Int. J. Environ. Res., 5(2):255-270, Spring 2011
ISSN: 1735-6865

Anaerobic Removal of COD from High Strength Fresh and Partially Stabilized Leachates and Application of Multi stage Kinetic Model

Safari, E.[1*], Jalili Ghazizade, M.[2], Shokouh, A.[3] and Nabi Bidhendi, Gh. R.[2]

[1] Department of Civil Engineering, Queen's University, Ellis Hall, 58 University Avenue, Kingston, Ontario, K7L 3N6, Canada

[2] Graduate Faculty of Environment, University of Tehran, P.O.B.14155-6135, Tehran, Iran

[3] Department of Civil and Environmental Engineering, Amirkabir Technical University, Tehran, Iran

Received 23 Feb. 2010; Revised 2 Oct. 2010; Accepted 10 Oct. 2010

ABSTRACT: High strength fresh leachates generated at a new disposal trench, compost plant and partially stabilized leachate of an older trench were characterized in terms of anaerobic degradation at laboratory batch scale at 35°C. Fresh leachate had extremely high COD of 66,710 – 89,501 mg/L along with low pH of 4.1-5.9 in contrast to older and therefore partially stabilized leachate with a COD of about 19,000 mg/L and higher pH of 8.4. Filtration of fresh leachate samples showed to have considerable effect on continuation of degradation as for the unfiltered samples, degradation nearly stopped after a slight reduction in COD. As a first attempt, it was shown that a considerably better fit was achieved for COD variations of filtered fresh leachate samples using first order multistage kinetic model based on which hydrolysis was found to have the smallest rate, therefore being the rate limiting stage in anaerobic degradation process.

Key words: Landfill, Soluble substrate, High strength leachate, Anaerobic degradation, Multistage kinetic model

INTRODUCTION

Landfilling of municipal solid waste (MSW) has been economically quite accepted method for municipal solid waste (MSW) disposal throughout the world. (El-Fadel and Findikakis, 1997; Komilis *et al.*, 1999; Surmacz-Gorska, 2001). From an environmental perspective the two main issues associated with land disposal of wastes are landfill gas (LFG) and leachate, which are generated as the landfill develops and the waste undergoes biological degradation (Haarstad and Maehlum, 1999; Kurniawan *et al.*, 2006). Landfill leachate, which is often characterized as a high strength wastewater with high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), chloride and ammonia nitrogen (Keenan *et al.*, 1984, Nwabanne *et al.*, 2009, Abdul Aziz *et al.*, 2010, Saeedi *et al.*, 2010) has also a varying quality corresponding to landfill age. Leachate strength depends on a number of influencing factors among which climatic conditions, waste characteristics and disposal scheme and state can considerably alter the leachate quality (Wintgens *et al.*, 2003). Leachate management and treatment should be considered as an integrated part of landfill operation (Kennedy and Lentz, 2000). Leachate treatment methods must be selected in accordance with the actual characteristics of the particular leachate (Zhang *et al.*, 2006, Renou et al, 2008); however efforts are to be made in minimizing the leachate strength through upstream management. Leachate strength can be considerably different from one landfill to another and especially from one country to another. Composition of MSW in developing countries is significantly different from developed ones in terms of organic content. As an instance MSW in developing countries has often very high organic fraction in contrast to developed countries. The high organic waste can lead to generation of strong leachate containing high concentrations of organic substrate expressed as COD and BOD_5 of over tens of thousands of ppm. High strength leachate can mainly be characterized as having high organic content, ammonia nitrogen and chloride (Safari and Nabi, 2007). Even in arid and semiarid climates (e.g. many cities in Iran), a considerable amount of leachate is generated resulting

---

*Corresponding author E-mail: edwin.safari@ce.queensu.ca

from the high moisture content that is associated with the relatively high fraction of organic materials in the waste (Safari and Baronian, 2002). Typical leachate treatment processes and systems found in the literature seem to deal with rather lower COD concentrations. Although treatment processes having been efficient in removal of certain constituents from leachate in many cases in other countries, the removal characteristics and kinetics could be different in case of high strength leachate as found in most waste dumpsites in Iran. Various physical, chemical and biological processes can be and often are involved in leachate treatment (Renou *et al.,* 2008). Neither of physical or chemical processes can be considered complete treatment processes as the contaminant of interest is either chemically transformed into other compounds within sludge texture or physically removed from solution. On the other hand, biological reactions transform the organic compounds into more stable inorganic materials and gas products. Although, biological methods are usually preferred over physicochemical ones to remove the majority of pollutants (Henze *et al.,* 1995), application of biological treatment alone cannot provide a complete treatment scheme considering the leachate characteristics and a combination of physical, chemical and biological methods are required (Zgajnar Gotvajna *et al.,* 2009, Berrueta *et al.,* 1996; Robinson and Barr, 1999; Chiang et al., 2001; Iaconi *et al.,* 2006; Tsilogeorgis et al., 2008; Kochany and Kochany, 2009; Wang *et al.,* 2009). However biological treatment processes can be considered as the core stage in the overall treatment system as there is a relatively high organic content in the leachate (Bohdziewicz and Kwarciak, 2008). Considering the high concentration of organic compounds within landfill leachate, anaerobic processes seem to be favorable at least as the first stage of biological treatment systems (Bohdziewicz et al, 2008, Wang and Banks, 2007 and Maranon et al, 2006). The main reasons behind this are lower operating costs, less sludge production and more importantly possibility of biogas generation for energy recovery purposes (Kennedy and Lentz, 2000). Anaerobic treatment process is furthermore preferred for treatment of high strength leachate such as young landfill leachate, with high BOD and BOD/COD ratio (Surmacz-Gorska, 2001).

Land disposal of waste and partial composting of the organic fraction of the MSW are the sole waste disposal methods in Iran (Rasapoor *et al.,* 2009; Nasrabadi *et al.,* 2008, Abduli *et al.,* 2007). Waste is disposed of in land with limited or no environmental control measures. Most of the waste dumps are constructed over natural clayey deposits which can act as a natural barrier towards migration of leachate to subsurface environments. The depth of groundwater, if any regional aquifer system exists, in many cases (i.e. arid and semiarid regions) may well be in excess of tens to hundreds of meters. However, leachate generated at such sites is often drained through the natural barrier underneath the dumpsite into existing depressions or constructed ponds where it is stored with no further treatment. The ponds often experience overflow to nearby seasonal or permanent surface water bodies due to incompatible capacity. The ponds can be a few meters deep resulting in anaerobic degradation of organic rich leachate and consequent emission of malicious odors and greenhouse gases. In most of the larger cities, the dumpsites are accompanied with a compost plant, where a portion of the incoming MSW undergoes Windrow composting process followed by handpicking of non-compostable (i.e. nonorganic) materials from the incoming waste stream. Due to the high moisture content of the incoming waste, significant amount of leachate is also generated at the compost facility both underneath the receiving pad or conveyer belt as well as the fermentation hall. In fact leachate generated at compost plants is the moisture content in excess of the field capacity of the waste under practically no mechanical stress.

The main objective of this study was to make an initial assessment on the possibility of anaerobic treatment of the extremely high strength leachate streams generated at Mashhad landfill and the associated compost plant. This paper presents the results of leachate characterization and laboratory scale anaerobic degradation characteristics. Attempts were made for the first time also to preliminarily characterize the anaerobic degradation kinetics using multistage kinetic models in addition to single stage first and second order ones.

Mashhad Landfill operating since 1975 is located in an arid region southeast of city of Mashhad and currently receives over 1400 tons of MSW every day. A compost plant was also recently implemented and is operated at 300-400 tons of MSW per day. The waste being disposed of at this site has about 65% by weight of organic material (i.e. mainly food waste) which has a high (i.e. about 70% by dry weight) of moisture content. Landfill has no constructed bottom liner. However the waste disposal trenches are developed over a natural clayey deposit which can in turn act as a barrier to downward migration of leachate. This can be confirmed by the fact that considerable amount of leachate is typically drained out of the trenches and flows to a nearby pond due to gravity. The natural topography of the site is slightly modified to form waste disposal trenches where waste is dumped and covered with local soil on a daily basis. Trenches are filled with waste and when full, are covered using a layer of local soil with no additional impermeable and topsoil layers.

The site experiences an annual precipitation and evaporation of about 250mm and 2000mm respectively. The significantly higher rates of evaporation compared to precipitation would suggest small amounts of leachate generation at the site. On the contrary, considerable flow rates of leachate (i.e. over 120m^3/d) are observed even during dry season. At the compost plant where incoming waste is transferred to a handpicking line followed by a fermentation hall, about 25-35 m^3/d of leachate is generated and collected in an underground tank. This relatively high amount of leachate can be associated with the high organic fraction of the MSW which in turn has high moisture content. In addition, this high moisture of the organic fraction of the waste coupled with the low rate of atmospheric precipitation results in a strong undiluted leachate rich in organic compounds in particular at the early stages of waste disposal.

