Asian Journal of Water, Environment and Pollution, Vol. 16, No. 3 (2019), pp. 91-97.
DOI 10.3233/AJW190037

The Efficiency of Anaerobic Biological Method Integrated with Fenton and Nanosilica Absorbent in the Treatment of Solid Waste Leachate

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Received July 27, 2018; revised and accepted November 28, 2018

Abstract: Environmental damages and pollution induced by the leachate of landfills are a source of concern for citizens. The present empirical study explored the anaerobic treatment of mature leachate of Saravan-Rasht in Guilan province, Iran and the efficiency of the Fenton process at pH 3-8 under different Fe^{2+} and H_2O_2 rates and oxidation retention time of 15-135 minutes using the Bench-scale method in laboratory conditions. In addition, the impact of nanosilica absorbent at the rates of 0.25-6.5 g L^{-1} was examined at retention times of 15-75 minutes and pH 3-11. BOD, COD and TSS removal efficiency was measured at all stages. It was found that BOD, COD and TSS removal efficiency at leachate anaerobic treatment stage was 63.7, 37.95 and 21% in the sample containing seed. BOD, COD and TSS removal efficiency exhibited an ascending trend in nanosilica absorbent as retention time was increased from 15 to 75 minutes, reaching 73, 70 and 58% at the retention time of 75 minutes, respectively. The results revealed that to treat mature leachate, anaerobic treatment should be first applied to remove biodegradable organic matter, and then the Fenton process and nanosilica absorbent should be used to remove resistant organic matter.

Key words: Anaerobic treatment, Fenton process, leachate, nanosilica absorbent, biodegradation.

Introduction

Site selection for the landfill has always been a serious challenge for humankind. The improper choice of the site may pollute water, soil, and air (Derakhshandeh and Beydokhti, 2014). The environmental hazards and contaminations by landfill leachate are a source of concern for common people (Asha and Latha, 2013). Leachate is very strong wastewater and a dark-coloured smelly liquid that percolates through the waste material and contains a wide range of suspended and dissolved organic matters, pathogens, and toxic compounds like heavy metals and heavy organic material (Atmaca, 2009). These factors combine together to produce a dark waste whose characteristics depend on landfill age (Javier et al., 2008).

Young leachate is usually formed within less than two years of the landfill and contains more organic fraction with relatively lower molecular weight than old leachate that is produced during anaerobic phase stabilization more than 10 years after waste disposal. Old leachate mainly contains organic matter, humic acid, and fulvic acid with relatively high molecular weight and stable properties resulting from less degradable organic matter. Leachate may contain high concentrations of several hazardous pollutants simultaneously. As landfill ages, the concentration of biodegradation-resistant matter with high molecular weight, e.g. humic and fulvic

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compounds, is increased. Young leachate can be treated with biological process, whilst it is inefficient for old leachate (Asha and Latha, 2013). The quality and quantity of landfill waste vary with the age of landfill. The leachate of urban landfills is characterized by high concentrations of organic matter, salts, nitrogen, and toxic elements (Sumanaweera, 2010).

The composition of leachate determines its treatability. Leachate is treated with different processes including anaerobic decomposition, chemical oxidation, chemical sequestration, activated carbon adsorption, and membrane processes (Haapea et al., 2002). Anaerobic treatment methods are more suitable for treating denser leachate. They have lower operating costs and create pathogen-free sediments (Im et al., 2001). Anaerobic process is the technology of the recent decade for waste treatment. It not only needs no air storage but also generates methane (Fang and Liu, 2001). CH_4 and CO_2 constitute the main products of final anaerobic digestion process. Anaerobic digestion is used for the disposal of organic waste in order to alleviate environmental hazards. Bio treatment processes cannot remove resistant organic matter, and further treatments are required for their removal (Ozturk et al., 2003). These processes are appropriate for the treatment of waste leachate at their initial stages where they have a high BOD_5/COD ratio, but they cannot be properly used to treat old leachate, which have a lower BOD_5/COD ratio and higher concentrations of toxic matter that is non-biodegradable (Yang and James, 2007).

