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Combination of Coagulation-Flocculation and Ozonation Processes for Treatment of Partially Stabilized Landfill Leachate of Tehran

Hamzeh Ali Jamali, Amir Hossein Mahvi, Ramin Nabizadeh, Foorogh Vaezi and Ghasem Ali Omrani

School of Public Health and Center for environmental Research,
Tehran University of Medical Sciences, Tehran, Iran

Abstract: In this study, samples of partially stabilized landfill leachate were taken from the artificial pond connected to the Tehran landfill site. The average characteristics were: COD=130000 mgl^{-1}, BOD_5 =47000 mgl^{-1}, color=40000 mgl^{-1} (Pt-Co), NH_3-N=2700 mgl^{-1} and pH= 7.7. An integrated technique consisted of coagulation/flocculation and ozonation processes was examined, to enhance COD and color reduction and increase the biodegradability of the leachate (i.e., the ratio of BOD_5/COD) for the further treatment. The coagulation of leachate samples was accomplished by addition of different coagulants including ferric chloride, aluminum sulphate, ferrous sulphate and poly-aluminum chloride in various coagulant and pH values. Results of these tests showed that among traditional coagulants the best coagulant for treatment of the leachate is ferric chloride in combination with an anionic polyelectrolyte (Magnafloc LT25). Maximum COD and color removal rates for 41% and 70% had been achieved by addition of 2.5g l^{-1} of ferric chloride as Fe^{+3} respectively. But, still final COD values were high (more than 70g l^{-1}) indicating the additional treatment steps is required.Thus, ozone as a strong oxidizing agent was applied to treat this pre-coagulated leachate. The ozone dosages used were in the range of 20 to 180 gO_3 per liter of the leachate. After oxidation, the maximum BOD_5 increase was about 10% for ozone treatment at applied dose of 40g per liter of leachate and the ratio of BOD_5/COD was increased from 0.36 up to 0.45.The maximum color removal was 81% by applying a high ozone dose of 180 g O_3/L. As expected, the COD of the leachate decreased with the increase of ozone dose. But, as the applied ozone dose increased above 200 gO_3 per liter of leachate, the COD profile started to reach plateau since the organic matters remained in the leachate were hard to oxidize. Therefore combination of coagulation-flocculation and ozonation is not sufficient for treatment of this leachate and for further treatment some other methods such as GAC adsorption and membrane filtration should be applied.

Key words: Landfill leachate · Coagulation-flocculation · Ozonation · Tehran

INTRODUCTION

Landfill is one of the most commonly methods for disposal of municipal solid waste around the world [1]. After land filling, solid waste undergoes physico-chemical and biological changes. Therefore, the degradation of the organic fraction of the waste is accomplished and the phenomenon generates a highly polluted wastewater called "leachate" [2]. The main sources of percolating water are rain fall, irrigation and moisture content of solid wastes [3].

In general, leachate generated from young acidogenic landfills are characterized by high BOD (3000-13000 mgl^{-1}), high strength COD (30000-60000 mgl^{-1}), high NH_3-N (500-2000 mgl^{-1}) and the ratio of BOD/COD equal to about 0.4-0.7). High COD and BOD concentrations and BOD/COD ratio in young leachates candidate it to anaerobic treatment prior to aerobic process [4-6]. With the increasing age of landfill, biodegradable fraction of organic compounds are decomposed over a period of long time, resulting in the production of stabilized leachate, which is usually characterized by high concentrations of NH_3-N (3000-5000 mgl^{-1}), COD(5000-20000 mgl^{-1}) and BOD/COD ratio of less than 0.1 [7,8]. Commonly, most of the organic contents of aged leachate have a high molecular weight and are recalcitrant compounds such as humic and fulvic substances, which are not easily degradable [9].

Corresponding Author: Dr. Amir Hossein Mahvi, School of Public Health and Center for environmental Research, Tehran University of Medical Sciences, Tehran, Iran

Therefore, aged leachate cannot be treated by using biological processes or natural system such as leachate recirculation [10]. As a result, the treatment processes for this kind of leachate are chemical precipitation, coagulation-flocculation [11], advanced oxidation such as Fenton's treatment [12-15], reverse osmosis [16, 17].

Tehran is one of the most crowded metropolises in Asia with a population over 10 million in 2007. Every day; Tehran municipality should manage about 6000 tons of solid wastes generated from residential and commercial sources which about 60% of these wastes are organic. Almost all of the solid wastes are transported to Tehran landfill site which is located in south of Kahrizak area (southeast of Tehran). This site covers a surface area of about 500ha and it has been in operation since 1975.

