samples at pH = 7, 5, 11, 9, 3, and 1 with a fixed dose of 1,200 mg/L, and the coagulation process was performed for 2 min under rapid mixing at 150 rpm, 20 min under slow mixing at 30 rpm, and 30 min under the settlement. Then, the samples were taken from the supernatant, then COD and turbidity tests were performed; according to the results, the optimum pH was determined for coagulant function.

Poly aluminum chloride was added to the samples at pH of about 11, 9, 7, 5, 3, and 1 at a constant PACl dose of about 1,000 mg/L. Then, the coagulation process was done. COD and turbidity tests were performed on the supernatant of samples, and the best pH was determined for the coagulant function. The 1 N sulfuric acid and soda solutions were used to adjust the pH of samples.

After determining the optimal pH for both coagulants, the dosage of 50; 100; 250; 500; 750; 1,000; and 1,500 mg/L of the coagulants, ferric chloride, and PACl were used at this optimal pH to achieve the best dose for the best pH. TSS, COD, and turbidity tests were carried out on the supernatant of the samples. To determine the most appropriate concentration of coagulant-aid, the polyelectrolyte at the concentrations of 0.1, 0.2, 0.5, 1, 1.5, and 2 mg/L was used with two main coagulants with the determined optimal pH and dose. After the jar test, the parameters of TSS, COD, and turbidity were measured to determine the best concentration of coagulant-aid.

Ozone was added to the wastewater sample after determining the best conditions in terms of coagulant type and concentration, the coagulant- aid, pH, and after determining the removal efficiency of the wastewater qualitative parameters. After the coagulation and flocculation processes, the ozone function was examined, then the best time and concentration were determined to reduce the wastewater qualitative parameters. At this stage, ferric chloride was used as a superior coagulant as it removes a higher percentage of COD compared to PACl.

In order to determine the equilibrium time of ozonation, first, the leachate samples were under the coagulation process by ferric chloride coagulant and coagulant-aid of polyelectrolyte with optimal pH and concentration of ferric chloride. Then, the above samples were exposed to a constant dose of ozone at 15, 30, 45, 60, 90, 120, and 180 min. After ozonation, the parameters were measured, and the optimized balance time of ozonation was determined (i.e., the most appropriate time in which maximum COD and TSS removal were done). On the next step, to determine the effective dose of ozone, the leachate samples of garbage were exposed to ozone at three concentrations of 2.14, 6.42, and 10.7 g/min, and its optimal equilibrium time after coagulation with ferric chloride and polyelectrolyte. After ozonation, the remaining COD and TSS were identified. The optimal dose of ozone was determined according to the maximum COD and TSS removal efficiency.

On the ozonation stage, ozone was added to the raw leachate of waste, then ozone best contact time, best concentration, and pH were determined to reduce the qualitative parameters of leachate. To determine the balance time of ozonation on the raw leachate, raw leachate samples were exposed to ozone at the leachate pH and constant concentrations of 6.42 g/min at the exposure time range of 15, 30, 45, 60, 90, 120, and 180 min. Qualitative experiments were performed on ozonized samples after the above times, and the optimal equilibrium time (optimal exposure time of ozone) was determined, that is, the most appropriate time in which maximum TSS and COD removal was done. Besides, to determine the effective dose of ozone, the raw leachate was in exposure to ozone at concentrations of 2.14, 6.42, and 10.7 g/min, besides the optimum balance time. After ozonation, the optimal ozone dose was determined according to the maximum COD and TSS removal. In the next step, to determine the optimal pH of the sample in ozonation, first, the initial pH of raw leachate samples was measured by pH meter, and then pH of samples was set by one normal soda and one normal sulfuric acid in the range of 3, 5, 7, 9, and 11. These samples were ozonized at the equilibrium time of 120 min and with the ozone concentration of 6.42 g/min. After ozonation, the parameters were measured to identify the impact of the pH solution on the ozonation performance and also that of effective pH on the COD and TSS removal. Jar test experiments were done on the ozonation of samples with superior coagulants, namely ferric chloride at various concentrations and different pH after determining the best equilibrium time, ozone concentration, and suitable pH for the ozonation. Then, the best concentration of the coagulant and suitable pH were determined for the performance of this matter's best amount.