Considering the two main sources of leachate generation (i.e. the disposal site and the compost plant), leachate sampling was carried out in two sessions from relatively young landfill trench (i.e. <1 year of age), relatively old landfill trench (i.e. >10 years of age) and from the tank receiving leachate from the two main components of the compost plant (i.e. receiving pad and the fermentation hall). The first session of leachate sampling was carried out through taking triplicate samples from the channel originating from underneath a trench which had been in operation for more than ten years. This is referred to herein as old trench leachate (OTL). This trench however was closed having reached its final capacity and a separate new trench was opened at the time of second leachate sampling session. The leachate sampled from this section of the landfill is referred herein to new trench leachate (NTL). Considering the fact that the leachate generated at the compost plant is stored in the underground tank for one to three days after which it is transferred to the leachate storage pond using a tanker, and that it is generated from the same type of waste being disposed of in the landfill, it was assumed to represent fresh leachate (FL). General quality constituents of the three leachate samples along with the concentrations of selected heavy metals are summarized in Tables 1 and 2 respectively.

As shown in the Tables 1 and 2 fresh leachate samples taken from the compost plant (FL) are significantly stronger in terms of concentrations of the main constituents. Concentration of total (i.e. unfiltered) and soluble (filtered using paper filter No. 40) COD of FL were about 4.7 times greater than that of OTL; indicating a considerable degradation of waste/

Table 1 . General quality constituents of leachates from Mashhad landfill and compost plant (values in mg/L except for pH)

Leachate	pH	BOD$_5$	COD		Cl^-	$NH4^+$-N	Total suspended Solids (TSS)
			Filtered	Unfiltered			
OTL	8.4	7,500-10,000	16,500	19,000	4,698-5,158	620-1,185	195-325
NTL	5.4*-5.9	-	66,710*	77,090*	5,998-6,098	740-985	18,124*
FL	4.1-5.1*	27,500-47,000	77,760*	89,501*	3,998-4,198	505-855	12,260-20,556*

*Quality of the samples used in anaerobic degradation tests, TSS: Total Suspended Solids

Table 2. Selected heavy metal constituents of leachates from Mashhad landfill and compost plant (values in mg/L except for pH)

Leachate	Zn	Ni	Cu	Cd	Fe	Mn	Pb	Cr	Hg
OTL	0.07-0.23	0.09-0.15	0.01-0.05	ND-0.01	1.02-1.08	0.04-0.05	0.07-0.57	0.02-0.06	0.009-0.012
NTL	4.77-5.26	0.17-0.22	0.03-0.10	0.06-0.07	10.64-11.66	0.38-0.49	0.80-0.89	NM	NM
FL	3.03-6.12	0.44-1.80	0.01-0.09	0.01-0.07	9.35-86.4	4.70-5.88	0.31-1.89	0.26-0.72	0.008-0.011

ND: Not Detected, NM: Not Measured

leachate organic content over a period of more than 10 years of old trench operation. Furthermore, concentration of NH_4^+-N is about the same in NTL, FL and OTL suggesting presence of anaerobic conditions within the old trench with practically no opportunity for the ammonia to be oxidized. Chloride as a conservative indicator of leachate quality was also found to be about the same in the three samples. More importantly, pH can be considered as a reasonable indicator of leachate (or landfill) age. Younger leachate typically has a low pH value of (e.g. about 5 as found in this study for FL and NTL). As the leachate quality deteriorates over time, the pH rises up (e.g. 8.4 as found in this study for OLT).

The high TSS in FL and NTL which was found to be orders of magnitude greater than that of OTL is a worthwhile observation. The low TSS concentration of OTL can be resulting from the fact that the leachate to some extent undergoes natural filtering when infiltrating through the layers of daily cover soil and the disposed of waste being placed over a long period of time. It appears that the fresh leachate (e.g. FL) has considerably high concentration of TSS. However it should be noted that the suspended solids within FL were relatively coarser particles consisting of mainly waste particles. These particles could have been removed through initial sieving step of the compost plant. The suspended particles of the NTL on the other hand were rather fine soil particles. This observation was done through visual comparison of the samples and it can be recommended to characterize the suspended solids by size and type in future studies. Particle size and soil type can influence the sorption process of heavy metals (Abduli and Safari, 1999). In general, heavy metal concentrations were not found in a range that could potentially slow down or inhibit the anaerobic degradation process. Heavy metal concentrations were found consistently orders of magnitude higher in NTL and FL which had a low pH compared to OTL with relatively higher pH values. This can be associated with the fact that most of the heavy metal content of the leachate can be in dissolved form at lower (i.e. acidic) pH values rather than possibly having been adsorbed (i.e. solid phase) on solid particles within the landfill and/or the leachate.

MATERIALS & METHODS

This study was carried out through the steps as shown in Fig. 1. After characterizing leachate streams in terms of general quality constituents and heavy metals as described above, an attempt was made to analyze anaerobic biodegradability through laboratory scale batch tests using mixture of OTL and FL following the same proportion determined at the site along with filtered and unfiltered samples of NTL and FL. Different kinetic models including simplified multistage kinetic models were tested on the soluble COD reduction observations. The main objective of this part of the study was to provide a basis for further treatability studies through answering the key questions being the extent and rate of anaerobic degradation (in terms of soluble COD removal) of high strength leachate with no pretreatment. It is worth noting that for the NTL and FL samples where TSS concentration was found to be considerably high, filtration was assumed to influence the anaerobic degradation process.

Experimental setup

All anaerobic degradation experiments were carried out at 35°C in 2.5l amber glass jars equipped with ports for occasional sampling and gas extraction. Three sets of batch experiments were done as follows:

1-A triplicate mixture of OTL and FL at a mixing ratio of 5(OTL) to 1(FL) representing the corresponding generation rate of leachate at OTL and the compost plant were tested. This mixture had a pH of 8.7, mixed liquor suspended solids (MLSS) of 1975 mg/L and a COD of 24840 mg/L. The reactors were seeded using 350 ml of sludge obtained from the anaerobic reactor of a local wastewater treatment plant.
2-Unfiltered NTL and FL
3-Filtered NTL and FL

The quality of the leachate samples used in the latter two tests is shown in Table 3 in terms of pH and COD concentration.

Kinetics of anaerobic degradability

Various kinetic models have been presented to describe biological degradation of organic compounds, in this case anaerobic degradation. The most popular models are Michaelis-Menten, Monod and simplified

Table 3. Characteristics of leachate samples used for the experiment

Reactor No.	1	2	3	4
Sample	Unfiltered NTL	Filtered NTL	Unfiltered FL	Filtered FL
pH	5.43	5.76	5.06	5.47
COD (mg/L)	77090	66710	89501	77760

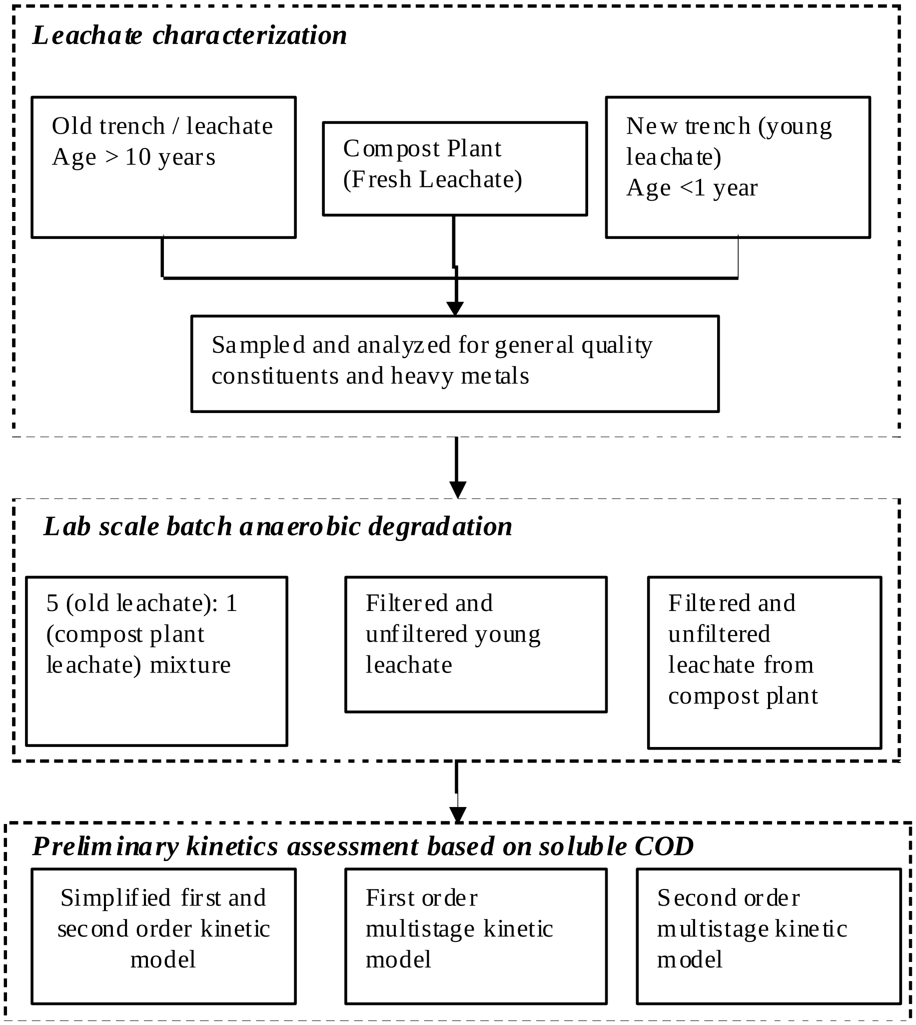

Fig. 1. Process of characterization of the leachates and their anaerobic degradation for Mashhad landfill and compost plant