Trench method is applied for disposal of these municipal solid wastes. Since the landfill was not properly lined with clay or other synthetic geomembrane, the exact quantity of produced leachate is not known, but it is estimated that about 80-90l leachate per ton of solid wastes is produced. To date, no leachate management program has been applied at this site. At the lowest point of this landfill, leachate reaches to the surface, forming an artificial pond.It covers about 12 ha (1200m*100m) with a depth of about 1.5m. There is not any program for treating the leachate. Consequently, this pond constitutes a real threat to the fauna and flora of the surrounding areas and the whole environment.

The objective of this research was to determine the common features of partially stabilized landfill leachate and its treatability by combination of coagulation-flocculation and ozonation processes.

MATERIALS AND METHODS

For characterization of partially stabilized leachate of the Tehran landfill, 25 points were selected around the pond as the distances between them were 104m. Then in the period of this study (12 months) composite samples were taken from the leachate of the pond between May 2007 and May 2008. Samples were transported to the laboratory in 30Lplastic carboys and were analyzed within 2 days. Preservation of samples if required had been done by storing at 4°C. The following parameters were measured: pH, BOD_5, COD, color, alkalinity, ammonia, total kjeldahl nitrogen (TKN), total phosphorous, total suspended solids (TSS), volatile suspended solids (VSS), sodium, potassium and chloride. All analyses were carried out according to standard methods for the examination of water and wastewater [18]. Selected samples were then repeatedly analyzed in order to validate/evaluate the obtained results and for reaching to the accepted analytical error (±5%). All the chemicals used for these analyses were in analytical grade. Coagulation-flocculation experiments were performed in a conventional jar-test apparatus equipped with four backers. The experimental procedure consisted of three subsequent stages; the initial rapid mixing stage of 3 min at 120 rpm, the following slow mixing stage of 25min at 40 rpm and the final settling step for 30 min. The pH values of samples were adjusted to the desired levels by addition of the appropriate amounts of 6N sodium hydroxide or 6N sulfuric acid. Chemical reagents used as coagulants included $Al_2 (SO4)_3$, $18H_2O$, FeSO4, H2O, FeCl3, 6H2O, Fe2 $(SO_4)_3$ and poly aluminum chloride (PAC). The addition of an anionic polyelectrolyte (Magna floc LT25) in combination with these coagulants was also examined. After the settling period, the supernatant was withdrawn from the beaker and was checked by chemical analysis. The withdrawal of sample was accomplished from a point about 2cm below the liquid level in the beaker by a pipette and finally the volume of the produced wet sludge was estimated by watching the sludge level at the bottom of the glass beaker. The experimental set-up for oxidation of partially stabilized leachate is shown in Figure 1.

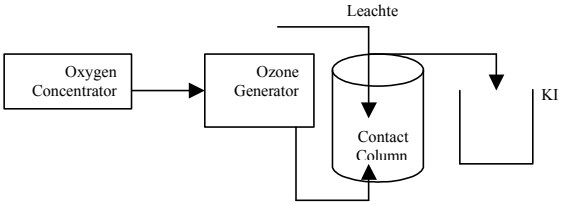

Fig. 1: Flow diagram for ozone treatment system.

As shown in Figure1, ozonation experiments were carried out in a laboratory batch bubble reactor, consisting of a glass column with a height of 100cm and internal diameter of 5cm. One liter of the pretreated leachate sample was then placed in the reactor. At this time, the height of sample was reached to about 50 cm. The ozone-air mixture was then supplied to the system through a schott ceramic porous diffuser (porosity 8-18 μm), inserted in the bottom of the reactor. Oxygen with a purity of 90% was produced by an oxygen concentrator (with a capacity of 3L/min) and delivered to the ozone generator (ARDA Co, Model 6-5-11015. Nominal ozone output at STP: $5gh^{-1}$). The air flow rate was adjusted at $2lmin^{-1}$.

For determination of the ozone dose ozone, in the feeding gas was first collected into a 10% potassium iodide solution and it was then measured in the solution by standard iodometric titration method [18]. Residual ozone in the out flow gas was also trapped and measured as described above. Ozone consumption was calculated by subtracting the amount of ozone in the outflow gas from the amount of ozone in the feeding gas.

The ozone dosage that was used in the experiments was $5gh^{-1}$ and the reaction times of ozonation experiments were varied between 1h to 48h.

RESULTS AND DISCUSSION

The main characteristics of the partially stabilized (aged) leachate samples studied in this project are presented in Table1.