First, the coagulation and flocculation process was performed on ozonized samples with superior coagulants at pH of 3, 5, 7, 9, and 11 with a constant dose of 1,000 mg/L. The pH samples were adjusted by 1 N soda and 1 N sulfuric acid. Then, samples were taken from the jar container of supernatants, then COD, TSS, and turbidity tests were conducted to determine the optimum pH for coagulant function. After determining the optimal pH for ferric chloride, the concentrations of 50; 100; 250; 500; 750; and 1,000 mg/L were used at this optimal pH to obtain the best concentration of coagulant for the best pH. TSS, COD, and turbidity tests were carried out on the supernatant samples in a jar container.

All tests on the leachate are based on the Standard Methods for the Examination of Water and Wastewater, 22nd ed., the measurement method of COD and B-5220 is based on this book. The reason for choosing this method is its feasibility to assess different types of samples. pH is the acidity or alkalinity of the solution measured by pH meter. TSS is the total suspended solids of leachate measured by the D-2540 standard method. To determine the turbidity of water and wastewater, the intensity of scattered light of a source is reduced by suspended particles of the sample, and it deviates. The intensity of scattered light is measured by an instrument. The measurement unit of turbidity is NTU. Excel software was used to analyze the results and to draw the graphs.

3. Result and discussion

The coagulants of $FeCl_3$ and PACl were compared to determine the optimal pH on the COD and TSS removal (Fig. 1); the coagulant dose was 1,200 and 1,000 mg/L, respectively.

According to Fig. 1, the pH had a great effect on the removal of organic leachate charges. The maximum removal rate of COD and TSS was obtained for ferric chloride at a pH of 11 (removal efficiency of 37.2% and 42%, respectively) and poly aluminum chloride at a pH of 5 (removal efficiency of 30.4% and 36.6%, respectively). Alkaline pH, increased iron solubility leads to an increase in their concentration in solution. In ferric chloride, the formation speed of flocs increases due to the rapid reaction of the iron ion with water hydroxide ion and slight solubility factor of hydroxide, thus iron composes the insoluble deposit of $Fe(OH)_3$, and the coagulation is done more rapid and more complete. Simultaneous with the formation of deposit, the colloidal particles of water are also trapped in the layers of them and have been deposited with them. This process forms the basis of the particles trap mechanism in deposit and reduces COD and TSS. Therefore, the organic matter removal at a dose of 1,000 mg/L can be due to the phenomenon of particles trapping in the deposit. Rivas et al. [10] investigated the leachate coagulation and flocculation. Ferric chloride was used for coagulation and flocculation, and its pH became lower than typical pH (7–8) by acidification of the sample before coagulation. The results were as follows: the optimal dose of 1,500 mg/L (0/01 M) of ferric chloride (Fe^{3+}) at the optimal pH of 3.5 had COD removal efficiency of 40%. In this way, the removal mechanism is irregular nuclei formation of metal hydroxide due to reduced pH and organic matter absorption on the surface of the deposits and, finally, their settlement. Our study is consistent with Taghipoor [27] study carried out on fresh leachate by coagulation and flocculation process as a pretreatment before ozonation Tehran University. He compared Ferric chloride and aluminum and reached to COD and TSS removal efficiency of 34% and 54%, respectively, by addition of 1 g/L of ferric chloride to the raw leachate at pH = 10. He found that ferric chloride is more effective than alum in the leachate parameters removal. COD removal efficiency reduction compared to our research is due to a more leachate organic charge compared to our study. First, PACl is absorbed to positively charged particles by the formation of diverse aluminum, neutralizing the charge. On the other hand, insoluble colloids aluminum hydroxide has been formed by continuance increase of the coagulant dose so that the colloids are unstable, and TSS are reduced by depositing them. TSS and turbidity reduction is also decreased COD. In Lin and Chang's [32] study about leachate treatment, poly aluminum chloride and a polymer coagulant-aid were used for the coagulation and flocculation process. The applied polymer ratio was 10 wt.% of the main coagulant. Optimum pH was obtained equal to 5 or lesser for coagulation and flocculation, and COD removal efficiency was 55%, which is appropriate in operation given to the simplicity of this process. The optimum pH is consistent with our optimum pH.

In Fig. 2, the effect of different concentrations of coagulants (ferric chloride and PACl) is shown without a combination with a coagulant-aid in the leachate parameters removal at the optimal pH.