Chemical treatment methods that are based on hydroxyl radical (OH°) are called advanced oxidation processes (AOP) (Perez et al., 2002). Organic matter oxidation by Fenton solution, referred to Fenton reaction, is a type of AOP (Lopez et al., 2004). This reaction can destroy many organic compounds with no toxic side effects. Another major advantage of this method is the simultaneous oxidation and coagulation that can remove more organic matter (Barbusinski and Filipek, 2009). The Fenton reaction method is relatively inexpensive and needs less time than other AOPs (Tengrui et al., 2007). Nanosilica is a very strong absorbent that is widely used in the industry. Due to its higher specific area, nanosilica has higher absorbance potential than the micrometre state at the nanoscale (Tzvetkova and Nickolov, 2012).

The present study aimed to explore the efficiency of anaerobic, Fenton, and nanosilica absorbent processes on the treatment of landfill leachate in terms of the removal of BOD, COD, and TSS. Also, the impact of pH was investigated on the removal performance of coagulant and nanosilica absorbent. The experiment focused on anaerobic biological integration with Fenton and nanosilica absorbent for leachate treatment in the Saravan region of Guilan Province, Iran.

Materials and Methods

To conduct the assays, 60 litres of raw old leachate of Saravan, Rasht were poured into polyethylene containers and were transferred to the laboratory of Department of Health, the Guilan University of Medical Science in Rasht, Iran. BOD, COD and TSS were analyzed by standard methods. Also, pH was measured by pH-meter (Testo 230) (Clesceri, 2005).

Laboratory Model

Five reactors made of glass were prepared with the volume of three litres (Figure 1). They were filled with 2.5 L leachate, 250 mg L^{-1} activated sludge as seed, and 3 mg L^{-1} dry milk as the nutrient. Then, they were capped, and a tube was mounted for biogas discharge. Then, the reactors were placed on a magnetic stirrer with the retention times of 5, 10, 15, 20, or 25 days. The control sample contained raw leachate without seed, but the other conditions were the same.

Optimum pH in the Anaerobic Reactor

The pH of the reactor containing anaerobic biotreatment + seed was 7.72 for 20-day retention time and it was 8.82 in the reactor containing control raw leachate for 20-day retention time. The present *in vitro* experiment explored the anaerobic treatment of mature leachate of

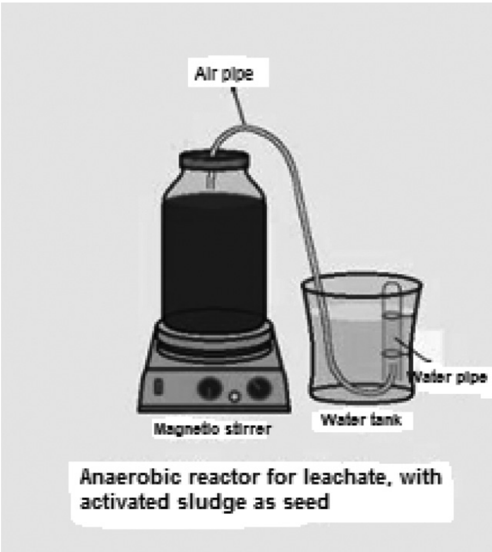

Figure 1: Anaerobic reactor with the retention time of 5-25 days.

Saravan and the efficiency of the Fenton process at pH 3-8 with different concentrations of Fe^{+2} and H_2O_2 at the retention time varying in the range of 15-135 minutes using the Bench-scale method. Also, the effect of nanosilica absorbent at various rates (0.25-6.5 g L^{-1}) was examined at the retention times of 15-75 minutes and pH of 3-11. At all stages, we evaluated the efficiency of BOD, COD and TSS removal.