Coagulation/Flocculation Experiments: The best conditions for coagulation-flocculation experiments were specified by considering COD and color removal rates. Table 2 shows the optimal condition of these experiments.

Table 1: Physicochemical parameters of partially stabilized leachate of Tehran

Parameter	No. of Samples	Range	Average±S.D
pH	24	7.5-7.8	7.7±0.3
Conductivity($mscm^{-1}$)	24	65-70	68±12
Color(Pt-Co unit)	24	38000-45000	40000±1250
TS(gl^{-1})	24	42.64-150	145.5±25
TSS(gl^{-1})	24	40.66-52.5	45.5±8
VSS(gl^{-1})	24	19.91-23.3	19.8±5
FSS(gl^{-1})	24	25.75-32.45	28.5±9
BOD_5(mgl^{-1})	24	40000-50000	47000±1800
SO_4^{-2}(mgl^{-1})	24	2000-3000	2400±350
NO_3-N(mgl^{-1})	24	4.5-100	20±25
NO_2-N(mgl^{-1})	24	0-5	2.5±0.8
NH_3-N(mgl^{-1})	24	2200-2900	2700±800
TKN(mgl^{-1})	24	2570-3300	2900±900
TDS(gl^{-1})	24	82.98-110.5	98.5±25
COD(mgl^{-1})	24	120000-150000	130000±2500
K^+(mgl^{-1})	25	55000-75000	68200±200
Na^+(mgl^{-1})	24	30000-40000	36100±500
Cl^-(mgl^{-1})	24	13100-16250	15120±400

Table 2: Optimal condition of coagulation-flocculation of the leachate

Coagulant	Coagulant concentration (mgl^{-1})	Polyelectrolyte	Polyelectrolyte concentration (mgl^{-1})	pH
Alum	1500	Magnafloc LT25	150	8
Ferric chloride	2500	Magnafloc LT25	250	10
PAC	2000	Magnafloc LT25	200	7
Ferrous sulphate	2500	Magnafloc LT25	250	8

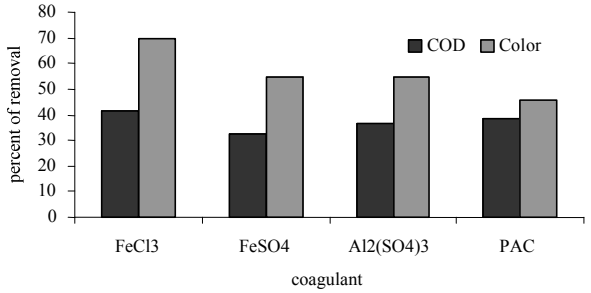

Fig. 2: Optimum results of leachate treatment by Coagulation-Flocculation with the various coagulants.

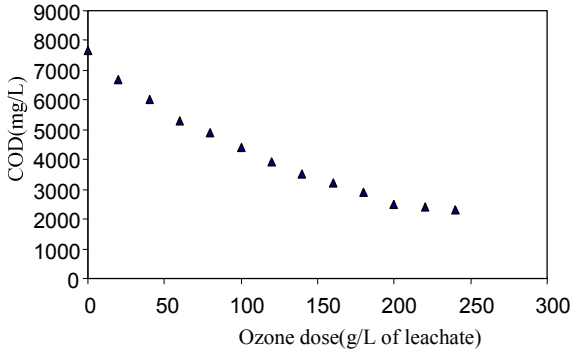

Fig. 3: The effect of Ozone dose on the reduction of COD

The results of COD and color removal under the optimum conditions determined for each coagulant can be seen in Fig. 2.

Ozonation Procedures: As it was revealed that the optimum conditions of primary coagulation were obtained when ferric chloride and an anionic polyelectrolyte used together, ozonation experiments were accomplished on the effluent of this primary leachate treatment. Results of the ozonation experiments are all presented in Figures 3 to 6.

Figure 3 shows the COD concentrations of the pre-treated partially stabilized landfill leachate after oxidation as a function of the applied ozone dose. As it is expected the COD of the leachate had decreased with increasing the applied ozone dose.

As the Ozone dose increased above $200gO_3$ per liter of the leachate, the COD profile started to reach a plateau since the remained organic matters in the leachate were difficult to oxidize.

Figure 4 demonstrates the changes in BOD_5 as a function of Ozone dose. As shown in figure, BOD_5 increased to about 10% when Ozone dose increased to 40 gO_3 /L of leachte.