first order reaction models (Tchobanoglous *et al.*, 2003; Liu *et al.*, 2004; Kurian *et al.*, 2006; Meima *et al.*, 2008; Cokgor *et al.*, 2009, Renou et al, 2008, Degirmentas and Deveci, 2004, Lopez and Borzacconi, 2008). The well known first and second order kinetic models which were employed in this study to fit the variations in soluble COD concentration are presented in Equation 1 and 2.

$S_t = S_0e^{-kt}$ **Equation 1**

$S_t = S_0/(1+S_0kt)$ **Equation 2**

Where; S_0 and S_t are the soluble COD concentration at the start of experiment and at time *t* (in days) respectively.

Furthermore, anaerobic degradation process can be summarized into three main stages of hydrolysis, acidogenesis and methanogenesis. The main issue to be addressed when trying to model the kinetic in this case would be the segregation of the phases each following different reaction rate constants. Accordingly three reaction rate constants of k_1, k_2 and k_3 can be taken into account for the phases of hydrolysis, acidogenesis and methanogenesis respectively. Various compounds are produced through the very stages of anaerobic degradation which cannot simply be integrated into one single model. Therefore as a simplified model of practical applicability, COD (in this case soluble COD) was considered as a main indicator; changes of which was assumed to demonstrate the state of anaerobic reactions. The simplified multistage COD based kinetic model is presented in Equation 3 for multistage first order model and in Equations 4 and 5 for multistage second order model (Degirmentas and Deveci, 2004).

The kinetics of anaerobic degradation of soluble COD of the leachate samples was assessed based on simplified first order and second order reactions in accordance with Equations 1 and 2. Furthermore, an attempt was made to fit the observations of soluble COD concentration to first order and second order multi-stage reaction kinetic models.

$$S_t = S_0.e^{-k_1 t} + k_1 S_0(e^{-k_2 t} – e^{-k_1 t})/(k_1 – k_2)$$

$$+ k_1 k_2 S_0\{[(k_2-k_3)e^{-k_1 t} – (k_1-k_3)e^{-k_2 t} + (k_1-k_2)e^{-k_3 t}]/[(k_1-k_2)(k_2-k_3)(k_1-k_2)]\}$$ **Equation 3**

Where; k_1, k_2 and k_3 are the reaction rate constants for hydrolysis, acidogenesis and methanogenesis respectively.

A solution to the second order kinetic model (Equation 4) was introduced also by Degirmentas and Deveci (2004) as shown in Equation 5.

$$dS_A/dt = -k_1 S_A^2$$
$$dS_B/dt = k_1 S_A^2 – k_2 S_B^2$$ **Equation 4**

$$dS_C/dt = k_2 S_B^2 – k_3 S_C^2$$

$$dS_D/dt = k_3 S_C^2$$

Where; S_A, S_B, S_C and S_D are the concentrations of the original organic compounds (as further referred to as S_0), hydrolysis products, volatile fatty acids and biogas respectively.

$$S_t = (A) + (B + (1/(C(D + ((E H)/(H+(FG)))))))+(I+(JK))+(((L+M)N)/O$$ **Equation 5**

Where;

$A= S_0/(1+k_1 S_0 t)$

$B= k_1 S_0/(2k_2+2t\ k_1 k_2 S_0)$

$C= 2k_2(1+tk_1 S_0)$

$D= -k_1^{0.5}(k_1+4k_2)^{0.5}S_0$

$E= 2(k_1+4k_2)^{0.5}S_0$

$F= (1+tk_1 S_0)^{(-(k1+4k2)\wedge 0.5))/(k1\wedge 0.5)}$

$G= k_1 S_0 + k_1^{0.5}(k_1+4k_2)^{0.5}S_0$

$H= -k_1 S_0 + k_1^{0.5}(k_1+4k_2)^{0.5}S_0$

$I= k_1 S_0/(2k_3+2t\ k_1 k_3 S_0)$

$J= k_1(k_1^2+4k_1 k_2+4k_2 k_3)^{0.5}S_0^2)$

$K= 2(k_1+4k_2)^{0.5}k_3\ (1+tk_1 S_0)$

$L= (k_1^2+4k_1 k_2+2k_2 k_3)S_0$

$M= (k_1+4k_2)^{0.5}(k_1(k_1^2+4k_1 k_2+4k_2 k_3)^{0.5}S_0^2)$

$N= (-1+(k_1+4k_2)^2)k_3^2(1+tk_1 S_0)$

$O= 2(k_1+4k_2)k_3(1+tk_1 S_0)$

RESULT & DISCUSSION

For the first series of tests, anaerobic biodegradability of the mixed leachate samples was assessed through monitoring pH, MLSS and COD. Variation in pH of the leachate within the three reactors is shown in Fig. 2. on an average basis. The initial relatively high pH value can be associated with the effect of larger portion of partially stabilized leachate of the landfill mixed with smaller fraction of fresh leachate of the compost plant. Generally no significant variation was observed in pH value, as it stayed

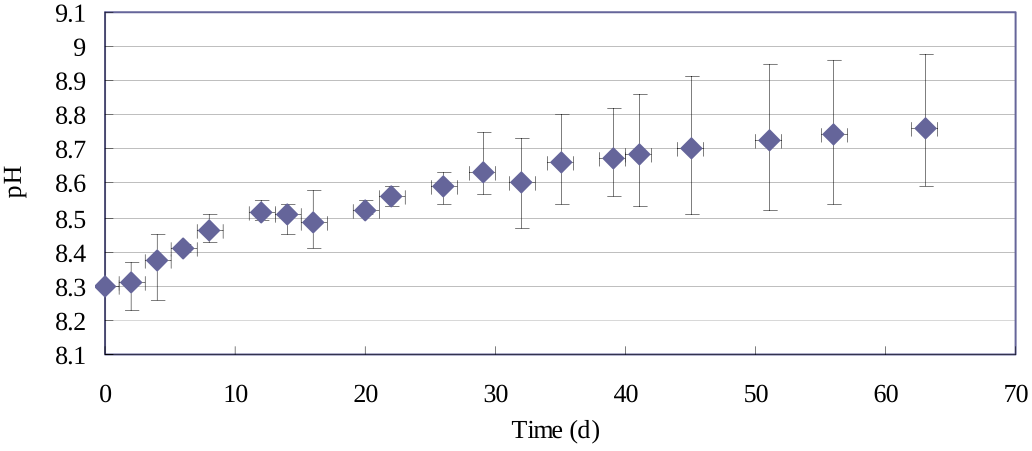

Fig. 2. pH changes in anaerobic rectors in the first series of tests

relatively constant between 8.2 and 8.9 appropriate for biological degradation to take place.

Another indicator of biological degradation is MLSS; variation of which for the first test series is shown in Fig. 3. Generally it is expected that MLSS concentration increase gradually because of micro-organisms growth and multiplication, although at considerably lower rates in anaerobic processes compared to aerobic ones (Millot and Courant, 1992). Observations indicated an increasing trend in MLSS of the reactors. On an average basis the initial MLSS of 1985 mg/L showed an increase up to 3448 mg/L at the time of termination of the experiment (Fig. 3). The observed MLSS growth fit to an exponential curve at a rate of 0.01 d^{-1}.

