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COMPARISON OF COAGULATION-FLOCCULATION, OZONATION AND FENTON PROCESSES FOR THE TREATMENT OF MUNICIPAL SANITARY LANDFILL LEACHATE

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Abstract

This experimental study was conducted to investigate the effect of coagulation-flocculation (CF), ozonation (O), coagulation-flocculation after ozonation (O/CF), ozonation after coagulation-flocculation (CF/O) and Fenton processes on the Tekirdağ Province Municipal Sanitary Landfill leachate treatment in the city of Tekirdağ. Also, the effects of $Al_2(SO_4)_3$ and $FeCl_3$ dosages on coagulation-flocculation process, oxidation time on ozonation process and H_2O_2 and $FeSO_4$ dosages on Fenton process in the removal of chemical oxygen demand (COD) were studied. The following parameters were analyzed for characterization study: pH, conductivity, COD, dissolved COD, total suspended solids (TSS), NH_4-N and alkalinity. The study shows that in CF, $FeCl_3$ was effective for all three samples in terms of COD removal and the removal efficiencies for Sample 1, 2 and 3 were 40.5%, 46.8% and 55.2%, respectively. The amount of ozone applied in ozonation process was 1 g O_3 per hour and after 120 minutes ozonation the COD removal efficiencies were insufficient and 14.5%, 24.4% and 31.8%, respectively. In all treatment methods the best removal efficiencies were obtained as 80.2%, 79.6% and 78.8%, respectively by Fenton process. The COD values for Samples 1, 2 and 3 after the Fenton process were found to be 509, 456 and 397 mg/L, respectively. It was also determined that the removal efficiencies of coagulation-flocculation process which applied after ozonation were 70.4%, 74.4% and 67.7%, respectively and close to the Fenton process.

Key words: coagulation-flocculation, fenton, landfill leachate, ozonation

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1. Introduction

Disposal of solid waste by landfills is still one of the most common options worldwide for municipal solid waste management (Di Maria and Sisani, 2017). Landfill leachate is the result of percolated rainwater and moisture passing through the layers of wastes in landfills (Koshy et al., 2007). Various chemical and biological reactions take place during the filtration of precipitation water falling into the solid waste landfill area. As a result, inorganic and organic compounds transfer from waste to leachate. The amount of leachate that will occur in the landfill area varies depending on the amount of rain and evaporation in the region and the compression during the filling (Trankler et al., 2005). Furthermore, the amount of leachate formed in landfills depends on the composition of the waste, the age of the landfill, the size of the area, the climatic conditions and the degree of permeability of the last cover layer (El-Fadel et al., 2002).

The physical, chemical and microbiological contents of the leachate originating from the landfills are quite complex and variable. The content of leachate is affected by environmental conditions, reactions occurring at the landfill, and the dynamics of the decomposition process occurring at the site (El-Fadel et al., 2002; Kjeldsen et al., 2002). Landfill

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leachate is usually dark in color, with very bad smell, high organic and inorganic load bearing wastewater containing a wide variety of pollutants (Yao, 2017). The composition of leachate depend on the content of the stored wastes and the age of the landfill area.. Leachate from young areas contains more pollutants than mature landfills (Goi et al., 2009). Variety groups of pollutants are present in leachate: dissolved organic matters, macro inorganic compounds, inorganic salts, heavy metals, humic compounds, nitrogenous compounds, and microorganisms (Costa et al., 2019; Yao, 2017). Therefore, it is very difficult to treat leachate by conventional methods to meet environmental standards. Combinations between conventional and advanced treatment methods are increasingly being investigated for the removal of pollutants from solid waste leachate. Therefore, a single method cannot be applied for the treatment of these extremely complex and variable wastewater (Costa et al., 2019; Renou et al., 2008; Wiszniowski et al., 2006).

The leachate treatment system must be flexible enough to produce the same quality wastewater despite changes in the leachate. Combinations of physical, chemical and biological methods should be used to achieve such flexibility (Kochany and Lipczynska-Kochany, 2009). Currently, there are various technologies for the treatment of leachate that aim to reach the standards set by the legislation. Various methods can be used in the treatment of leachate: biological processes (activated sludge, aerobic, anaerobic methods, etc.), physico-chemical processes (adsorption, coagulation-flocculation, oxidation, etc.), membrane filtration, advanced oxidation (Fenton, UV/H_2O_2, photo-Fenton, UV/O_3, etc.), and/or natural systems (Costa et al., 2019; Raghab et al., 2013; Renou et al., 2008; Varadarajan et al., 2020; Wiszniowski et al., 2006). Biological treatment methods are generally suitable for the treatment of young leachate (e.g. leachate from storage areas less than 1-2 years). Biological treatment methods are not suitable for the treatment of mature leachate more than 5-10 years age. Therefore, many physicochemical processes are being studied or used for the pre-treatment or complete treatment of mature leachate (Deng, 2007).

