Environmental Technology
Vol. 31, No. 14, 14 December 2010, 1635–1640

Removal of COD and colour from young municipal landfill leachate by Fenton process

Tuba Yilmaz, Ahmet Aygün, Ali Berktay and Bilgehan Nas*

Department of Environmental Engineering, Selcuk University, 42075, Konya, Turkey

(*Received 5 January 2010; Accepted 17 May 2010*)

Landfill is a common solution for the final disposal of municipal solid waste in Turkey. In recent years, studies of landfill leachate treatment by Fenton process have indicated that these methods can effectively reduce concentrations of organic contaminants and colour. The aim of this study is to investigate the removal efficiencies of colour and organic matter as COD from young municipal landfill leachate and the effect of operating conditions such as initial pH and Fenton's reagent dosage. Leachate was collected from municipal sanitary landfill located in city of Konya, Turkey. The main characteristics of the leachate were: pH = 7.25, colour = 3510 ptCo, COD = 38200 mgL^{-1}, BOD_5 = 22000 mgL^{-1}, ratio of BOD_5/COD was 0.58 and alkalinity as $CaCO_3$ = 10250 mgL^{-1}. It is observed that presenting a high value of COD and BOD_5 and the rate of BOD_5/COD values indicate that the leachate can be defined as young. The treatment of the leachate by Fenton process was carried out in a batch reactor. Under the optimal operation conditions (initial pH = 3, 2000 mgL^{-1} Fe^{2+} and 5000 mgL^{-1} H_2O_2), 55.9% of the initial COD and 89.4% colour were removed.

Keywords: COD removal; colour removal; Fenton process; landfill leachate; oxidation process

1. Introduction

Sanitary landfills are the primary method currently used for municipal solid waste disposal in many countries, and especially young leachate generated from landfills is a high-strength wastewater exhibiting acute and chronic toxicity. Untreated leachates can permeate groundwater or mix with surface waters and contribute to the pollution of soil, groundwater, and surface water [1].

Landfill is a common solution for the final disposal of municipal solid waste (MSW) in Turkey. Turkish Statistical Institute has been collecting data on waste by applying annual surveys to industrial establishments and municipalities. According to TURKSTAT data for the year 2006, there are 22 sanitary landfills, 4 composting plants, and 3 incinerations plants in Turkey [2]. Of the 25.28 million tonnes of waste collected in municipalities in 2006, 37.3% was disposed of in a sanitary landfill [3]. The Ministry of Environment and Forestry requires the municipalities to find out their MSW landfill site and treat landfill leachate. Therefore, treatment of landfill leachate is very important for the municipalities in Turkey.

Leachate from the young sites has higher concentration of pollutants than old landfills. With time, the pH of leachate moves from slightly acid to neutral, and the ratio of BOD/COD decreases [4].

Usually a combination of physical, chemical and biological methods are used for treatment of landfill leachate since it is difficult to get efficient treatment by one of these methods alone [5,6]. Aerobic, anaerobic and anoxic processes are the biological methods for leachate treatment and are usually used in combination [7,8]. Air stripping and adsorption are major physical methods whereas coagulation, flocculation and chemical oxidation are chemical treatment methods especially for COD removal from landfill leachate [9,10].

Landfill leachate is a coloured liquid formed primarily by the percolation of precipitation through open landfill or through the cap of the completed site and compaction of the wastes in landfill site. The decomposition of organic matter such as humic acid may cause the water to be yellow, brown or black [11]. There are several techniques used for colour removal. These include chemical precipitation, adsorption through granular activated carbon, nanofiltration, ozonation, radiation, UV photolysis, chemical coagulation, biological treatment with various additives, anaerobic process, fluidized biofilm process, and advanced oxidation with UV/H_2O_2 processes [12].