Fenton Process Study in Biotreated Leachate

The Fenton process was studied once the anaerobic stage was terminated. The study used H_2O_2 solution with 35% mass percent, 1.13 mass density, and iron (II) sulfate content ($FeSO_4.7H_2O$). At the first stage in which Fe^{2+} had the rates of 200-2200 mg L^{-1} and H_2O_2 had the rates of 500-5500 mg L^{-1}, the reaction was triggered at various pH's of 3-8 using H_2O_2/Fe^{2+} mass to volume rate with the contact time of 60 minutes. Then, at a constant weight ratio of H_2O_2/Fe^{2+} in which the optimal pH was selected, the experiment was carried out under contact times of 15-135 minutes to find out the optimal retention time for the Fenton process.

Different quantities of H_2O_2 at the concentrations of 500-5500 mg L^{-1} were added to the sample with the optimal Fe^{2+} derived from the previous stage at optimal contact time and the optimal pH derived from the first and second stages. Then, the optimal quantity of H_2O_2 was derived and finally, the optimal molar ratio of H_2O_2/Fe^{2+} was calculated. All assays were conducted discontinuously in a 1L beaker using Jar-test device at ambient temperature (Kargi and Pamukoglu, 2003).

Nanosilica Efficiency

After nanosilica was prepared, the leachate derived from the Fenton process at the contact time of 15-75 minutes was placed on a shaker with nanosilica absorbent. After the optimal contact time was found, the experiment was continued at pH of 3-11 and the optimal pH was selected for TSS, COD and BOD removal. The experiment was carried out at optimal pH and contact time derived from stages 1 and 2 with different nanosilica rates of 0.25-6.5 g L^{-1}, and the optimal rate of nanosilica for TSS, COD and BOD removal was determined. Data were analyzed in MS-Excel Software Package.

Results and Discussion

Raw Leachate Specifications

The samples were analyzed in the laboratory to find out the specifications of the raw leachate (Table 1). As Figures 2 and 3 illustrate, BOD, COD and TSS removal

Table 1: Specifications of raw leachate in Saravan

Variable	*Quantity*
BOD	1400 mg L^{-1}
COD	2630 mg L^{-1}
pH	8.2
TSS	3580 mg L^{-1}

efficiency was increased as the retention time was increased to 20 days, reaching 63.7, 37.95 and 21% in leachate with seed and 25, 15.58 and 36.55% in control leachate, respectively. When retention time exceeded 25 days, the efficiency started to decrease. So, the optimal retention time was found to be 20 days for the anaerobic reactor. Rahimi et al. (2016) and Agdag and Sponza (2005) reported that COD removal efficiency was increased to 64.86 and 89% in anaerobic digestion at the retention time of 15 days, respectively (Rahimi et al., 2016). In Ghosh et al. (2013) and Kahar et al. (2017), BOD, COD and TSS removal efficiency reached 85.9, 79.3 and 51% after 35 days, respectively (Kahar et al., 2017). Our findings are partially consistent with Rahimi et al. (2016).

At the H_2O_2 rate of 500-5500 mg L^{-1} and Fe^{2+} rate of 200-2200 mg L^{-1}, the highest BOD, COD and TSS removal efficiency was observed at pH 3, so it was selected as the optimal pH. Ahmadian et al. (2014) reported that COD removal efficiency was increased as pH was enhanced to 3. When solution pH increases

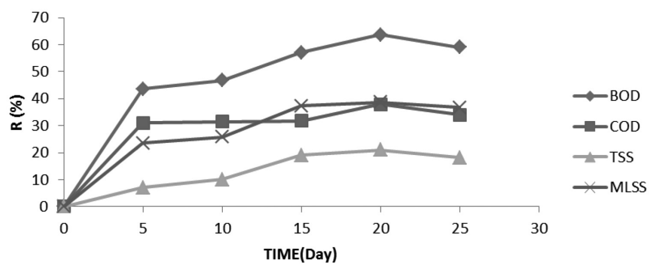

Figure 2: BOD, COD and TSS removal efficiency in anaerobic biological treatment of leachate + seed at retention times of 5, 10, 15, 20 and 25 days.