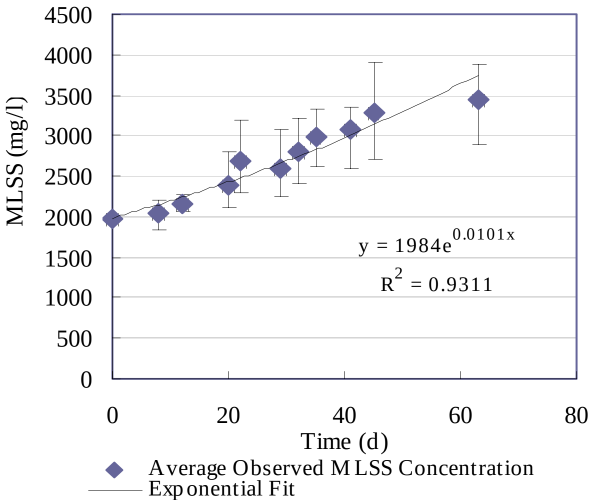

Fig. 3. Variation of average MLSS concentration in three anaerobic reactors in the first series of tests

As shown in Fig. 4. variations in concentration of soluble COD in the first series of tests indicated a relatively rapid decrease in about 15 days from the commencement of the experiment after which the COD concentration remains fairly constant over time. The initial high COD concentration of 24,840 mg/L in the three reactors was reduced to about 1500 mg/L for all reactors. This corresponds to an overall COD removal efficiency of about 94%. However, COD level remains almost constant at about 1500 mg/L which is yet a high concentration as compared to effluent discharge standards (i.e. 100 mg/L based on Iranian National Environmental Regulations). The reason behind this COD concentration level off seems to lie in the decreased ratio of organic carbon to ammonia nitrogen which can in turn slow down or inhibit the anaerobic degradation process. Other factors resulting in the COD removal stabilization could be the high chloride concentration along with low nitrate and phosphate concentrations. However further research is required to quantify the effect of inhibiting factors such as ammonia nitrogen, chloride and low concentrations of phosphate and nitrate.

The simplified first order kinetic model was fitted to the variation of soluble COD concentration in three reactors to an acceptable level as shown in Fig. 5(a,b & c). The first order model was also fitted to the average COD concentration as shown in Fig. 6. The corresponding reaction rate constants (i.e. *k*) were estimated to be 0.050, 0.049 and 0.049 d^{-1} for reactors 1, 2 and 3 respectively as shown in Table 4. Simplified second order kinetic model based on COD was also fitted to the same concentration variation. Good fit of second order model was also achieved for the three reactors as shown in Fig. 7(a,b & c) for three reactors in the first series of tests and Fig. 8. for the average concentration variation resulting in *k* values of 5.04E-6, 6.36E-6 and 4.41E-6 l/mg.d as shown in Table 4. Furthermore attempt was made to fit the simplified multistage kinetic models (first and second order). However no good fit was achieved neither using multistage first order nor second order models.

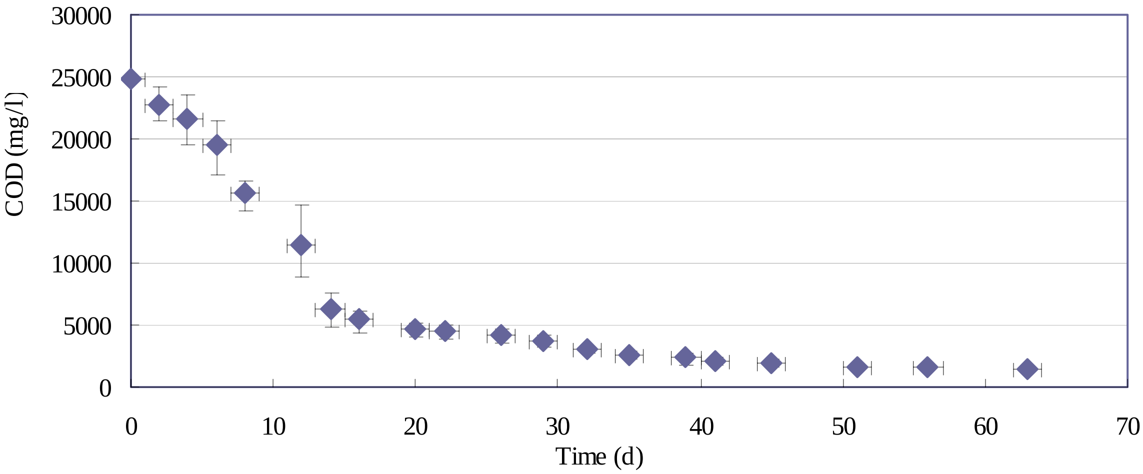

Fig. 4. Variation in average soluble COD concentration in three anaerobic rectors in the first series of tests

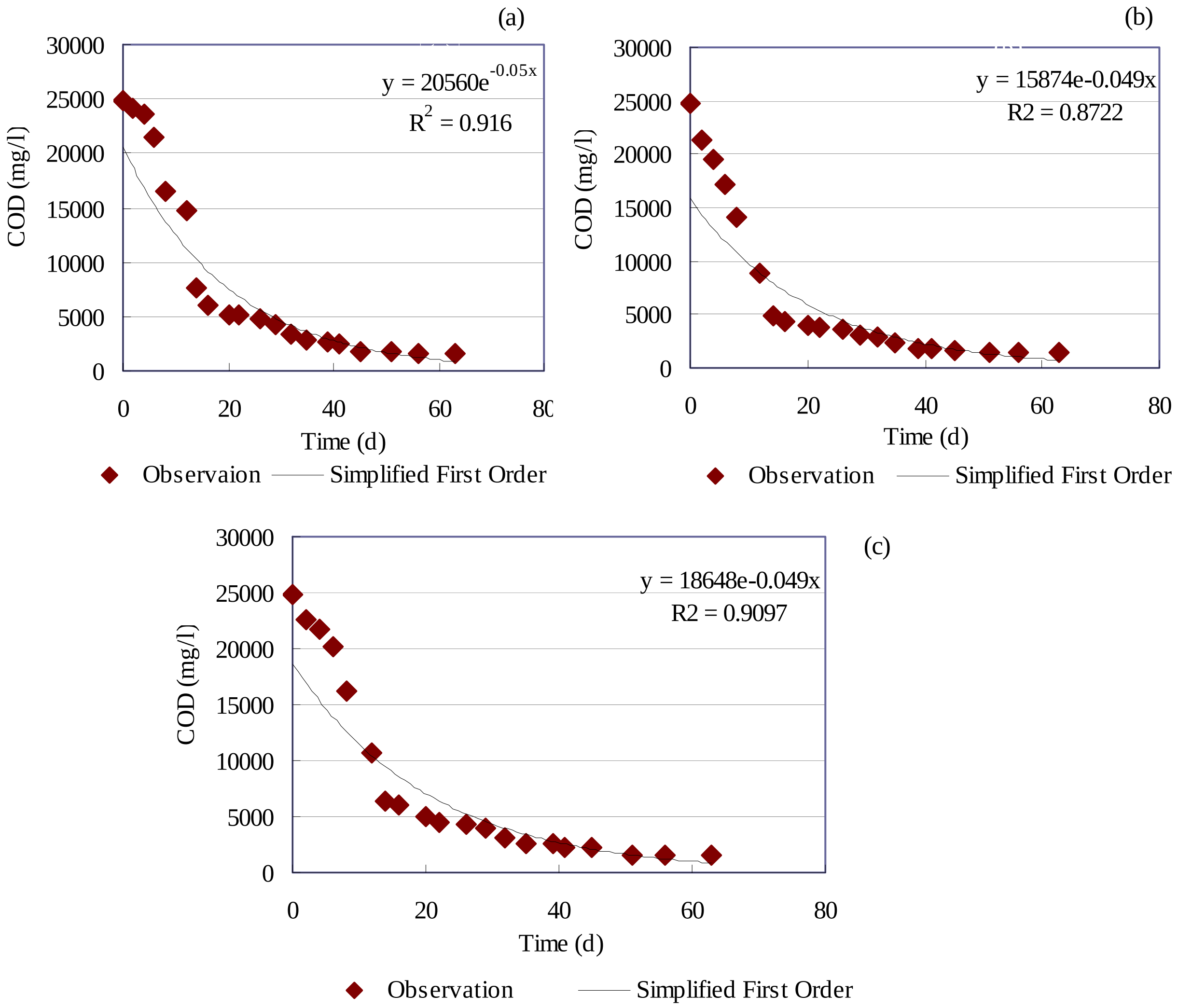

Fig. 5. First order kinetic model fitted to observed soluble COD concentration in (a) Reactor 1, (b) Reactor 2 and (c) Reactor 3 in the first series of tests

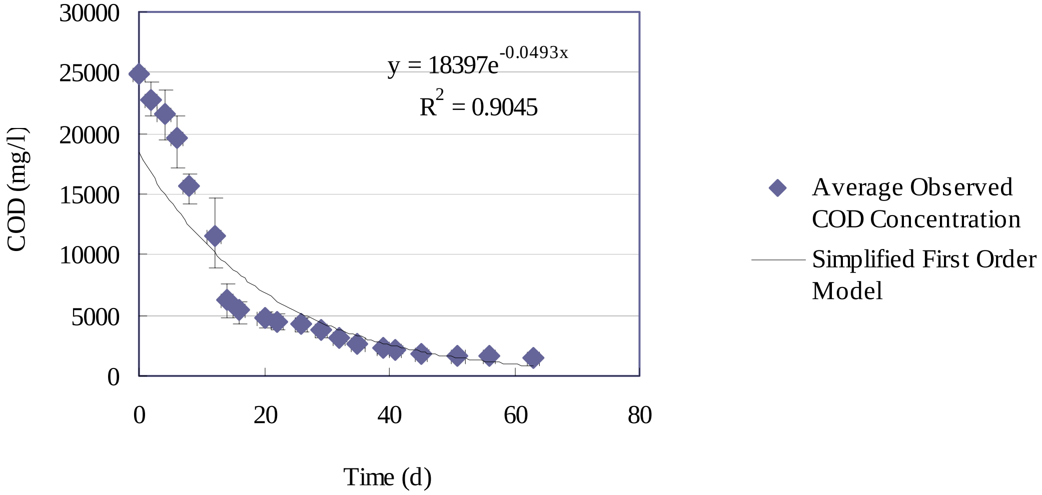

Fig. 6. First order kinetic model fitted to average observed soluble COD concentration in three reactors in the first series of tests