In recent years, studies of leachate treatment by conventional Fenton, photo-Fenton and electro-Fenton processes have indicated that these methods can effectively reduce concentrations of organic contaminants

*Corresponding author. Email: bnas@selcuk.edu.tr

ISSN 0959-3330 print/ISSN 1479-487X online

DOI: 10.1080/09593330.2010.494692
http://www.informaworld.com

and colour [1]. Goi *et al.* [4] reported that Fenton process can be used preferable treatment method by taking account the effective chemical oxygen demand, dissolved organic carbon removal and biodegradability improvement. Iron and hydrogen peroxide are two major chemicals determining operation costs as well as efficacy. To understand better and improve the Fenton process, numerous studies have been conducted to find the optimal reaction conditions and investigate the fundamental natures of the process.

Zhang *et al.* [13] diluted raw old landfill leachate to desired values and investigated the effects of reaction time, pH, molar ratio of H_2O_2 to Fe^{2+}, feeding modes, temperature, dosages and initial COD. They found that oxidation was so fast and 30 minutes was enough to complete the reaction. The optimum pH is 2.0–3.0 and it is indicated that organic removal increased as dosage increased at the favourable H_2O_2 to Fe^{2+} molar ratio (1.5). At 1000 mgL^{-1} initial COD concentration removal efficiency was 57.4% whereas it was 42% at 2000 mgL^{-1} COD. By adding H_2O_2 step by step, removal efficiencies increased slightly higher.

Lopez *et al.* [14] evaluated the application of the Fenton process as pre-treatment for the old landfill leachate from a municipal landfill located in southern Italy (COD = 10540 mgL^{-1}) with the objective of improving its overall biodegradability (BOD_5/COD ratio) up to a level compatible with a biological treatment ($BOD_5/COD \geq 0.5$). The maximum amount of COD that could be removed by the Fenton pre-treatment was about 60%, using reagent dosages of 10000 mgL^{-1} of H_2O_2 and 830 mgL^{-1} of Fe^{2+}.

Most of Fenton studies focused on leachates in old landfills [13–18] but in this study, Fenton process was used for treatment of young landfill leachate. The leachate was supplied from Konya Municipal sanitary landfill. Removal efficiencies of colour and organic matter as COD and the effect of operating conditions such as initial pH and Fenton's reagent dosage were investigated.

2. Materials and methods

2.1. *Materials and analytical methods*

For this study leachate from solid waste landfill in the Konya Municipal area was used. The population of the city is about 950,000. Landfill occupies 24 ha area with an average height of 8 m in the total area of 350 ha at the present time. The average flow rate of leachate is about 100 m^3/day. Samples were collected from the solid waste landfill with age of less than 5 years old. They were placed in 60 L plastic containers to be transported to the laboratory and stored at 4°C in refrigerator. The composition of the investigated leachate was reported in Table 1. Considering the value of BOD_5/COD ratio (0.58) and high contents of COD, BOD_5 and alkalinity the leachate was classified as 'young' [19].

Table 1. Composition of the investigated landfill leachate.

Parameter	Value
pH	7.25
Colour (Pt-Co)	3510
Chemical oxygen demand (COD) (mgL^{-1})	38200
Biochemical oxygen demand (BOD_5) (mgL^{-1})	22000
BOD_5/COD	0.58
Alkalinity (mgL^{-1} $CaCO_3$)	10250
Cl (mgL^{-1})	3240
Fe (mgL^{-1})	7.27
Pb (mgL^{-1})	0.204
Cd (mgL^{-1})	0.118
Cr (mgL^{-1})	0.661
Cu (mgL^{-1})	<0.01
Ni (mgL^{-1})	0.385
Zn (mgL^{-1})	0.177
Mg (mgL^{-1})	698
Ca (mgL^{-1})	139.5

pH, COD, BOD_5, colour, chlorine and alkalinity were analyzed in the laboratory according to the methods given in the Standard Methods [20]. pH measurements were done by using the WTW Multiparameter 340i. Closed reflux colorimetric method (Method 5220 C) was used for COD analysis. Colour was analyzed by spectrophotometer method (Method 2120 C), BOD was analyzed (Method 5210), and alkalinity by the means of titration method (Method 2320 B) as dictated by Standard Methods [20]. Heavy metals (Fe, Pb, Cd, Cr, Cu, Ni, Zn) and Ca-Mg measurements were performed using the Perkinelmer Optima 2200 DV ICP-OES.