Fig. 2a indicates that increased ferric chloride increases the removal efficiency of organic charge and TSS. These productivity gains continued up to the concentration of 1,000 mg/L (removal rate of 43.3% for COD and 49.2% for TSS) and then started to decline. Therefore, the optimal dose of $FeCl_3$ was considered 1,000 mg/L. An increased coagulant dose, especially the ferric salts, is suitable to remove the colloidal particles and turbidity due to the use of alkaline, but if the ferric chloride dose is increased too much, iron concentration is increased in the solution. When metal salts, such as ferric chloride, are added to water at high concentrations, the deposit of insoluble metal hydroxides ($Fe(OH)_3$) is produced immediately due to the reaction with water. Further, Fig. 2 shows the difference in TSS reduction efficiency, which is more than COD at higher coagulant concentrations. As Fig. 2b shows, the increased PACl increases the reduction rate of organic charge and turbidity, and this upward trend continues to the concentrations up to 750 mg/L; thus, the maximum reduction efficiency of COD and TSS is observed, which is 38.8% and 42.4%, respectively. Later, a slight reduction in efficiency has occurred. However, PACl performance at the optimum concentration of 750 mg/L is lower than the ferric chloride performance at the same concentration (43.3%). It could be concluded that poly aluminum chloride often reduces the coagulant dosage and produces the concerned salts due to high charging density. Ntampou et al. [33] study the

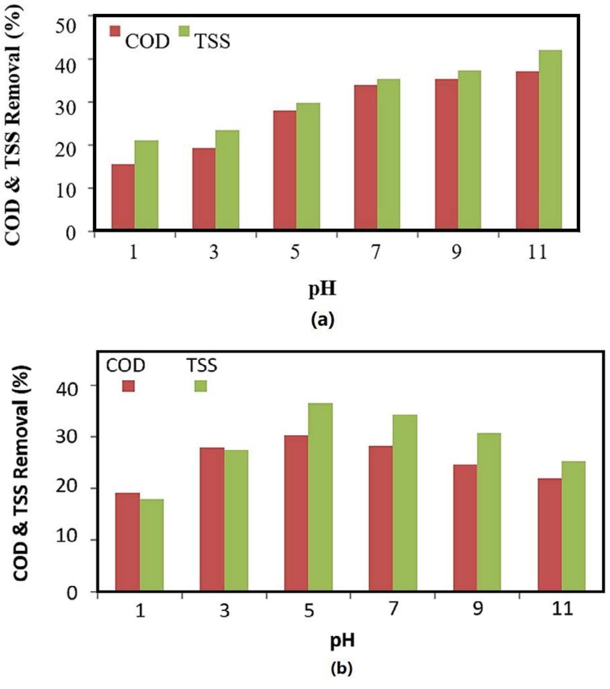


Fig. 1. TSS and COD removal rate by (a) a constant ferric chloride dose of 1,200 mg/L at different pH and (b) a constant PACl dose of 1,000 mg/L at different pH.

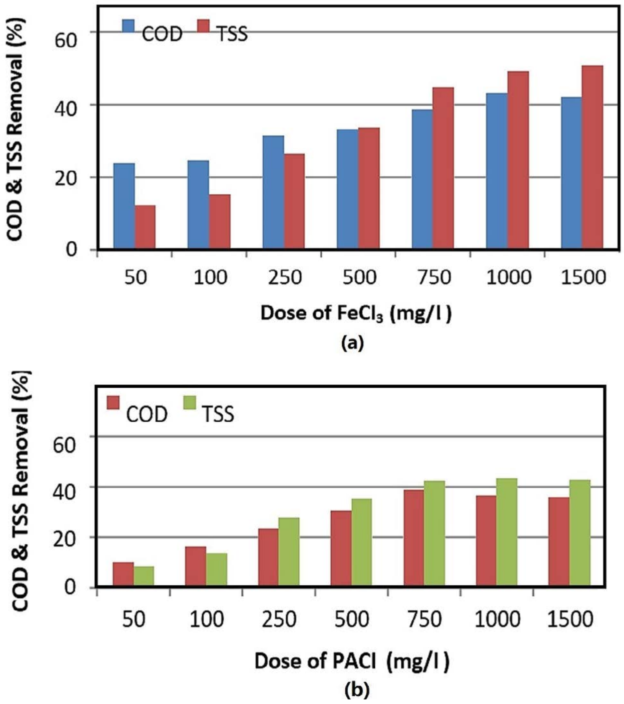


Fig. 2. TSS and COD removal percent (a) at different concentrations of ferric chloride at pH = 11 without coagulant-aid and (b) at various concentrations of PACl at pH = 5 without coagulant-aid.