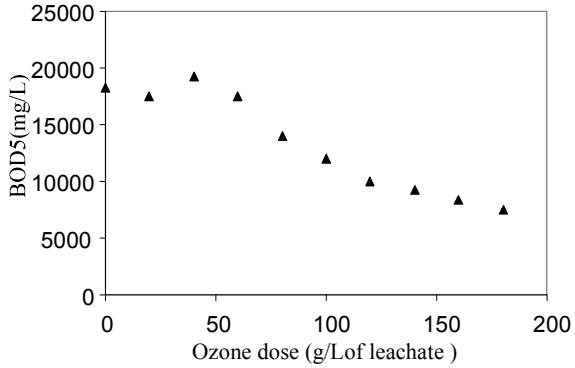

Fig. 4: The effect of Ozone dose on BOD_5.

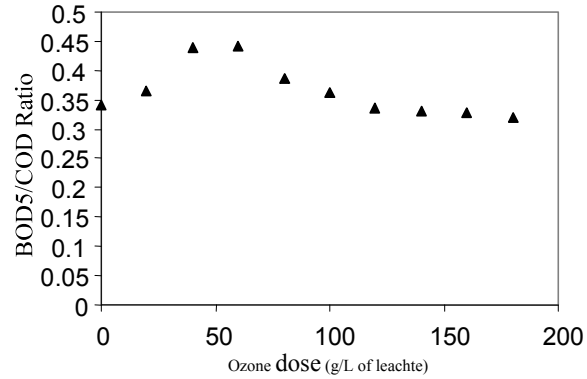

Fig. 5: The effect of Ozone dose on BOD_5/COD ratio

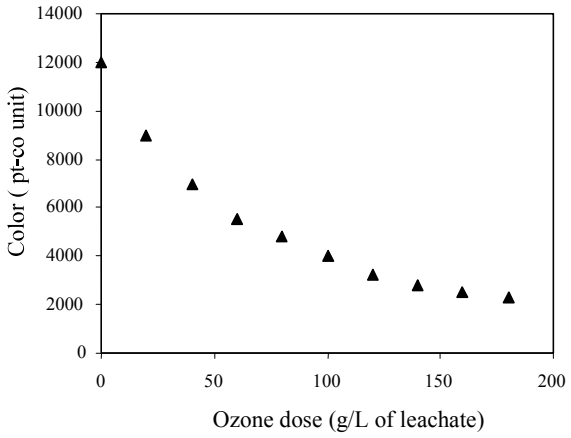

Fig. 6: The effect of Ozone dose on color

Figure 5 presents the relationship between the BOD_5/COD ratio and the applied Ozone dose.

By applying an Ozone dose of $120gl^{-1}$, a color removal efficiency of 73.5% was observed. But a by further increasing of ozone dose, the color removal efficiency was slightly increased and the maximum color removal efficiency reached to 81%.

The characteristics variations of leachate are attributed to a number of facts, such as composition of deposited solid wastes, landfill age, hydrogeology of landfill site, specific climate conditions and water flowing through the landfill [19]. According to Table 1, we conclude that old leachate with a BOD5/COD ratio of 0.36 could be considered as a relatively stabilized waste. Thus, using biological processes for further treatment of these wastes may be ineffective and other methods such as chemical coagulation could be applied. It is an accepted fact that complete removal of phosphorous is possible by coagulation-flocculation, whereas N removal is mainly dependant upon colloidal particulates removal [20]. Thus, most of the N compounds which can be removed are of albuminoidal type (just like N in proteins). Nevertheless, if biological treatment should be accomplished after physicochemical processes, control of treatment becomes critical since the effective growth of bacteria is directly dependant to the amount of BOD_5: N: P ratio. On the other hand, this ratio deviates from its original amount (100:5:1) after chemical treatment.

In this project, determination of the optimum conditions for coagulation- flocculation had been accomplished by controlling the variables of COD and color (see Figure 2 and Table 2). However, it should be noted that precipitation and adsorption of ferric cations in leachate samples is highly affected by humic compounds and efficiency of the coagulation. Therefore, the required dosage of ferric salts in wastewater treatment is primarily specified by the concentration of natural organic compounds. Of course, the concentrations of these compounds in the leachate are normally more than wastewaters.