2.2. *Experimental procedure*

Batch experiments were set up in 500 mL beakers. Jar test equipment was used for mixing and worked at 120 rpm. Mixing procedure lasted one hour following by a 30 minute settling. After the completion of the reaction, samples from supernatant were taken. Sufficient amount of MnO_2 was added [21] into the samples and pH was kept around 7.5–8.0 to prevent H_2O_2 interference with COD analysis. Residual H_2O_2 was checked by using test strips (Merck Merekoquant Peroxide Test) [22]. Acidic and alkaline conditions were provided using 3 M sulfuric acid and 10 M sodium hydroxide and checked with a pH-meter. Granular ferrous sulfate ($FeSO_4.7H_2O$), H_2O_2 (35% w/w), manganese (IV) oxide, NaOH, and H_2SO_4 98% of AR were supplied by Merck.

To start with, optimum pH was investigated. For this purpose, six different pH values (2.0, 2.5, 3.0, 3.5, 4.0 and 4.5) were selected. During this procedure, in order to obtain the molar ratio of 5.5, H_2O_2 and Fe^{2+} concentrations were kept constant at 10000 mgL^{-1} and 3000 mgL^{-1}, respectively. Later on, optimum Fe^{2+} dosage was determined. In order to achieve this, varying dosages of Fe^{2+} between 1000 and 6000 mgL^{-1} were used while H_2O_2 was constant at 10000 mgL^{-1}. Finally, utilizing the optimum dosages of Fe^{2+}(2000 mgL^{-1}) and pH (pH=3), optimum H_2O_2 concentration was determined. The applied H_2O_2 concentrations were chosen within the range of 1000–10000 mgL^{-1}.

3. Results and discussion

3.1. Effect of pH

In Fenton process, pH is one of the important parameters. It affects the activity of both the oxidant and the substrate, the speciation of iron and hydrogen peroxide decomposition [13]. At low pH, addition of H_2O_2 can increase the oxidation efficiency. From other studies, it was reported that a wide range of pH can be used in leachate treatment [16]. In some studies, optimum pH was defined to be in a range of 2.5–3.0 [23,24] or 4.0 [25]. In this study, pH range was selected considering all these values and pH range 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 were examined at 3000 mgL^{-1} Fe^{2+} and 10000 mgL^{-1} H_2O_2 concentrations. In Figure 1, effluent COD and its removal efficiencies are given. At pH 2.0 effluent COD was 32120 mgL^{-1} with 15.92% of COD removal. By increasing pH, COD removal efficiency increased. Maximum COD removal was achieved at pH 3.0 and removal efficiency was 48.1%. Over pH 3.0, effluent COD increased and removal efficiency decreased to 31.6%.

Colour is a specific property of the leachate. Fenton process has been widely used in colour removal applications. So, in this study colour removal efficiency of Fenton process on leachate was investigated. During the studies, over 95% of colour removal was observed at all the pH values employed except pH 2.0. Although maximum removal was apparent at pH 3.5, COD removal efficiency was higher at pH 3.0. Considering this, pH 3.0 was selected as optimum pH for leachate treatment by Fenton process. At pH lower than 3.5, H_2O_2 and ferrous ions are more stable resulting in a redox system and decolorizing better. However, at pH values higher than 4.0, ferrous ions easily form ferric ions which have a tendency to produce ferric hydroxo complexes [26].