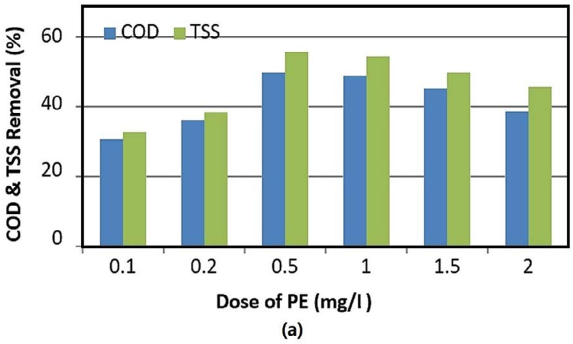
effective parameters were investigated in poly aluminum chloride and iron compounds in COD and color removal of leachate. Based on these results, the optimum pH range for the COD removal by PACl is 5.5, and under these conditions, COD removal efficiency of this leachate was achieved to 62% using 11 mM/L of poly aluminum chloride.

Fig. 3 indicates the effect of coagulant-aid at different concentrations on the performance of both coagulants, $FeCl_3$ and PACl, in the removal of leachate COD and TSS at optimum pH and concentration.

As observed in the above figures, by adding the coagulant-aid (with a concentration of 0.1–2 mg/L), the leachate parameter removal increased by both coagulants, and the diagram became ascending. Given the above figures, in ferric chloride, at polyelectrolyte concentrations of 0.5 mg/L, the highest percentage of COD and TSS is observed at 49.8% and 6.55%, respectively. Moreover, in PACl, maximize removal efficiency at a concentration of 1 mg/L polyelectrolyte is obtained for COD and TSS with 43.7% and 48%, respectively.

In total, in Fig. 4, the coagulants generally were compared with each other in terms of the reduction efficiency of organic charge and leachate suspended solids in combination with a coagulant-aid and without it.

As indicated in Fig. 4, both ferric chloride and PACl have higher yields in combination with coagulant-aid. Ferric chloride removal efficiency was higher than PACl in all conditions of removing COD and TSS, and it is better in coagulation and flocculation in combination with polyelectrolyte as a coagulant-aid. The addition of 0.5 g/L of polyelectrolyte is very effective in improving the process efficiency.



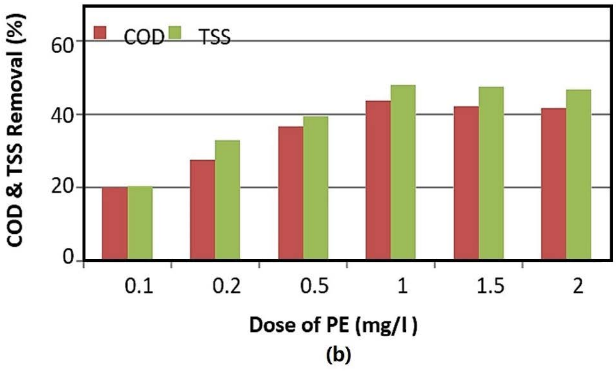


Fig. 3. TSS and COD removal percentage at different concentrations of polyelectrolyte at (a) pH = 11 and the ferric chloride concentration of 1,000 mg/L and (b) pH = 5 and poly aluminum chloride concentration of 750 mg/L.

According to the results, the ferric chloride, as a superior coagulant, was used in this stage. First, coagulation and flocculation were carried out in optimal coagulation conditions. The ozonation process was done on the surface wastewater of jar containers to obtain optimum balance and concentration of ozone. Fig. 5 reflects the efficiency of different time of ozonation, and thus shows the determination of the optimal balance time of ozonation in leachate contaminant parameters removal after coagulation and flocculation process with a superior coagulant ($FeCl_3$).

As seen in the above figures, in investigated time (180–15 min), increasing ozonation time reduces COD and TSS levels, and the curve becomes ascending. The maximum

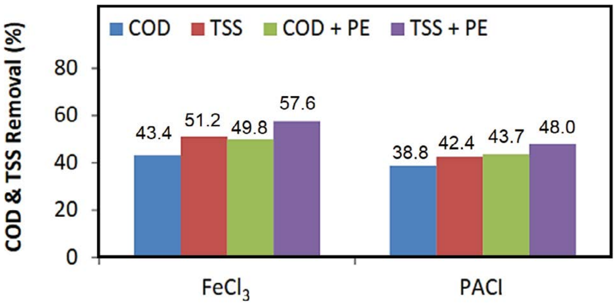
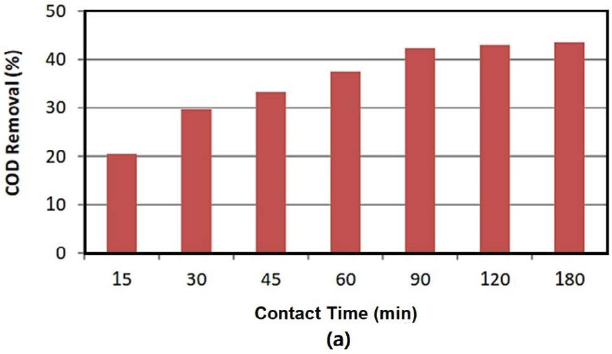