Fenton is an important advanced oxidation process used in the treatment of leachate. There are many studies on this subject in the literature (Abbas et al., 2020; Fang et al., 2005; Goi et al., 2009; Kamenev et al., 2002; Rivas et al., 2004; Vilar et al., 2006; Yılmaz et al., 2010). Goi et al. (2009) reported that the Fenton process was effective in the development of biodegradability and COD removal efficiency. In the Fenton process (Fenton, 1894), hydrogen peroxide is added to the wastewater in the presence of Fe salts, and hydroxyl radical which has strong oxidant properties are produced. These species ensure the rapid oxidation of organic materials (Deng and Englehardt, 2006). Fenton process is a multi-stage process that uses hydrogen peroxide (H_2O_2) to produce hydroxyl radicals (•OH) under acidic conditions, catalyzed by Fe^{2+}, in which the organic components are initially oxidized by •OH radicals. After oxidation under acidic conditions, the coagulation-flocculation of the organic substances and the precipitation of the coagulated organic materials in the neutral pH range are provided. When the Fenton process is applied, leachate with COD 93-34.920 mg/L has been shown to provide 30-95% COD removal (Singh et al., 2013). According to a study by Yılmaz et al. (2010), at the results of Fenton process applied to a leachate with initial COD concentration 38200 mg/L, color 3510 mgPtCo/L and pH 7.25, and Fenton conditions pH:3, 2000 mg Fe^{2+}/L and 5000 mg H_2O_2/L concentrations, COD removal efficiency was found as 55.9% and color removal efficiency was found as 89.4%.

Coagulation-flocculation and chemical oxidation processes are also used in order to treat landfill leachate. In the coagulation-flocculation process, which is one of the physicochemical processes, biodegradation of pollutants is not achieved, only phase transfer takes place (Ramos et al., 2019). In the studies, it was found that coagulation-flocculation, which is one of the physicochemical processes, is especially effective in the removal of large molecular weight pollutants in raw leachate (Gau and Chang, 1996; Goi et al., 2009). Coagulation-flocculation is a relatively simple technique that can be successfully used in the pre-treatment or post-treatment of landfills (Ntampou et al., 2006). Coagulation-flocculation is widely used to reduce the content of suspended or colloidal form of organics in water and wastewater (Teresa et al., 2007; Verma et al., 2012). However, since the coagulation-flocculation method cannot provide the biodegradation (oxidation) of organic matter alone, it is very common to use this method with oxidation in the literature (Goi et al., 2009; Monje-Ramirez and Orta de Velásquez, 2004; Ntampou et al., 2006; Wu et al., 2004).

The ozonation process is an attractive alternative for the treatment of leachate, due to the high oxidative power of ozone (Tizaoui et al., 2007). Over the past decade, many chemical treatment processes, including ozonation, have been proposed as an auxiliary approach or alternative for the treatment of leachate (Wu et al., 2004). Ozonation, one of the chemical oxidation processes, is considered a cost-effective approach to remove particularly recalcitrant pollutants and improve the performance of the biological treatment process which to be used later (Gomes et al., 2017; Wang et al., 2019). Recently, among chemical oxidation processes, ozonation is increasingly used as a pre-treatment or a post-treatment for leachate treatment (Goi et al., 2009) Many researchers have investigated the efficiency of ozonation in the treatment of landfill leachate (Fang et al., 2005; Kamenev et al., 2002; Ntampou et al., 2006; Vilar et al., 2006; Wu et al., 2004).

Municipal solid waste landfill is a solution widely used in Turkey for final disposal. In this study, the Fenton process, ozonation (O), coagulation-flocculation (CF), coagulation-flocculation after ozonation (O/CF) and ozonation after coagulation-flocculation (CF/O) of landfill leachate have been studied. The leachate was supplied from Tekirdağ Province Municipal Sanitary Landfill. The leachate was supplied from Tekirdağ Metropolitan Municipality Solid Waste Site. Tekirdağ is also an industrially developed region. In this area, besides municipal wastes, non-hazardous industrial wastes are also disposed of. The most important originality of the study is that it concerns the treatment of leachate from an area where complex waste (municipal and inert industrial wastes) is disposed. It is also the most comprehensive study conducted on the treatment of leachate from this region. Removal efficiencies of chemical oxygen demand (COD) and the effect of operating conditions such as Fenton's reagent dosages, ozonation time and optimum coagulant doses and optimum pH values were investigated. The aim of the study is to compare the effect of O/CF and/or CF/O on COD removal efficiency with the Fenton process, which includes oxidation-coagulation and sedimentation.