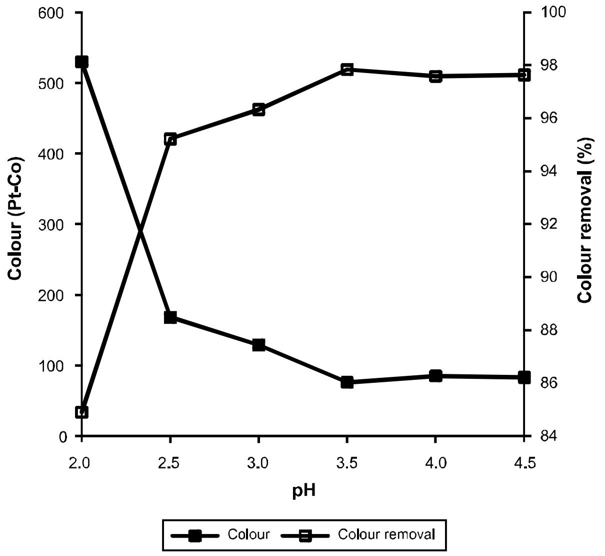

Figure 2. Effluent colour and its removal at different pH values (H_2O_2 = 10000 mgL^{-1}, Fe^{2+} = 3000 mgL^{-1}).

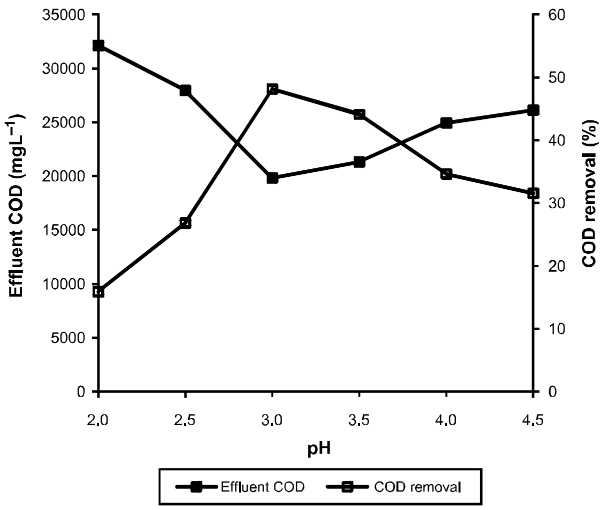

Figure 1. Effluent COD and COD removal at different pH values (H_2O_2 = 10000 mgL^{-1}, Fe^{2+} = 3000 mgL^{-1}).

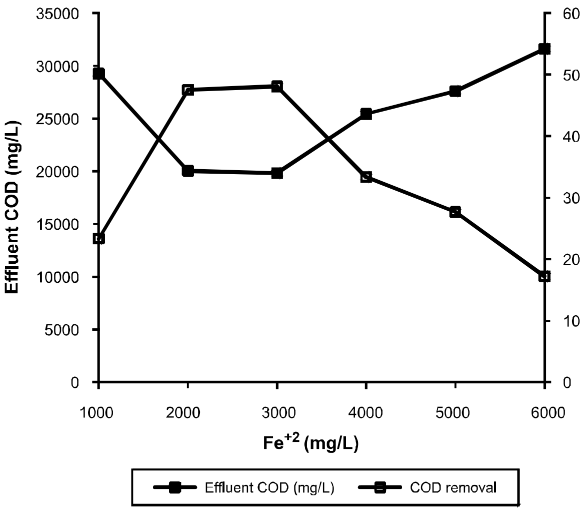

Figure 3. Effluent COD and its removal at different Fe^{2+} dosages (H_2O_2 = 10000 mgL^{-1}, pH = 3).

3.2. *Effect of Fe^{2+} dosages*

Effect of Fe^{2+} dosages on the COD removal efficiency is shown in Figure 3. At the concentration of 2000 mgL^{-1}, removal efficiency was 47.5% and it was accepted as optimum dosage. Although, COD removal was slightly high at the 3000 mgL^{-1} Fe^{2+} the difference was not significant. Effluent COD decreased by increasing the dosage of Fe^{2+}above 3000 mgL^{-1}. This result compares well with the study of Tang and Huang [27] in Fenton process for oxidizing organic pollutants, neither Fe^{2+} nor H_2O_2 should be overdosed due to their scavenging effect.