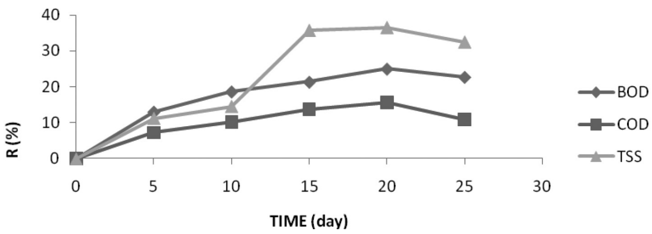

Figure 3: BOD, COD and TSS removal efficiency in anaerobic biological treatment of control leachate at retention times of 5, 10, 15, 20 and 25 days.

excessively, Fe^{2+} precipitates as $Fe(OH)_3$ resulting in the loss of Fe^{2+} concentration in the solution (Fu et al., 2009). This is in agreement with our findings. Our results for the retention time of 105 minutes is supported by Ahmadian et al. (2013)'s report (Figure 4).

Figure 5 displays the impact of Fe^{2+} concentration on TSS and COD removal efficiency at pH 3 and retention time of 105 minutes with constant H_2O_2 rate and Fe^{2+} rates varying in the range of 200-2200 mg L^{-1}. The optimal Fe^{2+} rate was found to be 1800 mg L^{-1}. Ahmadian et al. (2014) found that the optimal Fe^{2+} rate was 1600 mg L^{-1} for COD and TSS removal. The very high rates of Fe^{2+} inhibit the combination of OH radicals with Fe^{2+} ions and reduce the degradation of pollutants. The quantities reported by these researchers are lower than what we found in the present study.

Ahmadian et al. (2014) found that the optimal H_2O_2 concentration was 3000 mg L^{-1} for COD and TSS removal. Shafieiyoun et al. (2011) reported when the H_2O_2 concentrations was more than 2.7, consumption of hydrogen peroxide remained relatively constant, hence this concentarion was selected for the subsequent assays. The optimal H_2O_2 concentration was found to be 4500 mg L^{-1} in the present study (Figure 6). The values reported by these researchers are smaller than our findings.

The optimal concentration of hydrogen peroxide is important because firstly its excessive increase can escalate the cost of the process and secondly fewer activated hydroxyl radicals are formed, reducing the efficiency of oxidation process (Pignatello et al., 2006).

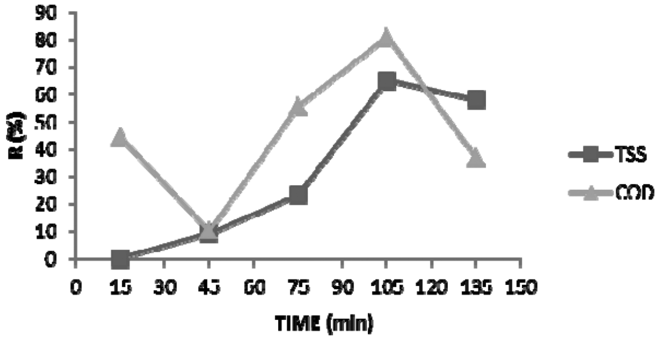

Figure 4: The effect of contact time on COD and TSS removal at pH 3 and H_2O_2/Fe^{2+} of 1800/4500.

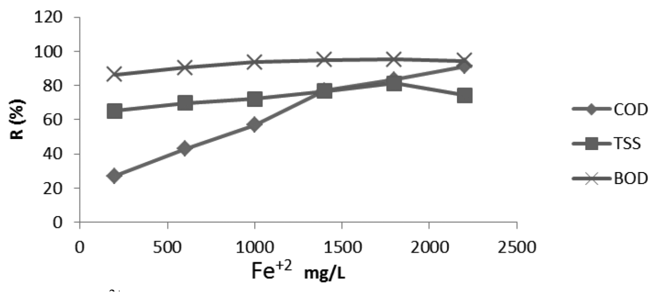

Figure 5. The effect of Fe^{2+} concentration on BOD, TSS and COD removal efficient at pH 3 and retention time of 105 minutes.