2. Materials and method

2.1. Landfill site and leachate characterization

The leachate was supplied from Tekirdağ Province Municipal Sanitary Landfill. This landfill area has been accepting waste since June 2008. At first, only mixed municipal wastes were accepted, and then, since it is the only landfill area in the region, non-hazardous wastes originating from industries have also started to be accepted to the area. The characterization data obtained in a study with this leachate are given in Table 1. The characterization study was carried out by the io Environmental Solutions Research and Development Company (io, 2011). The study was carried out as a solid waste landfill feasibility project. The characterization of the leachate was determined in the dry and rainy periods. As can be seen from Table 1, COD varied between 660-1985 mg/L in rainy seasons and between 2539-5400 mg/L in dry periods. pH ranged between 7.6-8.68 and TKN (Total Kjeldahl Nitrogen) values varied between 59-1236 mg/L.

As can be seen from the Table 1, heavy metal concentrations remained very low in both dry and rainy seasons. In the study done by Yao (2007), a table adapted from Alvarez-Vazquez et al. (2004) regarding the classification of leachate according to its composition is given. According to that table, age of leachate given in our study can be defined as bigger than 10 years age and stabilized in terms of COD, TKN, heavy metals and pH. According to the values given in the study by Costa et al. (2019), who shared a table adapted from Ziyang et al. (2009) and Farquhar (1989), our leachate was between 10-20 years age in terms of COD, between 5-10 years age in terms of TKN and bigger than 20 years age in terms of pH. The reason for these incompatibilities about age of this leachate is thought to be due to the new solid wastes and industrial inert wastes still being stored in this area.

2.2. Characterization of studied leachate samples

Samples to be used in the treatment studies were taken in 20 L acid washed polyethylene bottles. Samples taken from landfill leachate storage tank immediately transported to the laboratory and preserved and stored according to Standard Methods (APHA, 2005). pH and conductivity were determined in situ using appropriate devices; other parameters were determined according to Standard Methods (APHA, 2005). Three different samples were taken for characterization and treatment studies. The following parameters were analyzed: pH, conductivity, chemical oxygen demand (COD), dissolved COD, total suspended solids (TSS), NH_4-N, and alkalinity.

The characterization of the studied leachate samples is given on the Table 1. The characterization obtained in previous study made with this leachate was given in Table 1. As can be seen from Table 1 (io, 2011), heavy metal concentrations in leachate samples taken during rainy and dry periods are at very low levels. For this reason, heavy metal analysis was not performed in the samples used in purification and characterization in this study. As seen from the Table 2, COD is between 1874-2572 mg/L, pH is about 7.8, conductivity is between 10.56-20.1 mS/cm, and alkalinity is between 3814-6300 mg $CaCO_3$/L, NH_4-N is between 51-87 mg/L.

Table 1. Characterization of the landfill leachate in dry and rainy seasons (io, 2011)

Parameter	***Rainy***	***Dry***	***Dry***	***Dry***	***Rainy***	***Rainy***	***Dry***	***Mean±St.Dev.***
COD(mg/L)	660	2590	3070	5400	670	1985	2539	2416.3±1497.4
TSS(mg/L)	25	128	128	2605	35	100	75	442.3±883.7
TKN(mg/L)	59.3	631.5	276.5	1236	289	905	1214	658.8±38.4
T-P(mg/L)	0.37	0.24	2.92	2.78	0.69	3.49	3.03	1.9±1.3
T-Cr(mg/L)	<0.05	<0.05	<0.5	<0.5	<0.5	<0.5	<0.5	-
Cr^{+6}(mg/L)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-
Pb(mg/L)	0.31	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	-
Cd(mg/L)	<0.01	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	-
Cu(mg/L)	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	0.06	-
Zn(mg/L)	1.166	0.52	<0.25	0.96	1.17	2.19	0.03	1.0±0.7
Fe(mg/L)	4.02	5.7	0.37	<0.2	<0.2	1.55	0.98	2.5±2
pH	7.91	7.65	8.68	8.11	8.27	8.27	7.6	8.1±0.4

Table 2. Composition of studied landfill leachate samples

Parameter	*Sample 1*	*Sample 2*	*Sample 3*	*Mean*	*St-Dev*
pH	7.78	7.76	7.85	7.8	0.0
Conductivity (mS/cm)	20.1	19.98	10.56	16.9	4.5
Alkalinity (mg $CaCO_3$/L)	6300	5244	3814	5119.3	1018.7
TSS (mg/L)	380	334	244	319.3	56.5
COD (mg/L)	2572	2238	1874	2228.0	285.0
Dissolved COD (mg/L)	1477	1238	846	1187.0	260.1
NH_4-N (mg/L)	87	76	51	71.3	15.1

According to the study of Costa et al. (2019), the age of this leachate is between 10-20 in terms of COD and TKN and bigger than 20 years age in terms of pH. Similar to the results of the characterization study given in Table 1, differences regarding the age of the leachate were found in this study. This is thought to be due to the fact that new wastes and inert wastes are still being disposed of at the landfill.

2.3. Treatment methods

In the study, Fenton process, ozonation (O), coagulation-flocculation (CF), coagulation-flocculation after ozonation (O/CF) and ozonation after coagulation-flocculation (CF/O) of landfill leachate have been studied. Each set of experiments was made in duplicate for all treatment methods. Taking the mean values of these two sets, removal efficiencies were determined.