Figure 4 shows effluent colour and colour removal versus Fe^{2+} concentrations. Although colour removal was the highest at 3000 mgL^{-1} Fe^{2+} concentration and was 97.3%, 2000 mgL^{-1} was selected as the optimum dosage due to the higher COD removal. At this concentration, colour removal efficiency was 96.4% and effluent colour was 126 Pt-Co. Similar results were obtained in the study of Primo *et al.* [28] and they indicated that the remaining colour after oxidation was mainly due to the presence of iron in effluent. There was no clear difference in colour removal efficiency between the lowest and highest concentrations of Fe^{2+}. So colour in effluent was negligible. This change was probably due to changes in the nature of the compounds present in the leachate [28].

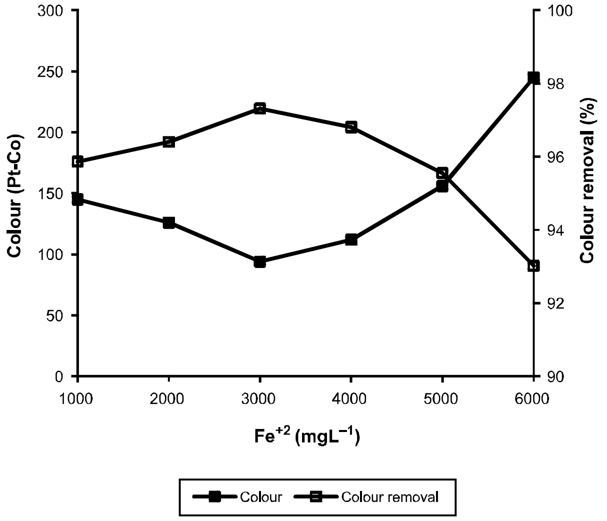

Figure 4. Effluent colour and its removal at different Fe^{2+} dosages (H_2O_2 = 10000 mgL^{-1}, pH = 3).

3.3. *Effect of H_2O_2 dosages*

The COD removal efficiency did not increase with the dosage of H_2O_2; from Figure 5 it can be noted that increases until a concentration of 5000 mgL^{-1} are achieved, then decreases occur. Landfill leachates are composed of a complex mixture of organic matter. During the oxidation step, more decomposition of organic matter provides more additional COD removal. This continues until formation of the end by-products of oxidation reactions are mainly made of short chain organic acids that are difficult to be further oxidized [14].

Figure 5 shows the effect of H_2O_2 dosages on the COD removal efficiency. The increase in the hydrogen peroxide concentrations resulted a decrease in the effluent COD. After 5000 mgL^{-1} H_2O_2 concentration

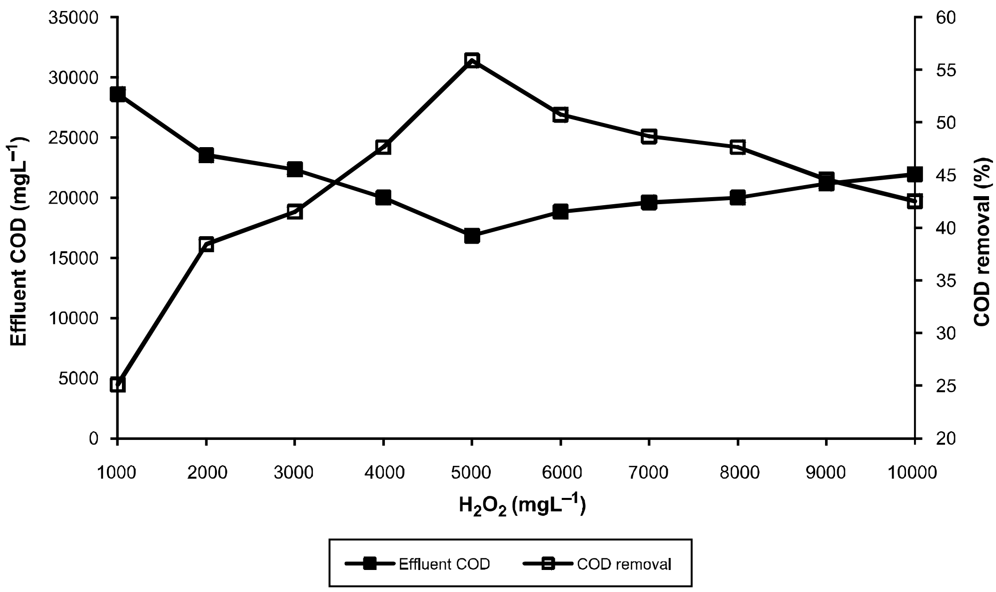

Figure 5. Effluent COD and its removal at different H_2O_2 dosages (Fe^{2+} = 2000 mgL^{-1}, pH = 3).