BOD, COD and TSS efficiency in the Fenton process was found to be 95.9, 75 and 88.4% at Fe^{2+} rate of 1800 mg L^{-1} and 95.3, 83.3 and 81.4% at H_2O_2 rate of 4500 mg L^{-1}, respectively.

Table 2: The effect of pH in the Fenton process

H_2O_2/Fe^{2+}	*pH*						*Removed COD or TSS (mg/L)*
	3	*4*	*5*	*6*	*7*	*8*	
500/200	840	950	1600	1699	1738	1779	COD
	465	255	160	545	760	625	TSS
1500/600	490	660	410	710	1210	1460	COD
	55	130	78	495	345	445	TSS
2500/1000	370	440	415	398	550	540	COD
	24	190	65	325	20	50	TSS
3500/1400	130	80	100	110	330	60	COD
	45	150	66	240	95	160	TSS
4500/1800	120	40	50	20	220	50	COD
	43	110	111	290	125	430	TSS
5500/2200	150	129	149	81	225	240	COD
	48	99	131	270	120	530	TSS

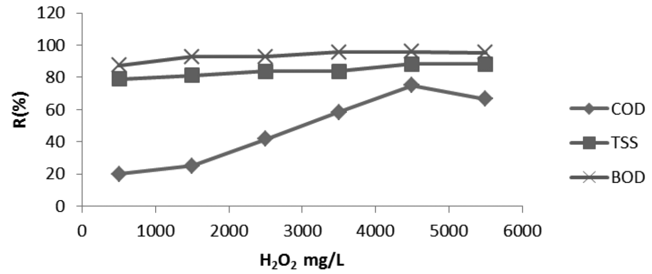

Figure 6: The effect of H_2O_2 on BOD, TSS and COD removal efficient at pH 3 and retention time of 105 minutes.

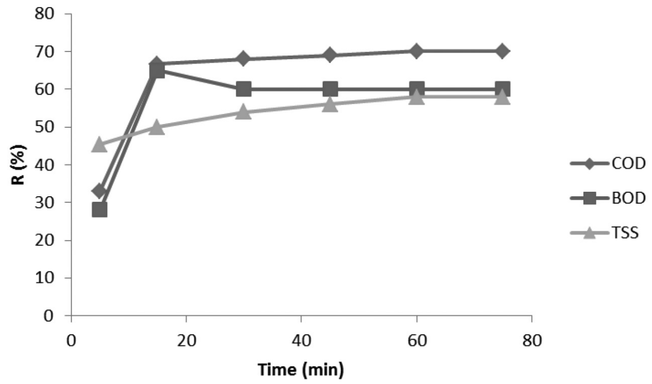

Figure 7. COD, TSS and BOD removal percent at different retention times with 4 g L^{-1} nanosilica absorbent.

Nanosilica absorbent had an ascending trend in TSS, COD and BOD removal after retention time of 15-75 minutes. BOD, COD and TSS removal efficiency at the retention time of 75 minutes was 73, 70 and 58%, respectively. Falahati et al. (2018) found that COD removal efficiency was 86% at contact time of 10 minutes and that as contact time was extended, the efficiency was. Lee Mao et al. (2012) reported that the optimal contact time was 30 minutes for alum and ferric chloride at the dosage of 2000 mg L^{-1} and that TSS and COD removal efficiency was 40 and 18% for alum and 90 and 52% for ferric chloride, respectively. Since the excellent integrity of nanoabsorbents increases their area remarkably, they can reach their maximum absorption potential in a short time (Yang et al., 2015). The results reported by Falahati et al. (2018) are consistent with our findings according to which BOD, COD and TSS removal efficiency had an ascending trend after the retention time of 15 minutes (Figure 7).