- *Fenton process*

The Fenton process experiments were conducted by using the jar test method. In the Fenton experiments H_2O_2 (35% w/w, Merck), $FeSO_4.7H_2O$ (Merck), NaOH and H_2SO_4 (Merck) were used. Experiments were carried out at a constant pH (pH 3) and at room temperature. Various H_2O_2 and $FeSO_4.7H_2O$ dosages have been used to determine optimum conditions for the best COD removal efficiency. H_2O_2 and $FeSO_4$ were used between dosages of 3300-16500 mg/L and 1650–13200 mg/L, respectively, for three samples (these doses were determined after a preliminary study for leachate). For the determination of optimum H_2O_2 dosages in COD removal, $FeSO_4$ was kept constant at 9900 mg/L and H_2O_2 dosages had been changed between 3300–16500 mg/L. After this study, optimum H_2O_2 was found and then optimum $FeSO_4$ study was performed. In this study, $FeSO_4$ doses were changed between 1650-13200 mg/L at optimum H_2O_2 doses. Firstly, each beaker was filled with 500 mL of the wastewater sample, and the pH was adjusted to 3 with 1 N H_2SO_4 solution. Then FeSO4.7H2O and H_2O_2 were added in required amounts into the wastewater. The wastewater sample was then rapidly mixed for 5 minutes at 120 rpm and the process continued with slow mixing for 25 minutes at 30 rpm. The samples were left for 1 hour for the reaction to continue. The pH was then adjusted to 7-8 with 1N NaOH to precipitate $Fe(OH)_3$ and prevent H_2O_2 from interfering with the COD test by decomposing H_2O_2 into O_2 and H_2O (Mandal et al., 2010). After waiting for 30 minutes, the supernatant was withdrawn for COD analysis. In addition, in order to prevent H_2O_2 interferences, H_2O_2 concentrations in the samples were measured with H_2O_2 photometric method (Merck Spektroquant Method, detection limit: 2-20 mg H_2O_2 /L) before the COD tests. If high levels of H_2O_2 concentrations that could interfere were measured, COD measurements were made after the samples were kept at high pH overnight.

- *Ozone oxidation (O)*

An ozone generator produced by Degremont and having a production rate of 1 g O_3 per hour was used for ozone oxidation. Ozonation system was operated in semi-continuous type, i.e., continuous with respect to the gas flow and batch with respect to solution. For ozonation, 2 liters of leachate were filled into a stainless-steel reactor with a capacity of 4 liters. Samples were taken at 15, 30, 45, 60, 90, 120 min for the analysis. Excess ozone gas was taken from the top of the reactor into a gas washing bottle containing KI solution. The amount of ozone in the waste gas was measured during the experimental study by taking samples from the KI trap and titrating the iodine in the samples with $Na_2S_2O_3$ (APHA, 2005). Optimum pH study has not been done in the ozonation process, ozonation has been studied at natural pH.

- *Coagulation–flocculation (CF) method*

The coagulation-flocculation (CF) experiments were conducted by using the Jar test method. Aluminum sulfate ($Al_2(SO_4)_3.18\ H_2O$) and ferric chloride ($FeCl_3.6H_2O$) were used for CF experiments. These chemicals were prepared as 10% solutions and 1NaOH and 1H_2SO_4 solutions were used to adjust the pH to 7.5. In addition, anionic polyelectrolyte was used in the flocculation study. The optimum dose study in CF experiments was carried out at pH: 7.5 based on previous experiments (experiments by staff in the facility). A series of jar test experiment applying 2 min. rapid mixing at 200 rpm, 15 min. slow mixing at 45 rpm and 30 min. for settling was conducted on 500 mL wastewater. Flocculation was carried out using 1‰ anionic polyelectrolyte.

- *Sequential coagulation-flocculation and ozonation*

In the study, COD removal efficiencies were determined by using ozonation (CF/O) after coagulation-flocculation and coagulation-flocculation (O/CF) after ozonation. In the CF/O study the wastewater obtained by using coagulants and coagulant doses, which gives the best results in coagulation-flocculation experiments, was then subjected to ozonation. In addition to these experiments, the leachate was first subjected to ozone oxidation and then to the coagulation-flocculation method. In these experiments performed after ozonation, previously determined coagulant doses were used as optimum doses. In the O/CF study, optimum coagulant and dose studies were not performed.

3. Results and discussion

3.1. Fenton process

Fenton process is a process that includes oxidation, coagulation and sedimentation. The best oxidation efficiency in the Fenton process occurs at about pH 3; the coagulation process that occurs after oxidation takes place between pH 7-8 and $Fe(OH)_3$ starts to precipitate at this pH (Goi et al., 2009). In this study the effect of pH change in Fenton process has not been investigated; studies have been conducted at acidic pH at pH: 3. Because at low pH, addition of H_2O_2 can increase the oxidation efficiency (Yılmaz et al., 2010). In addition, there are many studies in the literature that Fenton process is more efficient at pH:3 (Kochany and Lipczynska-Kochany, 2009; Yılmaz et al., 2010; Zhang at al., 2006).