Fig. 4. Comparison of two coagulants in combination with a coagulant-aid and without it, in COD and TSS removal at optimum conditions.



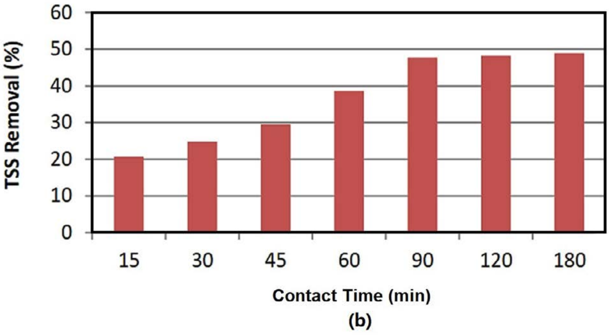


Fig. 5. (a) COD removal percentage and (b) TSS removal percentage at different times of exposure to ozone after coagulation.

reduction in parameters occurs in an exposure time of 90 min, which is 42.4% and 47.7% for COD and TSS removal, respectively. After the exposure time of 90 min, leachate parameters reduction is almost constant, and increased removal efficiency is very low and negligible compared with the exposure time of 90 min. Therefore, the optimal balance ozonation time is determined after 90 min coagulation and flocculation.

In Fig. 6, the effect of different concentrations of exposure ozone is shown in removing the parameters of leachate pollutants after coagulation and flocculation.

In Fig. 7, with a range of changes in ozone concentration (2.14–10.7 g/min), we found that the concentration of 6.42 g/min has maximum removal of COD and TSS (36.5% and 38.3%, respectively). Then, the concentration efficiency decreases significantly, which may be due to the dilution of the entrance ozone caused by increasing its capacity. Given the above figure, the best concentration of ozone is 6.42 g/min, causing the maximum removal of COD and TSS. In this regard, it has been reported that higher ozone dosage could have an inhibitory effect on the generation of hydroxyl radical through Eq. (1). In this way, ozone can react with hydroxyl radical and produces hydroperoxyl radicals with weaker reactivity compared to hydroxyl radical [34]. Hence, this reaction might suppress the COD and TOC removals in ozonation after coagulation.

$$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \qquad (1)$$

In research in Taiwan, about 72% of COD was removed in the combination method of coagulation–flocculation (by ferric chloride at the rate of 900 mg/L) and ozonation (at pH = 8.6 and dosage of 1.2 g/L). They found that coagulation and flocculation removed a variety of large molecules in the leachate to achieve high efficiency in the removal of organic substances combined with ozone-based advanced treatment processes. The difference between consumed ozone of our study and this study can be due to the mentioned reason, that is, the coagulation process operates properly due to lower hard-decomposable compounds as well as organic leachate charges and reduces the organic charge; thus, the amount of consumed ozone is reduced. The COD removal efficiency is suitable and almost equal in both studies [35]. According to our results, organic charge reduction of 71% is suitable at two processes (coagulation–flocculation and ozonation); however, the continuation of the treatment process is difficult as the residual material of the sample is severely resistant to treatment and cannot be treated. They can be treated only by a high dosage of ozonation or by using a suitable compound of other treatment methods. If we only want to use the mentioned processes, we should apply a higher amount of ozone and coagulant that is not economically justified.

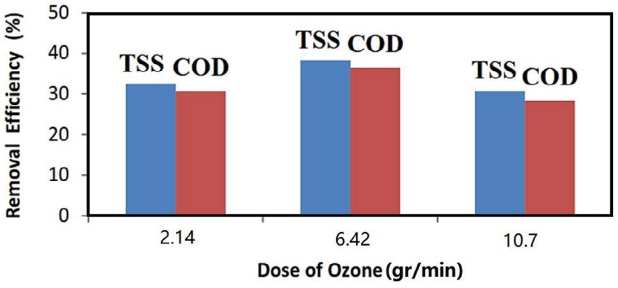


Fig. 6. COD and TSS removal efficiency at different concentrations of ozone after the coagulation.