Table 4. Results of Simplified first and second order kinetic model fitted to anaerobic degradation of first series of tests

Reactor	Initial COD (mg/L)	Final COD Removal (%)	Kinetic Model	Rate Constant k (d^{-1})	R^2	Kinetic Model	Rate Constant k (L/mg.d)	R^2
1	24,840	93.8	$COD_t=20560e^{-0.05t}$	0.05	0.916	$COD_t=24840/(1+0.125194t)$	5.04E-6	0.892
2	24,840	94.4	$COD_t=15874e^{-0.049t}$	0.049	0.872	$COD_t=24840/(1+0.157982t)$	6.36E-6	0.915
3	24,840	93.9	$COD_t=18648e^{-0.049t}$	0.049	0.909	$COD_t=24840/(1+0.109544t)$	4.41E-6	0.909
Average		94	$COD_t=18397e^{-0.049t}$	0.049	0.904	$COD_t=24840/(1+0.128671t)$	5.18E-6	0.893

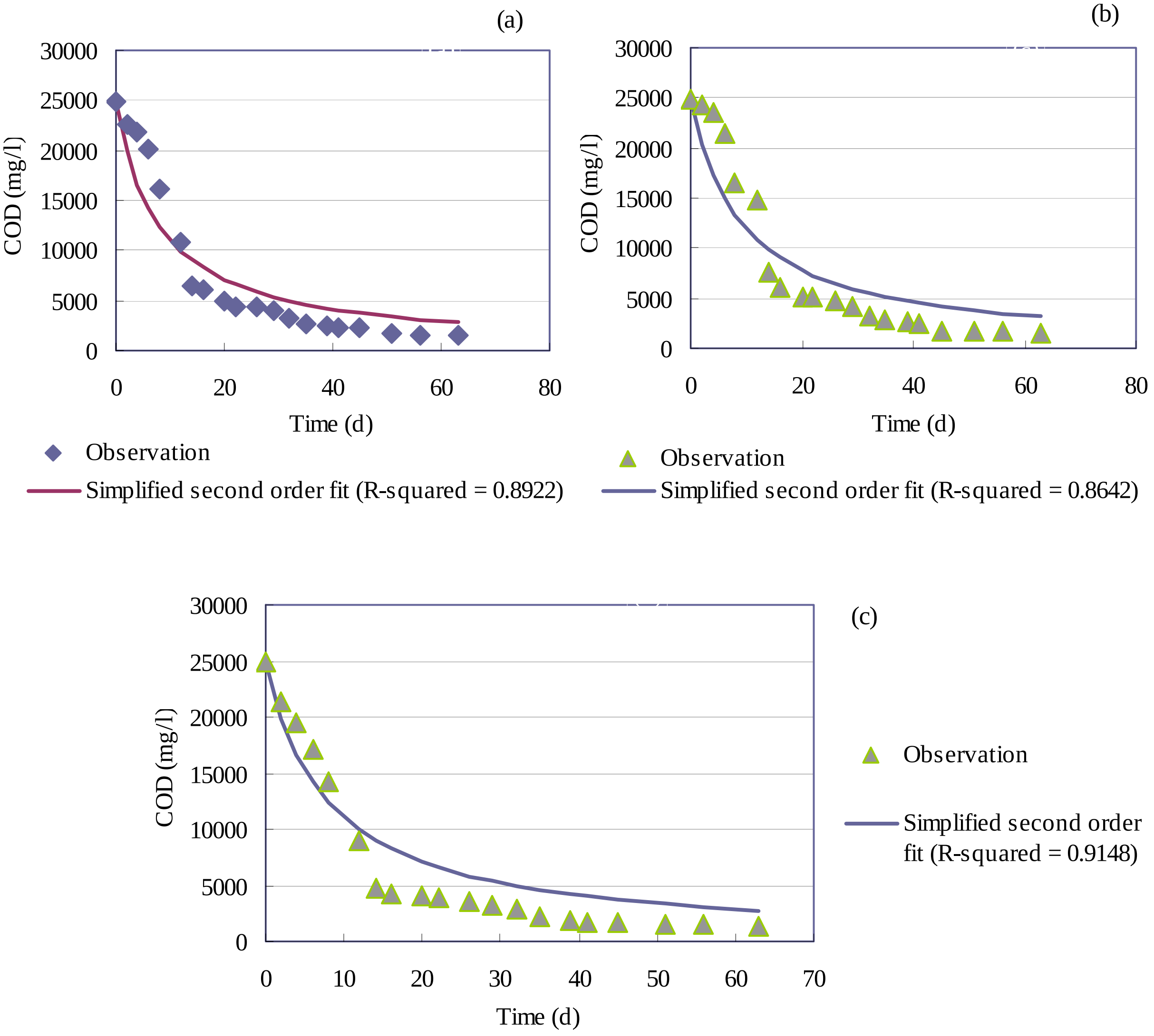

Fig. 7. Second order kinetic model fitted to observed soluble COD concentration in (a) Reactor 1, (b) Reactor 2 and (c) Reactor 3 in the first series of tests

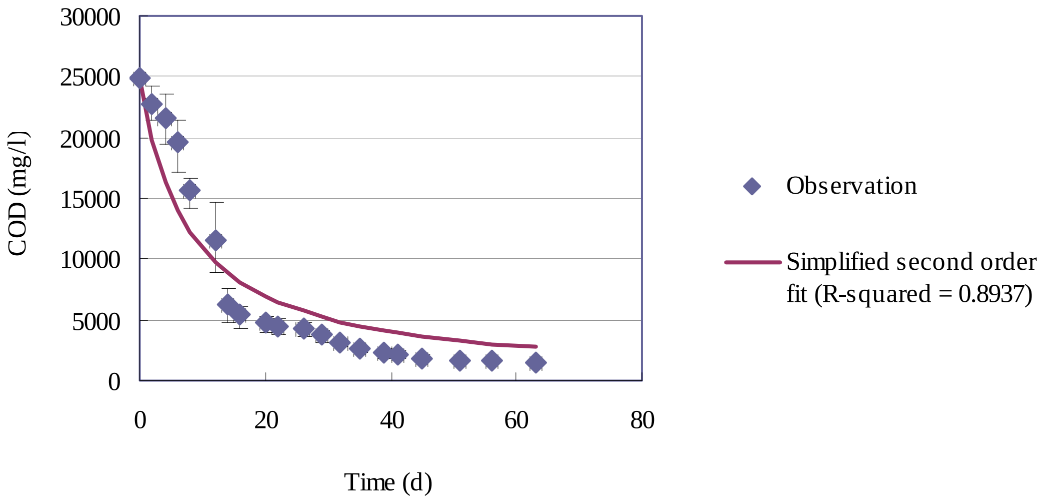

Fig. 8. Second order kinetic model fitted to average observed soluble COD concentration in three reactors in the first series of tests

The second series of tests were carried out using NTL and FL in filtered and unfiltered form to preliminarily assess the effect of filtration on the degradation extent and rate of anaerobic degradation. The main difference of these two leachate samples with the mixture used in the first series of tests lies in the considerably low pH and high COD concentration. As stated earlier, the leachate samples were used in filtered and unfiltered forms. The results of monitoring pH values indicated that for the unfiltered samples the pH value increased up to slightly less than 7.5 and remains constant at this level (Fig. 9). This showed that the biological degradation is inhibited whereas for the filtered samples as shown in Fig. 9, pH values increase substantially up to about 8.3 and the biological reaction continues.

This was confirmed by the results of COD concentration monitoring as shown in Fig. 10. Concentration of COD for the reactors with unfiltered leachate samples showed a slight decrease almost after 20 days after starting the experiment and remained almost constant afterwards. On the other hand the samples with filtered leachate (soluble COD) showed further considerable decrease in COD concentration over time. The biodegradation process was observed to be inhibited in Reactor 1 and Reactor 3 (i.e. reactors with unfiltered leachate samples).