effluent COD increased and at this concentration, removal efficiency was 55.9%. This was accepted as an optimum dosage and after this dosage, COD removal efficiency decreased. The presence of H_2O_2 in a large quantity can act as a scavenger for the OH radicals, thus reducing the kinetic rate of Fenton process [16].

Chloride and sulphate ions form complexes with iron and less reactive inorganic radicals than OH^-. These phenomena cause reduction of organic matter removal [29]. In this study, wastewater contains relatively high chloride ions (3240 mgL^{-1}), which could reduce oxidation of organic matter.

Figure 6 shows effluent colour and its removal against H_2O_2 concentration. At the lowest hydrogen peroxide concentration colour removal was high and removal efficiency was 54.4%. Colour removal increased as H_2O_2 dose increased and until 3000 mgL^{-1} significant effect on colour removal was obtained. So it was determined that the optimum dosage for COD removal was appropriate for colour removal, too.

In this study, 2000 mgL^{-1} Fe^{2+} and 5000 mgL^{-1} H_2O_2 at pH 3 were determined as optimum concentrations. These concentrations are equal to 4.16:1 molar ratio of H_2O_2 to Fe^{+2}. Such ratios can be variable according to the characterization of leachate. Thus, Pala and Erden [30] reported that molar ratio of H_2O_2 to Fe^{2+} was 1.6:1 whereas Kim and Huh [31] found an optimal molar ratio of H_2O_2 to Fe^{2+} 12.5:1 in batch tests. Also Lopez *et al.* [14] concluded a molar ratio of H_2O_2 to Fe^{2+} of 19.8:1 for the treatment of raw leachate in batch test.

At the optimum condition, BOD_5 was decreased from initial value 22000 mgL^{-1} to 10800 mgL^{-1}. BOD_5/COD ratio increased from 0.58 to 0.64. Similar findings were reported in other studies. Barnes *et al.* [32] indicated that by using Fenton process BOD/COD ratio increased from 0.44 to 0.71 and Goi *et al.* [33] found that it is increased from 0.35 to 0.71. In our study BOD/COD ratio increasing was relatively smaller than other studies due the leachate age and its composition.

4. Conclusions

In treatment of young leachate that contains relatively high COD, Fenton process can be used as a pretreatment or improving BOD_5/COD ratio stage. The effects of major parameters on the Fenton process were evaluated using a lab scale reactor. A figure of 55.9% of COD removal was obtained by Fenton process at the dosages of 2000 mgL^{-1} Fe^{2+} and 5000 mgL^{-1} H_2O_2. In colour removal studies, it was determined that Fenton had high efficiency on colour removal and over 88% of colour was removed at all dosages of reagents. Optimal molar ratios of H_2O_2 to Fe^{2+} in the treatment of landfill leachate by Fenton reactions are variable due to complex content of landfill leachate. Improvement in BOD_5/COD ratio by Fenton process was also investigated in this study and it was found that the ratio increased from 0.58 to 0.64. From all these results, Fenton oxidation has been found to be satisfactory for young landfill leachate treatment with a high of 38200 mgL^{-1} COD concentration. It can be concluded that Fenton process is effective on not only old leachate but also young leachate, too.