In the Fenton process, Fe^{2+} and H_2O_2 are two main chemicals that determine costs and organic matter removal efficiency (Mahmud et al., 2012). H_2O_2 plays a very important role as a source of •OH generation in Fenton's reaction (Deng, 2007; Wu et al., 2010). Effects of the H_2O_2 and $FeSO_4$ doses on the COD removal efficiencies are shown in Figs. 1-2 for three samples. Five H_2O_2 doses between 3300-16500 mg/L were tested at a fixed $FeSO_4$ dose of 9900 mg/L. From Fig. 1, it can be stated that COD removal efficiencies increase up to a certain point with the dosage of H_2O_2. At constant $FeSO_4$ dosage, COD removal efficiencies increased at doses up to 13200 mg/L for Sample 1, 9900 mg/L for Sample 2 and 6600 mg/L for Sample 3. At these dosages COD removal efficiencies were measured as 80.2%, 79.6% and 77.5% for Sample 1, Sample 2 and Sample 3, respectively. It is seen from Fig. 1 that H_2O_2 doses higher than optimum doses, reduces the removal efficiency. It is because the presence of large amounts H_2O_2 causes as a scavenger for the •OH radicals, thus reducing the efficiency of the Fenton process (Wu et al., 2010; Yılmaz et al., 2010).

After optimum H_2O_2 doses which were determined for each sample, optimum $FeSO_4$ doses were determined. As seen in Fig. 2, optimum $FeSO_4$ doses are 9900 mg/L, 9900 mg/L and 6600 mg/L for Samples1, 2 and 3, respectively. The COD removal efficiencies at these dosages are 80.2%, 79.6% and 78.8%, respectively. When the COD values of leachate samples were examined, it is seen that the sample with the lowest COD was the Sample 3. In addition, the sample with the lowest alkalinity and electrical conductivity was again the Sample 3. Alkalinity and electrical conductivity (dissolved salts) are thought to affect the Fenton reagents dosages, which were H_2O_2 and $FeSO_4$ doses. Because, the presence of high alkalinity or dissolved solids (various salts) can reduce the removal of organic matter in the Fenton process by forming complexes with Fe^{2+} and also scavenging •OH radicals (Kochany and Lipczynska-Kochany, 2009). In addition, chloride and sulphate ions (dissolved solids) form complexes with Fe^{2+} and less reactive inorganic radicals than •OH radicals. These phenomena cause reduction of organic matter removal efficiency (Yılmaz et al., 2010).

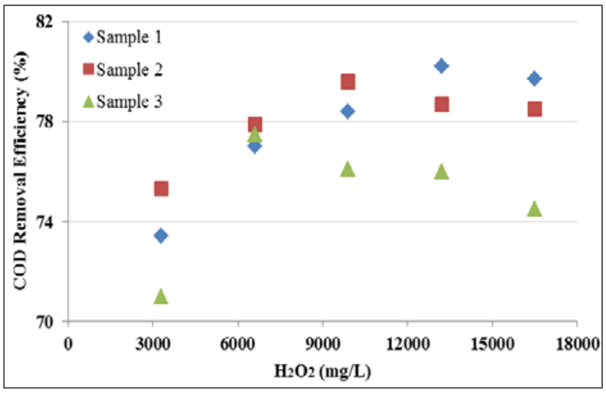

Fig. 1. Effect of H_2O_2 on COD removal efficiency (pH:3, $FeSO_4$: 9900 mg/L, time:2 h)

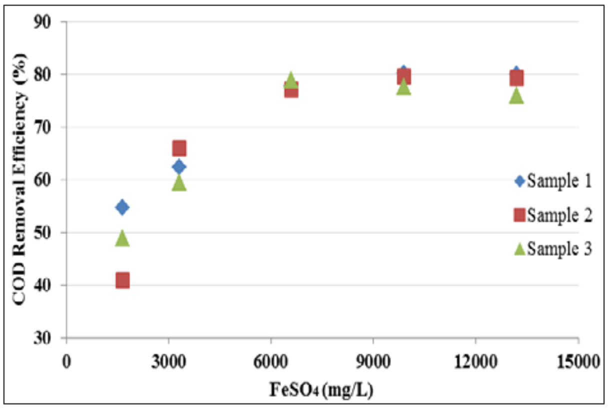

Fig. 2. Effect of $FeSO_4$ on COD removal efficiency (pH:3, H_2O_2:6600-13200 mg/L, time:2 h)