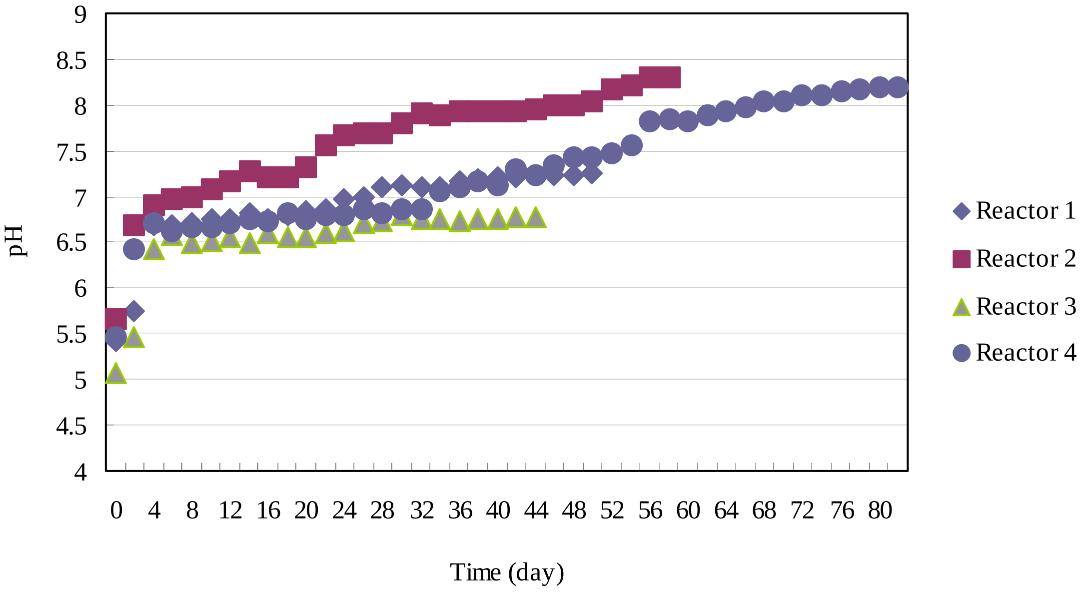

Fig. 9. Variations in pH of the leachate samples during anaerobic degradation process

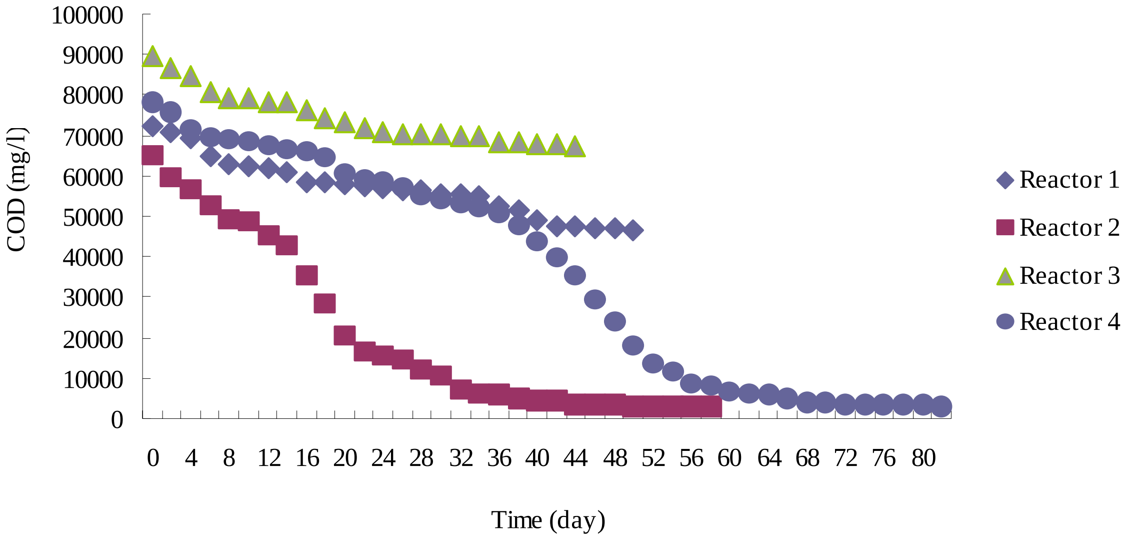

Fig. 10. Variations in COD concentration of the leachate samples during anaerobic degradation process

The reaction rate analysis was therefore performed for Reactor 2 and Reactor 4 where reactions where further reduction of COD was observed to significantly lower concentrations compared to the initial ones. The highest COD removal efficiency was observed at a pH range of about 7.5 to 8.3 for both reactors (Fig. 11). As shown in Fig. 8 and Fig. 10, the time taken for pH values to reach a level corresponding to the maximum COD removal efficiency was about 20 and 50 days for Reactor 2 and Reactor 4 respectively.

The kinetics of soluble COD reduction through anaerobic degradation as observed in Reactors 2 and 4 was first modeled using a simple first and second order scheme defined in Equation 1 and 2. The results are shown in Fig. 12. The first order kinetic model resulted in a *k* value of 0.052 d^{-1} (i.e. R^2 value of 0.947 compared to 0.815 for that of second order model). However an attempt was made to fit the observations to multistage first and second order models as described by Equation 3 and 5 respectively. The results of first order multistage fitting were found to be even better than simple first order for Reactor 2 (i.e. R^2 value of 0.987) whereas the second order multistage model did not provide a good fit and *k* values were found to be sensitive to initial values assigned for calculations. Levenberg-Marquardt nonlinear curve fitting procedure was employed for the multistage model fitting. The first order multistage model fitted to observations of soluble COD degradation in Reactor 2 is shown in Fig. 13. The resulting *k* values for hydrolysis, acidogenesis and methanogenesis were calculated to be 0.0993, 0.209 and 0.1636 d^{-1} respectively.

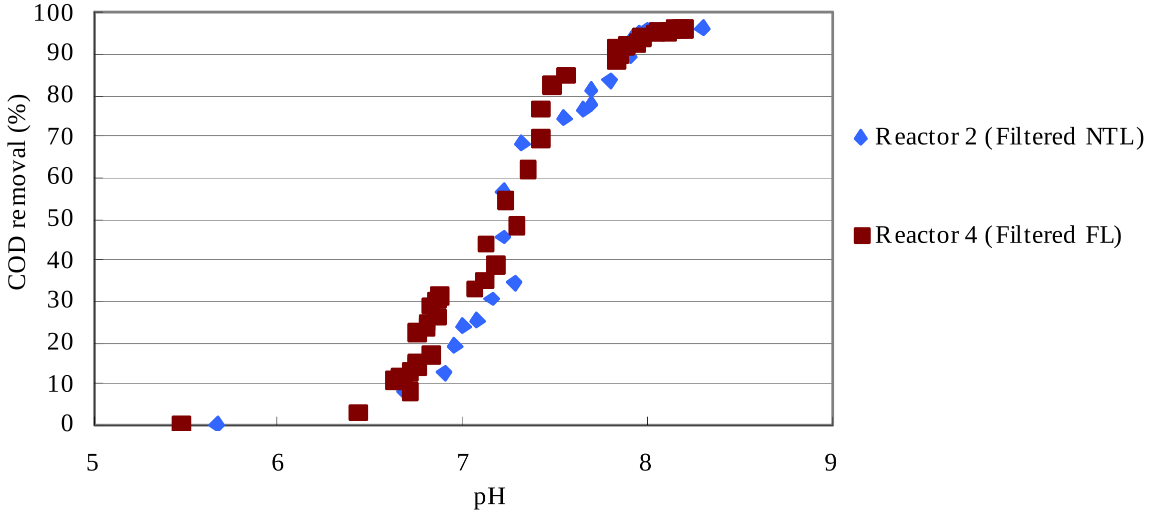

Fig. 11. COD removal efficiency versus pH variation for Reactors 2 and 4

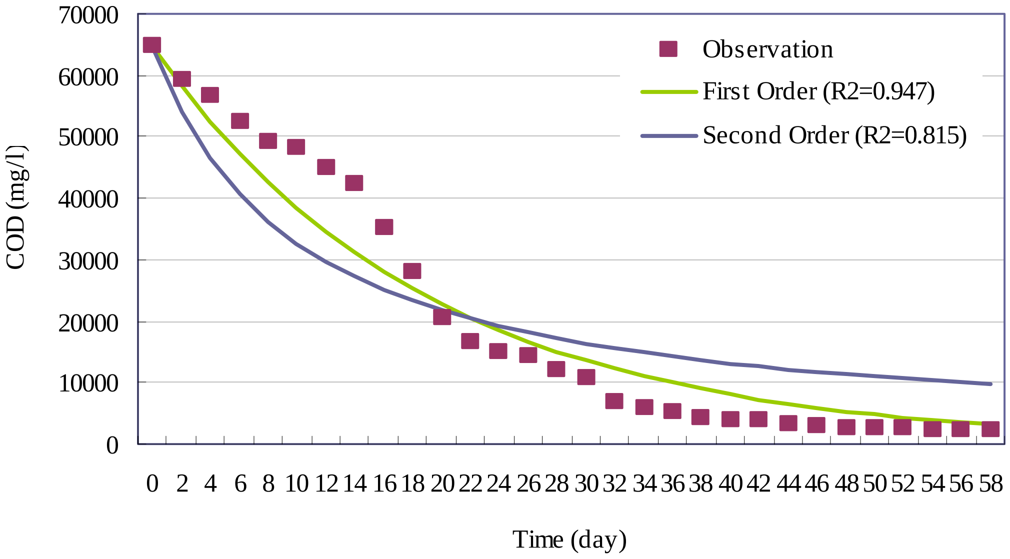

Fig. 12. First and second order kinetics fitted to soluble COD observations in Reactor 2 (Filtered NTL)