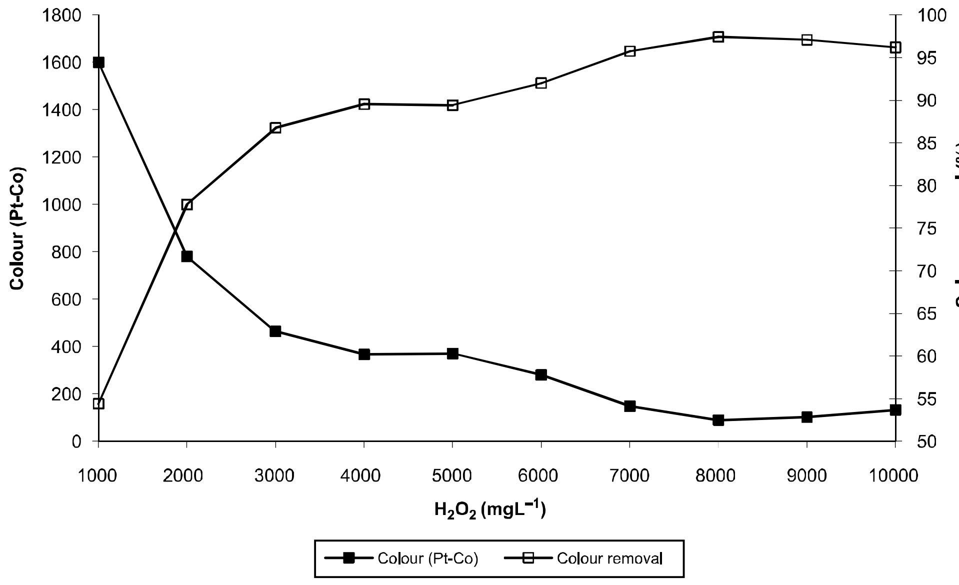

Figure 6. Effluent colour and its removal at different H_2O_2 dosages (Fe^{2+} = 2000 mgL^{-1}, pH = 3).

References

[1] Y. Deng and J.D. Englehardt, *Treatment of landfill leachate by the Fenton process,* Water Res. 40 (2006), pp. 3683–3694.

[2] TURKSTAT, Turkish Statistical Institute, Environmental Statistics. Solid waste statistics of municipalities 2008, http://www.turkstat.gov.tr; accessed 10 September 2008.

[3] B. Nas, T. Cay, F. Iscan, and A. Berktay, *Selection of MSW landfill site for Konya, Turkey using GIS and Multi-Criteria Evaluation,* Environ. Monit. Assess, 160 (2010), pp. 491–500.

[4] A. Goi, Y. Veressinina, and M. Trapido, *Combination of ozonation and the Fenton processes for landfill leachate treatment: Evaluation of treatment efficiency,* Ozone-Sci. Eng. 31 (2009), pp. 28–36.

[5] L. Chiang, J. Chang, and C. Chung, *Electrochemical oxidation combined with physical-chemical pretreatment processes for the treatment of refractory landfill leachate,* Environ. Eng. Sci. 18 (2001), pp. 369–378.

[6] D.H. Ahn, C. Yun-Chul, and C. Won-Seok, *Use of coagulant and zeolite to enhance the biological treatment efficiency of high ammonia leachate,* J. Environ. Sci. Heal. Part A 37 (2002), pp. 163–173.

[7] E. Castillo, M. Vergara, and Y. Moreno, *Landfill leachate treatment using a rotating biological contactor and an upward-flow anaerobic sludge bed reactor,* Waste Manage. 27 (2007), pp. 720–726.

[8] O.N. Agdag and D.T. Sponza, *Anaerobic/aerobic treatment of municipal landfill leachate in sequential two-stage up-flow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) systems,* Process Biochem. 40 (2005), pp. 895–902.

[9] D. Trebouet, J.P. Schlumpf, P. Jaounen, and F. Quemeneur, *Stabilized landfill treatment by combined physico-chemical-nanofiltration processes,* Water Res. 35 (2001), pp. 2935–2942.

[10] J.L. Morais and P.P. Zamora, *Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates,* J. Hazard. Mater. 123 (2005), pp. 181–186.

[11] A.I. Zouboulis, X.-L. Chai, and I.A. Katsoyiannis, *The application of bioflocculant for the removal of humic acids from stabilized landfill leachates,* J. Environ. Manage. 70 (2004), pp. 35–41.