In Table 3, COD removal efficiencies and COD values of the treated samples are given depending on the optimum H_2O_2 and $FeSO_4$ doses and H_2O_2/Fe^{2+} molar ratio. As seen from the Table 3, H_2O_2 doses and $FeSO_4$ doses are the lowest for the Sample 3 which had the lowest COD. In addition, it is seen that as the alkalinity and electrical conductivity decreased, higher removal efficiencies were obtained with lower H_2O_2 and $FeSO_4$ doses. The reason for this is that high anions and cations, that is, high conductivity and high alkalinity, causes the scavenging of the •OH radicals. Leachate containing significant amounts of anions and cations (electrical conductivity and alkalinity in Table 2) are known scavengers of •OH radicals and inhibitors of the Fenton reaction (Kochany and Lipczynska-Kochany, 2009). In this study, Sample 1 and Sample 2 which contain relatively high alkalinity and electrical conductivity than Sample 3, consume much higher Fenton reactants (H_2O_2 and $FeSO_4$) (Yılmaz et al., 2010). From Table 3, it is seen that samples with COD values between 1874-2572 mg/L need 3.5-5.1 H_2O_2/Fe^{2+} molar ratio in order to be properly treated by Fenton process.

3.2. Ozone oxidation (O)

Samples were subjected to the ozonation process for 120 minutes. The amount of ozone given in the ozonation system is 1 gram per hour. Since ozonation is carried out for 2 hours in the experiments, the total amount of ozone given is 2000 mg. The COD concentration of the Sample 1 is 2572 mg/L and 2 L of leachate was ozonated. In this case, the dose of ozone given is 2000 mg O_3/5144 (=2572*2) mgCOD = 0.38mg O_3/mgCOD. With the same method, the ozone doses of the Sample 2 and Sample 3 were 0.44 and 0.53 mgO_3/mgCOD, respectively. As a result of ozonation, COD removal efficiencies are shown in Fig. 3. As seen in Fig. 3, the highest removal efficiency was obtained in the Sample 3 which has the highest ozone dose, while the lowest removal efficiency was obtained in Sample 1 which has the lowest ozone dose. In addition, the alkalinity and electrical conductivity of the Sample 3 were the lowest. This is thought to affect COD removal efficiency by ozonation.

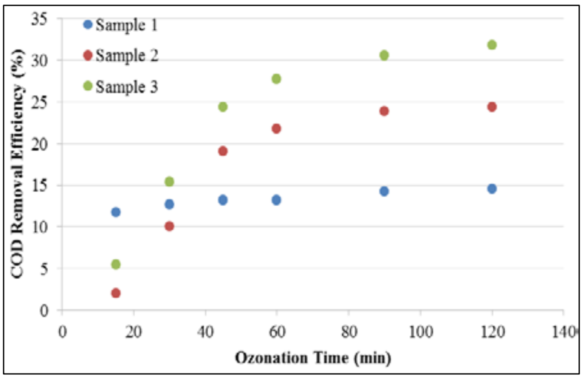

Fig. 3. Effect of ozonation time on COD removal efficiency (At natural pH)

Even after 120 minutes of ozonation of raw leachates, COD removal efficiencies did not exceed 14%, 24% and 32% in Sample 1, 2 and 3 respectively. Nevertheless, aromatic rings and unsaturated bonds that may be present in leachate may be shown, causing COD removal to be low. The rate of degradation of organic substances with ozone in the first 30 minutes is greater than the next 90 minutes as seen from the Fig. 3. From here, it can be said that the oxidation of organic substances, which can be easily oxidized, is completed in the first 30 minutes. As seen from the Fig. 3 the COD profile started to reach plateau since the organic matters remained in the leachate were hard to oxidize (Jamali et al., 2009). The reaction rate decreases after this period can be attributed to the presence of aldehydes, ketones and organic acids, which are thought to occur during ozonation in the wastewater and are slow to react with ozone (Ntampou et al., 2006).

3.3. Coagulation–flocculation (CF) method

In the CF method, the important operating conditions are pH, coagulant type and coagulant doses. In addition, the presence of inorganic and organic substances in wastewater is an important factor affecting the removal efficiency. In this study, pH 7.5 was studied, based on previous experiments (experiments by staff in the facility). Two different coagulants were studied which $FeCl_3$ and $Al_2(SO_4)_3$. COD removal efficiencies obtained using $Al_2(SO_4)_3$ and $FeCl_3$ are given in Table 4. The study shows that $FeCl_3$ was effective for all three samples in terms of COD removal efficiencies. The optimum dose for $FeCl_3$ appears to be 5660 mg/L in all three samples, and COD removal efficiencies were 40.5%, 46.8% and 55.2% for Samples1, 2 and 3, respectively. When $Al_2(SO_4)_3$ was used, it is seen that the highest removal efficiencies were obtained at 10000 mg/L coagulant doses and the removal efficiencies at this dose did not exceed 49.2%. These study results were compatible with many study results in the literature. Many studies have found that $FeCl_3$ was more effective than $Al_2(SO_4)_3$ as a coagulant. As a result, as shown in the literature, ferric coagulants are generally more effective than $Al_2(SO_4)_3$ salts in wastewater treatment (Jamali et al., 2009; Tatsi et al., 2003). As seen from the Table 3, the highest removal efficiencies were found for Sample 3 in both coagulant uses. The reason for this is thought to be that the particulate COD of Sample 3 is higher than the particulate COD of other samples (Table 2).