After treatment by coagulants, the pH of leachate samples had reduced to about 5.5. The reason of the pH drop is that cations of Fe^{+3} and Al^{+3} have acidic characters (they both are Lewis acids), therefore hydrolysis had been occurred at acidic conditions caused by precipitation of metallic hydroxides. Application of coagulation-flocculation for the removal of non-biodegradable organic compounds from hazardous landfill leachate was previously studied [21]. Although the doses required were identical ($0.035moll^{-1}$ of Fe^{3+} or Al^{3+}), with an initial COD concentration of $4100mgl^{-1}$, ferric chloride was found to give higher removal of organic compound (55%) than alum (42%). These results were in agreement with the previous study by in Greece [22]. At an initial concentration of 5690 $mgl^{-1}$and at pH 4.8, the maximum COD removal of 56% was achieved with 0.8 $gl^{-1}$of $FeCl_3$, as compared to 39% with $0.4gl^{-1}$of $Al_2(SO_4)_3$.

In another study, the application of coagulation-flocculation for the treatment of stabilized leachate from the Thssaloniki landfill (Greece) was performed [23]. Without pH adjustment, the addition of 1.5g/L of FeCl3 was able to increase the COD removal rate to 80%, while 1.5 $gl^{-1}$of Al^{3+} ions resulted in up to 38% reduction of COD. These results were in agreement with our findings and suggest that $FeCl_3$ is more effective than alum as a coagulant.

Generally, ferric coagulants are more effective than Al salts in wastewater treatment [21, 22]. Furthermore, it has been reported that the major cations formed by hydrolysis of polyaluminium chloride (PAC) are polynuclear products [such as $Al_{13}O_4$ $(OH)_{24}^{7+}$] which depolymerized when organic compounds are present [24]. This leads to reduction of PAC efficiency in wastewater treatment.

Figure 3 shows the COD changes of relatively stabilized leachate after oxidation with various dosages of Ozone. As indicated in this figure, COD removal reached up to 70 %(from 76700 to 23000mgl^{-1}) for 240gO_3/L of leachate. During the first stage (up to 20gO_3/L of leachate) COD value was decreased to 67030 mgl^{-1}. Similarly, Silva *et al*. [25] found Ozonation process disappointing with regard to COD removal at pH 4.5 and achieved only 48% COD removal at 3.0gO_3/L. As it reported, the major compounds of stabilized leachate are humic and fulvic acids with molecular weights in the range of 1000-10000 Da [26]. Humic compounds are composed of a skeleton containing alkyl/aromatic units with N and oxygen groups and double bonds. The main functional groups of these compounds are carboxyl acids, phenolic hydroxyls, ketones and quinon groups [27]. Compared to humic acids, the fulvic acids are less aromatic and they are largely composed of carboxylic acids, phenolic and ketone groups [28]. Therefore, they are less biodegradable than humic acids. We must know that by further Ozonation of leachate, the amount of readily biodegradable organic compounds decreases and thus changes the COD concentration discontinue.

As shows in Figure 4, BOD increasing may be caused by two phenomena: (1) Formation of oxidation- by products (OBP_S) with less molecular weight and thus better biodegradability and/or (2) diminishing the toxicity of few organic compounds after their oxidation by Ozone. The maximum increase of BOD occurred after applying 40 g Ozone per liter of leachate. This result is in agreement with the findings of Karrer *et al* [29]. who reported an increase in BOD_5/COD ratio and consequent increase of biodegradability after ozonation of leachate. However, when Ozone dosage had reached as high as 100mg/L, the ratio of BOD_5/COD had become plateau.

Figure 6 indicates that color of leachate has effectively reduced by ozonation. and significant decolorization was found to take place during ozonation, resulting in more than 80% reduction of color (from 12000 to 2300 Pt-Co units), which is similar with the relevant finding of others [25,30,31]. Ozonation has been often applied as a post- treatment (final polishing) step of colored wastewaters, resulting from the textile (dying) industry [32], but also from the fermentation [33], or from the paper mill industry [34]. During the current study, the initial dark brown color of the leachate sample attributed to the presence of humic substances, became light yellow as the oxidation reaction by Ozone was preceded. Furthermore, the decolorization rate was remarkably high during the beginning stages of ozonation reaction, as at 60gO_3/L of leachate, the observed color removal was more than 54%. After prolonged reaction time the removal of color was up to 80%. Color reduction principally is related to direct reaction of ozone with double bonds of carbon in the structure of color compounds which leads to production of colorless products such as aliphatic acids, ketons and aldehyds [35]. These reactions occur at a high rate and are approximately completed during the initial period of ozonatin process.

Data of previous researches also indicate that the rate of color removal is nearly two times greater than COD removal rate [36]. Oxidation of readily biodegradable compounds can occur during the short periods of reaction, but the rate of this oxidation decreases by time mainly because of formation of numerous less reactive by products such as aldehydes, ketons and organic acids in the initial periods of ozonation [35].

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