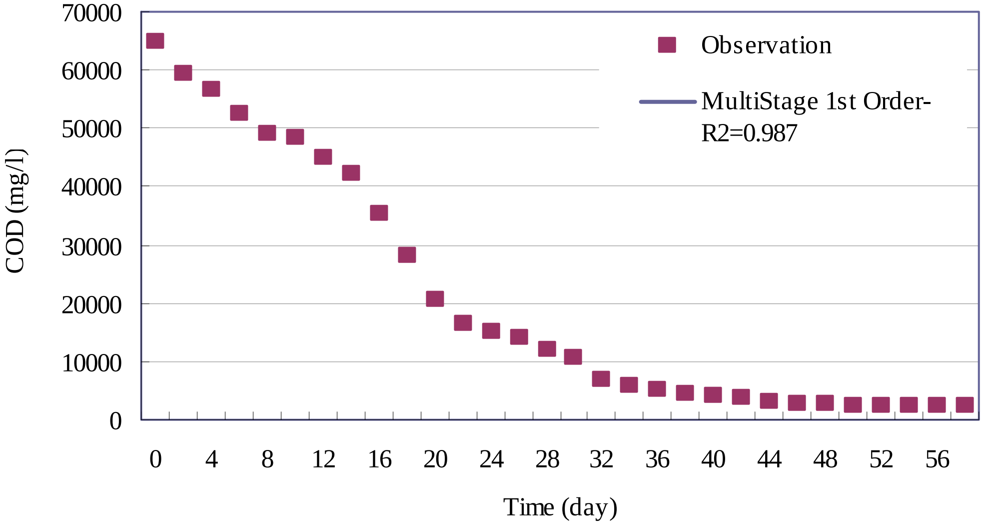

Fig. 13. First order multistage kinetics fitted to soluble COD observations in Reactor 2 (Filtered NTL)

These values indicate that the hydrolysis stage proceeds slower than acidogenesis and methanogenesis. Therefore hydrolysis could potentially be recognized as the rate limiting stage.

The same procedure was applied to Reactor 4. The results indicated that the single stage first and second order kinetic models did not provide reasonably desirable fits for Reactor 4 with R^2 values of 0.832 and 0.702 respectively (Fig. 14). In contrast to the simple first order model, the multistage first order model provided a substantially better fit with an R^2 of 0.95 and k values of 0.0691, 0.0802 and 0.0825 d^{-1} for hydrolysis, acidogenesis and methanogenesis respectively (Fig. 15). It appears that the reaction rates for Reactor 4 are lower than those of Reactor 2 and with smaller difference between the three stages. Attempts to fit the observations for Reactor 4 failed as the k values were found to be sensitive to initial assumptions. The results of the different kinetic models fitted to the observations of soluble COD degradation are summarized for Reactors 2 and 4 in Table 5.

CONCOLUSION

The leachate samples used in this study were found to be of substantial high strength. The extent of anaerobic biodegradability with no pretreatment other than filtering the suspended solids only for the fresh leachate samples was found to be above 94% in terms of soluble COD removal. In other words, it was shown that partially stabilized leachate combination yet of relatively high strength can be treated in anaerobic conditions with no pretreatment. It is also worth noting that despite the relatively high COD removal efficiency found in this study, there still

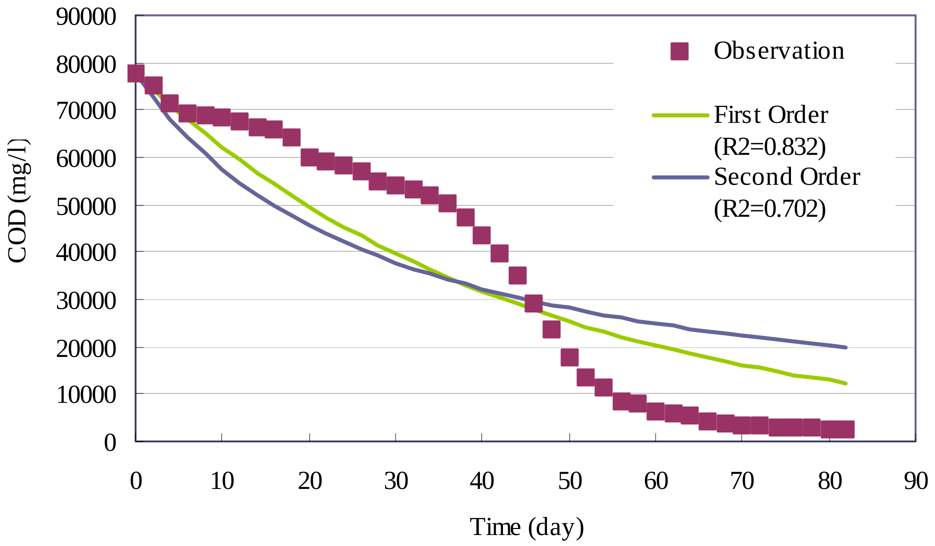

Fig. 14. First and second order kinetics fitted to soluble COD observations in Reactor 4 (Filtered FL)

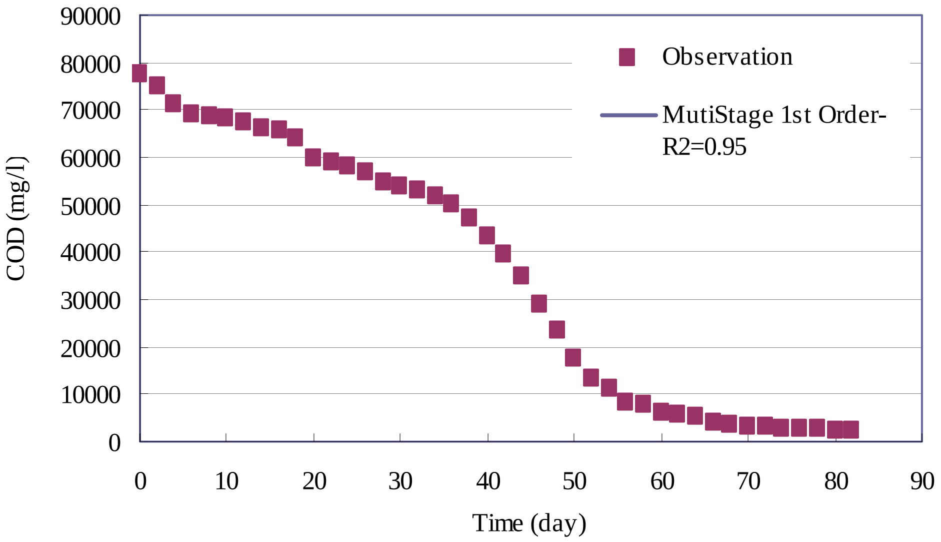

Fig. 15. First order multistage kinetics fitted to soluble COD observations in Reactor 4 (Filtered FL)

Table 5. Summary of kinetic models fitted to soluble COD degradation in filtered NTL (R2) and FL (R4)

Reactor/Model	**Simple First Order**		**Simple Second Order**		**Multistage First Order**			
	R^2	k (d^{-1})	R^2	k (L/mg.d)	R^2	k1 (d^{-1})	k2 (d^{-1})	k3 (d^{-1})
Reactor 2 (Filtered NTL)	0.947	0.052	0.815	15E-7	0.987	0.0993	0.209	0.1636
Reactor 4 (Filtered FL)	0.832	0.022	0.702	45E-8	0.950	0.0691	0.0802	0.0825

remains a residual COD concentration of about 1500 mg/L which was found to remain constant. This might be associated with the increased ratio of ammonia nitrogen to organic carbon along with high chloride concentrations at the mid to late stages of the experiment. Nevertheless, the results indicate that anaerobic degradation of partially stabilized landfill leachate could be promising as a main integrated part of a given leachate treatment system.