The above figure shows the descending trend of COD and TSS coincides with an increase of exposure time. In the early stages, the reaction of COD is rapidly decreased so that it reached 24.5% in the first 30 min; however, during oxidation, the compounds decomposed rapidly are removed, and the reaction rate becomes slower by increasing the reaction duration. This is due to the lower reactivity of intermediate products produced during the early time of ozonation. The highest removal efficiency of COD and TSS was obtained at the exposure time of 120 min, about 41% and 45%, respectively. The curve shows no significant descending later than 120 min, indicating complete oxidation of O_3 in COD removal. After that time, increasing exposure to O_3 time does not affect COD and TSS removal. The exposure time of 3 h was removed at COD of about 42%. However, due to the lower advantage compared to the exposure time of 2 h and saving energy, the balance time of 2 h was chosen as the optimum balance (equilibrium) time of ozonation.

Fig. 8 shows the effect of different ozone concentrations in reducing COD and TSS of raw leachate in the equilibrium time of 120 min.

According to Fig. 8 and the removal percentage of each ozone concentration, it was observed that ozone dilution at low levels (6.42 g/min) resulted in a slight increase in COD

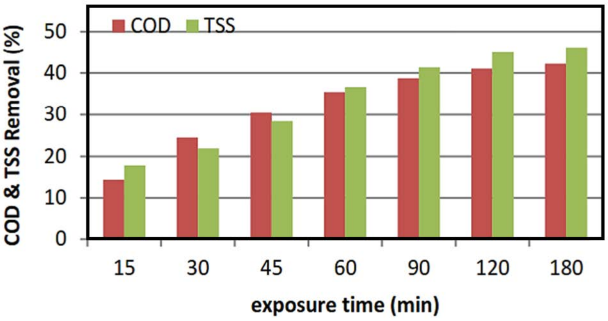


Fig. 7. Effect of ozonation on the removal of COD and TSS of the raw leachate.

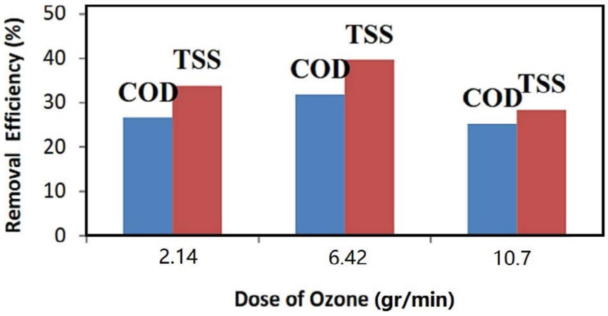


Fig. 8. COD and TSS removal efficiency at various times of ozonation at initial pH.

removal efficiency. Of course, the dilution of ozone (5 L/min) and its weight percentage reduction decreases COD removal efficiency as the amount of generated ozone is severely reduced per volume unit by increasing the gas flow rate.

In Fig. 9a, the effects of leachate pH are shown on the ozonation process. The investigation of the pH effect is performed at exposure time and the optimum concentration (120 min and 6.42 g/min).

According to Fig. 9a, it was found when pH is in the range of 9–8, in the presence of OH ions, ozone is quickly decomposed to highly reactive radicals of $OH^{\bullet}$. In an alkaline environment, many organic compounds that oxidize slowly by ozone can quickly oxidize by hydroxyl radicals. This phenomenon shows that an alkaline environment is a key parameter for enhancing the effect of ozonation. However, if pH is more than 9, bicarbonate ions convert to carbonate ions, which are the consumer of $OH^{\bullet}$ radicals and reduce the kinetics speed of the oxidation reaction.

At this stage, the raw leachate, obtained under optimum conditions, was ozonized. Then, the wastewater was coagulated with superior coagulant-aid (ferric chloride), and jar test results were obtained.