COD removal efficiencies for both coagulants increased by increasing the coagulant dosages to the optimum dosages. This result is mainly due to the optimum dose of coagulant producing flocs with good structure and consistency. In doses lower than optimum, the produced flocs were small and influence the settling velocity of the sludge (Ahmadi et al., 2017). Removal efficiencies decreased at higher coagulant doses for both coagulants. At higher doses than optimum, in addition to the formation of small flocks, the resting ability of the flock may occur (Ahmadi et al., 2017).

Table 3. COD removal efficiencies and COD values of the treated samples

Samples	***Optimum H_2O_2 (mg/L)***	***Optimum $FeSO_4$ (mg/L)***	***H_2O_2/Fe^{2+} molar ratio***	***COD Removal Efficiency (%)***	***COD (treated wastewater) (mg/L)***
Sample 1	13200	9900	5.1	80.2	509
Sample 2	9900	9900	4.4	79.6	456
Sample 3	6600	6600	3.5	78.8	397

Table 4. COD removal efficiencies obtained using $Al_2(SO_4)_3$ and $FeCl_3$ (pH:7.5)

$FeCl_3$ dosages (mg/L)	***$FeCl_3$ Removal Efficiencies (%)***		
	Sample 1	***Sample 2***	***Sample 3***
2330	25.9	22.1	40.2
3330	31.2	32.8	47.6
4330	36	40	51.8
5660	40.5	46.8	55.2
6660	38.4	45.2	53.3
$Al_2(SO_4)_3$ dosages (mg/L)	***$Al_2(SO_4)_3$ Removal Efficiencies (%)***		
	Sample 1	***Sample 2***	***Sample 3***
3330	27.2	26.8	36.4
5000	31.9	34.9	42.9
6660	34.6	39.3	48.3
10000	37	41.8	49.2
13330	35.9	40.2	46.2

3.4. Sequential coagulation-flocculation and ozonation

In the Table 5, COD removal efficiencies of CF alone, ozonation alone, CF applied after ozonation, CF/O and O/CF are given. As seen from the Table 5, the ozonation efficiency applied alone was very low. When ozonation was applied after CF (CF/O), the removal efficiencies were seen to be considerably higher, and for Sample 1, 2 and 3, it increased from 14.5% to 46.7%, from 24.4% to 55% and from 31.8% to 66.1%, respectively. The COD concentrations of the leachate decreased from 2572, 2238 and 1874 mg/L to 1371, 1007 and 635 mg/L respectively by CF/O process.

When the COD removal efficiencies of CF using $FeCl_3$ are analyzed from Table 5, it is seen that for Sample 1, 2 and 3 it is 40.5%, 46.8% and 55.2% respectively. When CF removal efficiencies were examined after ozone application, it is seen that ozone increased COD removal efficiencies of CF especially for Sample 1 and 2. As seen in Table 5, CF removal efficiencies after ozonation were 65.4% and 66.1% for Sample 1 and 2, respectively. The CF removal efficiency of Sample 3 after ozonation remained at 52.1%. According to these results, COD removal efficiencies for Samples1, 2 and 3 after O/CF process were measured as 70.4%, 74.4% and 67.3%, respectively. As the reason for the increase of CF efficiency after ozonation, it can be said that ozone decreases the colloidal charge density in humic substances that are likely to be present in leachate (Ntampou et al., 2006). The COD concentration of the leachate was reduced from 2572, 2238 and 1874 mg/L to 761, 573 and 612 mg/L respectively by O/CF process.

When the efficiency of the ozonation process after coagulation-flocculation is examined, it is seen that the efficiency of ozonation process alone is higher. The reason for this is the increase of Cl^- concentrations in the environment due to $FeCl_3$ used in CF process, and the fact that ozone oxidizes the Cl^- ion to Cl_2 gas and cannot oxidize the organic substance. Thus, oxidation of COD decreased due to Cl^-.

It can be concluded that O/CF process was more efficient than CF/O process in terms of COD removal efficiency. Various results have been reported in other studies that pre-ozonation of wastewater reduces the colloidal load density caused by various humic substances in wastewater (Ntampou et al., 2006; Tanaka et al., 2001). In addition, it has been reported by Edwards et al. (1994) that ozonation can oxidize large molecular weight organics, convert them into smaller particles and increase acidic functional groups. It is stated that this change increases the interaction between the organic matter and the coagulant agent (Ntampou et al., 2006).