[12] H.A. Aziz, S. Alias, M.N. Adlan, A.H. Faridah, A.H. Asaari, and M.S. Zahari, *Colour removal from landfill leachate by coagulation and flocculation processes,* Bioresource Technol. 98 (2007), pp. 218–220.

[13] H. Zhang, H.J. Choi, and C.P. Huang, *Optimization of Fenton process for the treatment of landfill leachate,* J. Hazard. Mater. 125 (2005), pp. 166–174.

[14] A. Lopez, M. Pagono, A. Volpe, and A.C.D. Pinto, *Fenton's pre-treatment of mature landfill leachate,* Chemosphere 54 (2004), pp. 1005–1010.

[15] Y. Deng, *Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate,* J. Hazard. Mater. 146 (2007), pp. 334–340.

[16] T.A. Kurniawan, W. Lo, and G. Chan, *Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate,* J. Hazard. Mater. 129 (2006), pp. 80–100.

[17] C.D. Iaconi, R. Ramadori, and A. Lopez, *Combined biological and chemical degradation for treating a mature municipal landfill leachate,* Biochem. Eng. J. 31 (2006), pp. 118–124.

[18] S.H. Gau and F.S. Chang, *Improved Fenton method to remove recalcitrant organics in landfill leachate,* Water Sci. Technol. 34 (1996), pp. 455–462.

[19] Y. Deng and J.D. Englehardt, *Electrochemical oxidation for landfill leachate treatment,* Waste Manage. 27 (2007), pp. 380–388.

[20] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater,* 21th ed., APHA, AWWA, WPCF, Washington DC, 2005.

[21] N. Azbar, T. Yonar, and K. Kestioğlu, *Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent,* Chemosphere 55 (2004), pp. 35–43.

[22] G.E. Ustun, S.K. Solmaz Akal, and A. Birgul, *Regeneration of industrial district wastewater using a combination of Fenton process and ion exchange* – a case study. Resour. Conserv. Recy. 52 (2007), pp. 425–440.

[23] H. Zhang, H.J. Choi, and C.P. Huang, *Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor,* J. Hazard. Mater. 136 (2006), pp. 618–623.

[24] D. Hermosilla, M. Cortijo, and C.P. Huang, *Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton process,* Sci. Total Environ. 407 (2009), pp. 3473–3481.

[25] F. Wang, D.W. Smith, and M.G. El-Din, *Application of advanced oxidation methods for landfill leachate treatment – A Review,* J. Environ. Eng. Sci. 2 (2003), pp. 413–427.

[26] S. Meric, D. Kaptan, and T. Olmez, *Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process,* Chemosphere 54 (2004), pp. 435–441.

[27] W.Z. Tang and C.P. Huang, *2,4-Diclorophenol oxidation kinetics by Fenton's reagent,* Environ. Technol. 17 (1996), pp. 1371–1379.

[28] O. Primo, M.J. Rivero, and I. Ortiz, *Photo-Fenton process as an efficient alternative to the treatment of landfill leachates,* J. Hazard. Mater. 153 (2008), pp. 834–842.

[29] E.M. Siedlecka and P. Stepnowski, *Application of Fenton and Fenton-like process for the oxidation of MTBE and its by-products in saline wastewaters,* Proceedings of the 10th International Conference on Environmental Science and Technology, 5–7 September, Kos Island, Greece, 2007.

[30] A. Pala and G. Erden, *Chemical pretreatment of landfill leachate discharged into municipal biological treatment systems,* Environ. Eng. Sci. 21 (2004), pp. 549–557.

[31] Y.K. Kim and I.R. Huh, *Enhancing biological treatability of landfill leachate by chemical oxidation,* Environ. Eng. Sci. 14 (1997), pp. 73–79.

[32] D. Barnes, X. Li, and J. Chen, *Determination of suitable pretreatment method for old-intermediate landfill leachate,* Environ. Technol. 28 (2007), pp. 195–203.

[33] A. Goi, Y. Veressinina, and M. Trapido, *Fenton process for landfill leachate treatment: evaluation of biodegradability and toxicity,* J. Environ. Eng. 136 (2010), pp. 46–53.