Fig. 9b shows the effect of pH changes of ozonized leachate on COD and TSS removal efficiency at the constant concentration of ferric chloride about 1,000 mg/L. according to Fig. 9b, the removal efficiency of COD and TSS is increased by increasing the ozonized leachate pH, and the curve is became ascending. The best removal efficiency was at a pH of 11, at a rate of 53.5% of COD and 52% of TSS. The above figure shows that TSS removal efficiency is more than COD at initial pH (5 and 3); however, the COD removal percentage becomes more than TSS at pH = 7 and more. Generally, a pH of 11 was selected as the best pH for optimal performance. Given to leachate pH changes at different times of ozonation, this study indicates that the initial leachate pH is increased by increased ozonation time; for example, it has increased from 7.7 to 9.8. The longer the ozonation time, the more sensible the pH increase, but if the ozonation time is slow, pH changes will not be much due to the creation of fewer side ozonation acidic products. Another reason for increased pH may be the discharge of carbon dioxide or volatile fatty acids from the reaction environment. In the study of some researchers, pH reduction was also observed due to the formation of secondary products with acidic nature, which is mainly oxalic acid [27]. Our results are almost consistent with Wang et al. [36] results on the leachate ozonation in Canada. They reached to COD efficiency of 70% at pH = 8.3 and an ozone dose of 3.6 g/L. One of the reasons for the relatively higher COD efficiency of leachate could be the lesser COD of the considered leachate. Based on the results, a pH of 9 is emphasized for ozonation because, in an alkaline environment, ozone decomposes to free radicals and, subsequently, produces $OH^{\bullet}$, leading to mineral material. Thus, the degradability of treated wastewater has been exacerbated before another treatment.

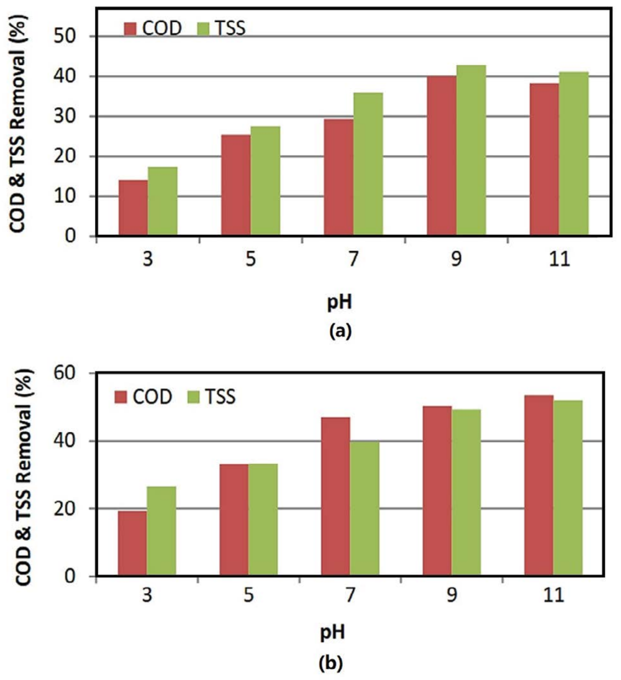


Fig. 9. Efficacy level of pH on COD and TSS removal at (a) 120 min of duration and ozone dose of 6.42 g/min (b) at constant ferric chloride dose of 1,000 mg/L at different pH.

In Fig. 10, the concentration changes impact of ferric chloride coagulant is shown on the removal efficiency of ozonized leachate contaminant parameters at the optimum pH of 11.

As indicated in Fig. 10, the curve is ascending from the concentration of 50–500 mg/L, and the maximum removal efficiency (59% of COD and 60% of TSS) is obtained at the concentration of 500 mg/L. Then, the removal efficiency has been stabilized, and there is no significant increase. Hence, the optimal dose of $FeCl_3$ for the COD and TSS removal of ozonized leachate is considered equal to 500 mg/L. The reason for the effective dose of coagulant reduction may be the electrical load reduction of leachate organic particles due to the preliminary ozonation of leachate. As a result, a small amount of coagulant is required for the effective removal of organic leachate materials. The results show that the optimum value of ferric chloride is reduced from 1,000 to 500 mg/L. It is a good result as the consumption of coagulant is reduced; thus, less sludge is produced, the sludge management costs are reduced, and higher efficiency is obtained in organic charge.

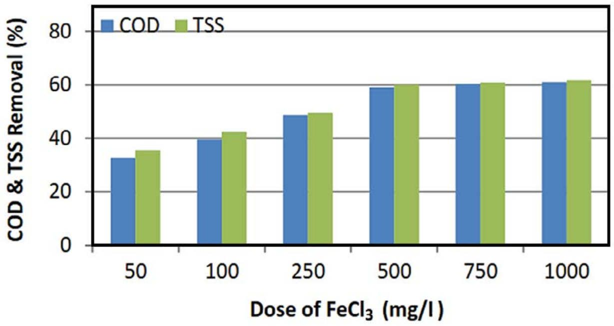


Fig. 10. COD and TSS removal percentage at different ferric chloride concentrations at pH = 11.