The results revealed that BOD removal efficiency increased with pH until it reached 6 beyond which the removal efficiency was improved until pH 9 (Figure 8). The optimal pH for TSS removal was found to be 7. Lee Mao et al. (2012) found that optimal removal efficiency of pollutants with ferric chloride and alum was obtained at pH 7 and afterward, it gradually declined. According to Pavithra and Shanthakumar (2017), pH's exceeding 6 were effective on BOD and COD removal efficiency. With nanosilica at pH 6, BOD and COD removal efficiency was 62.5 and 73.09%, respectively (Pavithra and Shanthakumar, 2017). Maleki et al. (2009) reported that iron hydroxides precipitate at pH 9 and that at lower pH's, hydrogen ions derived from the hydrolysis of the metals compete with organic ligands, resulting in lower efficiency of their removal. At higher pH's, hydroxide ions compete with organic compounds for metal absorption, and metallic hydroxyls mainly precipitate at these pH's. Our results are consistent with Maleki et al. (2009).

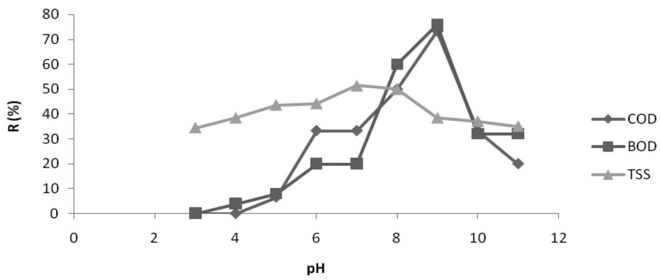

Figure 8. COD, TSS and BOD removal percent at different pH's with 4 g L^{-1} nanosilica absorbent.

According to Shabiinam and Dikshit (2011)'s results about coagulation with calcium hydroxide at the rate of 15 g L^{-1} showed that the highest COD removal efficiency was obtained at pH 8 reducing COD by 50%. At calcium hydroxide rate of 25 g L^{-1}, COD removal efficiency was over 69%. Lee Mao et al. (2012) reported that the highest effective removal efficiency of silica nanoparticles at the dosage of 4 g L^{-1} was 50.35 and 62.59% for BOD and COD removal, respectively. Nateghi et al. (2011) found that BOD and COD removal efficiency was augmented as poly aluminum chloride (PACl) coagulator was increased to 50 mg L^{-1}. We found that the optimal dosage for nanosilica absorbent was 1 g L^{-1} and BOD, COD and TSS removal efficiency was 28, 26.7 and 24.8%, respectively (Figure 9). These findings are in agreement with Nateghi et al. (2011) and Lee Mao et al. (2012). Our results revealed that in order to treat mature leachate that contains a high deal of non-biodegradable organic matter, we should first apply anaerobic treatment to remove biodegradable organic matter and then, we can proceed to the Fenton process and the use of nanosilica absorbent, that removes resistant, non-biodegradable organic matter, reduces the economical costs.

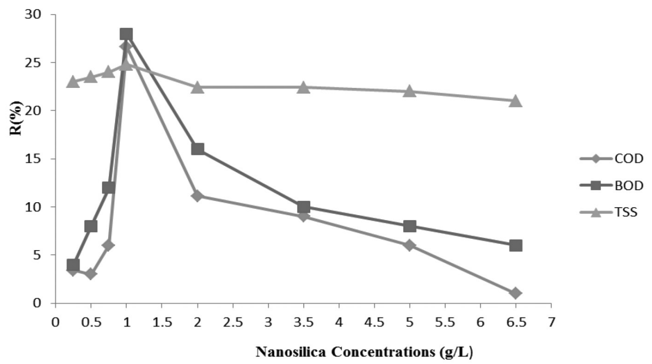

Figure 9. The effect of different dosages of nanosilica absorbent on COD, TSS and BOD removal process (retention time = 15 minutes, pH = 9).

Conclusions

The results revealed that to treat mature leachate, anaerobic treatment should be first applied to remove biodegradable organic matter, and then the Fenton process and nanosilica absorbent should be used to remove resistant organic matter.

Acknowledgements

This research was supported by Guilan University of Medical Sciences, Rasht, Iran.

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