3.5. Comparison of the treatment alternatives

Comparison of the methods used to treat the leachate studied is given in Fig. 4. When the Fig. 4 is examined, it is seen that the efficiency of CF and O processes alone is lower than CF/O, O/CF and Fenton process. Especially the efficiency of ozonation seems to be quite low compared to all other processes. When the CF process by using $FeCl_3$ is examined, it is seen that the removal efficiency of the samples is high due to the decrease in COD values of Sample 1, 2 and 3. In addition, Sample 3, which has the lowest total COD and the highest particulate COD ratio, had the highest COD removal efficiency in the CF process.

It is seen that the efficiency of CF applied alone without any pre-treatment was between 41%-55% depending on the CODs of the samples and their alkalinity and electrical conductivity. It is seen that the COD removal efficiency of CF applied after ozonation has reached to 65%. This is thought to be due to the separation of particulate organic matter into small pieces by ozonation and thus to better interact with the coagulant (Ntampou et al., 2006).

As known, Fenton process is a process in which oxidation-coagulation and precipitation occur together. When Fenton and CF/O and O/CF processes were compared, it was seen that the efficiency of Fenton process was more effective than the other two processes. As seen from the Fig. 4, the efficiencies of the O/CF process and Fenton processes are close to each other.

Table 5. COD removal efficiencies of treatment processes

Samples	***Removal Efficiencies (%)***					
	Only CF with $FeCl_3$	***CF after O***	***Only O***	***O after CF***	***CF/O (together)***	***O/CF (together)***
Sample 1	40.5	65.4	14.5	10.4	46.7	70.4
Sample 2	46.8	66.1	24.4	15.4	55.0	74.4
Sample 3	55.2	52.1	31.8	23.9	66.1	67.3

According to this result, oxidation process is applied for this leachate first, and then it will give better results if coagulation-flocculation is applied. As it is known, in the Fenton process, the oxidation process takes place at pH: 3, then coagulation and precipitation occur at pH: 7-8. It is thought that the most important reason for the COD removal efficiency up to 80% in Fenton process is that oxidation is carried out at suitable pH. Because in O/CF or CF/O processes, the optimum pH study has not been done in the ozonation step, ozonation has been studied at natural pH of the leachate.

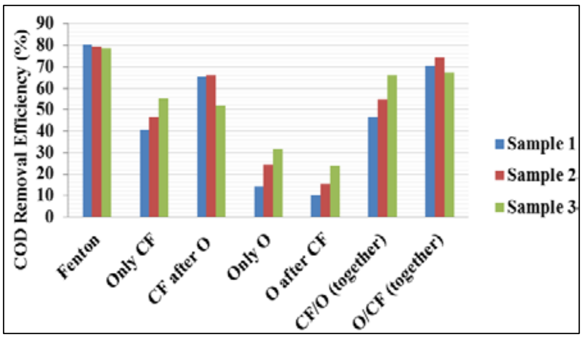

Fig. 4. Comparison of the treatment alternatives

4. Conclusions

In this study, the coagulation-flocculation, ozonation, coagulation-flocculation after ozonation (O/CF), ozonation after coagulation-flocculation (CF/O) and Fenton process were studied. In the study, comparison of these processes was made and the most appropriate treatment process was tried to be determined in terms of COD removal efficiency. The conclusions obtained in the study are summarized below:

- Parallel results were found in the samples taken three times and the best removal efficiencies were obtained by Fenton process. After the Fenton process, COD values for Samples1, 2 and 3 are 509, 456 and 397 mg/L, respectively. Although the Fenton process is the most efficient process, there are some difficulties in its operation. In order to apply this process, the pH value must first be reduced to around 3 and then brought back to neutral pH levels. This process may require a high cost in wastewaters with high alkalinity, such as this leachate studied.
- Although the efficiency of CF process alone does not seem very high, almost all of the suspended and colloidal substances are removed with this process. Therefore, the efficiency of biological treatment to be applied after this process may be high. It should be investigated whether the biological treatment process after CF will be the most economical method compared to all other methods to achieve lower COD concentrations.
- Coagulation-flocculation process after ozonation has removal efficiencies close to the Fenton process. It has been determined that ozonation increased the efficiency of the subsequent coagulation-flocculation process. This is believed to be due to the fact that the organic substance is broken down into smaller pieces by the ozonation process and interacts better with the coagulant, thereby increasing removal efficiencies. Moreover the CF/O method is considered to be easier to operate than the Fenton process.
- It has been determined that the ozone efficiency applied alone remains low, the removal efficiency was relatively high in the first 30 minutes, and the removal efficiency decreased in the next 90 minutes. It is thought that this is due to the fact that fast-oxidizing organics can break down in the first 30 minutes and by-products (aldehydes, ketones and organic acids), which are more difficult to decompose during the next ozonation period, are formed.
- By conducting pilot studies, removal efficiency and cost analysis of alternatives such as Fenton, biological treatment after ozonation or biological treatment after coagulation-flocculation should be done.

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