In Fig. 11, the final results of ozonation are shown before and after the coagulation–flocculation as well as the results of coagulation–flocculation itself.

As deduced from Fig. 11, the combination of two treatment methods is more effective than either of them. While leachate ozonation has a relatively good efficiency in COD and TSS removal after coagulation and flocculation, the pre-ozonation was more effective than it as a result of the conversion of non-biodegradable materials to biodegradable compounds, and it allocated the highest removal efficiency of organic matter and TSS of leachate [37]. In the case of coagulation–flocculation, as previously mentioned, among two coagulants of $FeCl_3$ and PACl, ferric chloride has a higher efficiency in COD and TSS removal compared to PACl. Ferric chloride has COD and TSS removal efficiency of about 49.8% and 55.6% to treat this leachate, respectively. The results are shown generally when the ozonation is done after coagulation and flocculation, coagulation and flocculation units have more ability to remove pollutants from the leachate compared to the combination of ozonation–coagulation and flocculation. In this research, COD removal efficiency was 75.8%, which is slightly improved compared to the former stage, which was 71%. The reason for it may be the electrical charge of leachate organic particles due to the initial ozonation of leachate. The optimum value of ferric chloride is reduced from 1,000 to 500 mg/L. It is a good result since the consumption of coagulant is reduced; thus, less sludge is produced, the sludge management costs are reduced, and higher efficiency is obtained in organic charge. In a study conducted on leachate in Greece, the researchers found that ozonation and following coagulation–flocculation cannot reduce COD of leachate to less than 200 mg/L, the wastewater output standard. The COD removal efficiency is about 78% at 4 mM concentration of ferric chloride and a dose of 2 g/h of ozone that would result in consumption coagulant dose reduction. This research is consistent with our study in terms of removal efficiency, coagulant dose reduction, and effective ozone dose. In that study, results show that the coagulation–flocculation/ozonation method is more effective than pre-ozonation [33]. Due to the leachate complex nature, high doses of ozone are not enough to treat it, and other treatment methods are needed to improve COD removal of leachate using the coagulation process as a pretreatment or varnishing stage before or after the ozonation. In the case of ozonation, pH adjustment effects on the coagulation by changing the electrostatic reaction between coagulants and organic molecules. The results indicate that a combination of coagulation–flocculation and ozonation could be considered as a combined approach for leachate treatment.

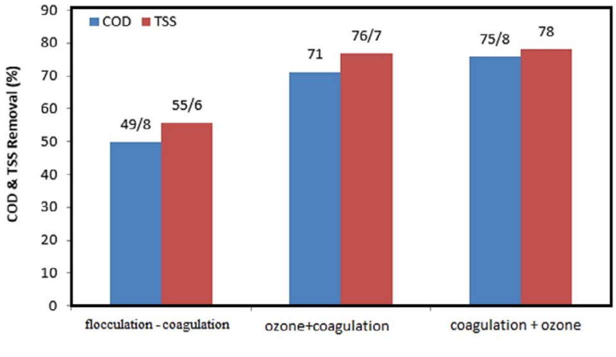


Fig. 11. Final results of ozonation before and after the coagulation and the coagulation itself in COD and TSS removal.

4. Conclusion

In this research, ferric chloride with a dosage of 1 g/L at pH = 11 had better efficiency than poly aluminum chloride (PACl) by being able to remove 49.8% of COD and 55.6% of TSS. Ozonation was performed at pH = 9 and the optimal dosage of 6.42 g/min for 120 min, and the wastewater was tested by ferric chloride under the jar test in the coagulation stage; it was found that ferric chloride could remove 59% of COD and 60% of TSS at optimum pH of 11 with a dosage of 500 mg/L. Ozonation after coagulation/flocculation of COD and TSS removal efficiency was about 75% and 78% at the optimal pH of 9 with a dosage of 6.42 g/min ozone respectively; whereas, this removal efficiency was 71% and 76.7% for COD and TSS in ozonation and then coagulation and flocculation process, respectively. As can be seen, the present study introduces the ozonation after coagulation/flocculation as an effective way for leachate treatment (COD and TSS removal). However, leachate characteristics, such as the nature of the solid waste and the concentration of organic contaminants to be removed, available purification efficiency, waste disposal options, the capability of process application, and economic factors, are key factors to be considered in the selection of the most appropriate process for leachate treatment.

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