An important observation was that filtration of high strength leachate showed to have significant effect on continuation of anaerobic biodegradation of organic content of the leachate. Removal of COD was shown to be halted for unfiltered samples after a few days with no substantial decrease in COD concentration. This study was not meant and therefore could not provide certain reasoning for the inhibition of anaerobic reaction due to presence of insoluble fraction of COD in the leachate. However, hydrolysis stage of anaerobic degradation of total COD which was found to contain 15% of insoluble COD seemed to be the growth limiting stage. This conclusion could be made in accordance with the relatively small increase in pH value of the reactors containing unfiltered leachate up to less than 7 where the pH remains nearly constant over more than 40 days after commencement of the experiment. This experiment was carried out for a specific high strength leachate and general conclusions could not be drawn on the effect of the insoluble COD on anaerobic degradation of leachate. Therefore further research is required to determine the observed inhibition process in similar situations. In any case it can be seen that a pretreatment in form of physical filtration could result in continuation of the anaerobic process. This can be of practical importance in cases where the core process for leachate treatment is to be anaerobic treatment.

Furthermore, anaerobic reaction kinetics was characterized for high strength leachate samples. The soluble COD concentration was considered to be the target quality constituent for the sake of practicality. Simple first and second order kinetic models were fitted to the observed values of soluble COD degradation. An attempt was also made to fit multistage first and second order kinetic models for the experimented anaerobic degradation of high strength leachate since similar studies (if any) were not found in the literature to the extent reviewed by the authors. The importance of multistage approach lies in the fact that the rate limiting stage(s) can be identified based on which proper measures can be employed to enhance the reaction. It was shown that the decreasing trend of soluble COD follows a first order (multistage) anaerobic reaction due to the nonlinear best fit to the observed data. Considering the reaction rate constants calculated for each of the three main stages (i.e. hydrolysis, acidogenesis and methanogenesis), it can be concluded that in this experiment, hydrolysis was the rate limiting stage having been associated with the smallest reaction rate constant. For the specific leachate samples tested in this study, first order multistage kinetic model provided considerably better fit in comparison to the single stage first and second order models. Further studies are recommended to evaluate the applicability of this kinetic model to different leachates of high strength. It was also shown that anaerobic degradation of the older leachate (i.e. partially stabilized) did not follow a multistage kinetic model. This can be associated with the fact that first stages of degradation might have already been completed as reflected in high pH values as compared to fresh leachate.

From a practical point of view, the results of this study suggest that a pretreatment of high strength leachate such as removal of suspended solids can enhance the anaerobic degradation rate. Repetition of this study for similar high strength leachates from different landfills is proposed for generalization purposes. Considering the fact that waste characteristics and leachate properties are to a large extent similar in different cities of Iran, results of this study can be of basic contribution to design of required leachate treatment systems.

ACKNOWLEDGEMENT

The project was carried out at Graduate Faculty of Environment of the University of Tehran supported by Organization for Waste Recycling of Mashhad Municipality.

REFERENCES

Abdul Aziz, H., Omran, A. and Zakaria, W. R. (2010). H2O2 Oxidation of Pre Coagulated Semi Aerobic Leachate, Int. J. Environ. Res., **4 (2)**, 209-216.

Abduli, M. A., Nabi Bidhendi, G. R., Nasrabadi, T. and Hoveidi, H. (2007). Municipal Solid Waste Management on the South Coastline of the Caspian Sea (Golestan, Mazandaran, and Guilan Provinces of Iran). Journal of Environmental Health, **70 (5)**, 34-37.

Abduli, M. A. and Safari, E. (2003). Preliminary analysis of heavy metals in Kahrizak landfill leachate: A conceptual approach. International Journal of Environmental Studies. **60 (5),** 491-499.

Berrueta, J., Gutierres, A. and Fueyo, G. (1996). Anaerobic treatment of leachates in a pilot-scale UASB: strategy of start-up. J. Chem. Technol. Biotech., **67**, 302–314.

Bohdziewicz, J. and Kwarciak, A. (2008). The application of hybrid system UASB reactor-RO in landfill leachate treatment. Desalination, 222, pp. 128–134.

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

Cokgor, E. U., Insel, G., Aydin, E. and Orhon, D. (2009). Respirometric evaluation of a mixture of organic chemicals with different biodegradation kinetics. Journal of Hazardous Materials, 161, pp. 35–41.

Degirmentas, I. and Deveci, N. (2004). Anaerobic treatment of antibiotic production wastewater and kinetic evaluations. Journal of Biochemistry, 136, pp. 177-182.

El-Fadel, M. and Findikakis, N. (1997). Environmental impacts of solid waste landfilling. Journal of Environment Management, 50, pp. 1–25.

Haarstad, K. and Maehlum, T. (1999). Important aspects of long-term production and treatment of municipal solid waste leachate. Waste Management Research, 17, 470-477.

Henze, M., Harremoes, P., Arvin, E. and Jansen, J. C. (1995). Wastewater Treatment: Biological and Chemical Processes. Springer-Verlag, Berlin, Germany.

Iaconi, C. D., Ramadori, R. and Lopez, A. (2006). Combined biological and chemical degradation for treating a mature municipal landfill leachate. Biochemical Engineering Journal, **31**, 118-124.

Keenan, J. D., Steiner, R. L. and Fungaroli, A. A. (1984). Landfill leachate treatment. Journal of WPCF, **56 (1)**, 27-33.

Kennedy, K. J. and Lentz E. M. (2000). Treatment of landfill leachate using sequencing batch and continuous flow upflow anaerobic sludge blanket (UASB) reactors. Water Research, **34 (14)**, 3640-3656.

Kochany, J. and Kochany, E. L. (2009). Utilization of landfill leachate parameters for pretreatment by Fenton reaction and struvite precipitation—a comparative study. Journal of Hazardous Materials, **166**, 248-254.

Komilis, D. P., Ham R. K. and Stegmann, (1999). The effect of municipal solid waste pretreatment on landfill behavior: a literature review. Waste Management Research, **17**, 10-19.

Kurian, R., Nakhla, G. and Bassi, A. (2006). Biodegradation kinetics of high strength oily pet food wastewater in a membrane-coupled bioreactor (MBR). Chemosphere, **65**, 1204–1211.

Kurniawan, T., Wai-hung, L. and Chan, G. (2006). Physicochemical treatments for removal of recalcitrant contaminants from landfill leachate. Journal of Hazardous Materials, **B129**, 80-100.

Liu, V. L., Nakhla, G. and Bassi, A. (2004). Treatability and kinetics studies of mesophilic aerobic biodegradation of high oil and grease pet food wastewater. Journal of Hazardous Materials, **B112**, 87-94.

Lopez, I. and Borzacconi, L. (2008). Modeling a full scale UASB reactor using a COD global balance approach and state observers. Chemical Engineering Journal, (Article in press).

Maranon, E., Castrillon, L., Fernandez, Y. and Fernandez, E. (2006). Anaerobic treatment of sludge from a nitrification-denitrification landfill leachate plant. Waste Management, **26**, 869-874.

Meima, J. A., Mora Naranjo, M. and Haarstrick, A. (2008). Sensitivity analysis and literature review of parameters controlling local biodegradation processes in municipal solid waste landfills. Waste Management, **28**, 904-918.

Millot, N. and Courant, P. (1992). Treatability characteristics of landfill leachate. landfilling of waste: Leachate, E and FN SPON, pp. 107-117.

Nasrabadi, T., Nabi Bidhendi, G. R., Yavari, A. R. and Mohammadnejad, S. (2008). Evaluating Citizen Attitudes and Participation in Solid Waste Management in Tehran, Iran. Journal of Environmental Health, **71 (5)**, 30-33.

Nwabanne, J. T., Onukwuli, O. D. and Ifeakandu, C. M. (2009). Biokinetics of Anaerobic Digestion of Municipal Waste, Int. J. Environ. Res., **3 (4)**, 511-516.

Rasapoor, M., Nasrabadi, T., Kamali, M., Hoveidi, H. (2009). The effects of aeration rate on generated compost quality, using aerated static pile method. Waste Management, **29**, 570-573.

Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F. and Moulin, P. (2008). Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials, **150**, 468-493.

Robinson, H. D. and Barr, M. J. (1999). Aerobic biological treatment of landfill leachates. Waste Management Research, **17**, 478-486.

Saeedi, M ., Rezaei Bazkiaei, A . and Torkaman, Z . (2010). Insights in Leaching Characteristic Assessment of Solidified Wastes Using Different Leach tests, Int. J. Environ. Res., **4 (3)**, 455-462.

Safari, E. and Baronian, C. (2002). Modeling Temporal Variations in Leachate Quantity Generated at Kahrizak Landfill. Proceedings of International Environmental Modeling Software Society (IEMSS 2002), Switzerland.

Safari, E. and Nabi B., Gh. R. (2007). Removal of Manganese and Zinc from Kahrizak landfill leachate using daily cover soil and lime. Journal of Waste Management, Elsevier, 1551–1556.

Surmacz-Gorska, J. (2001). Degradation of organic compounds in municipal landfill leachate. Publisher of Environmental Engineering Committee of Polish Academy of Sciences, Lublin.

Tchobanoglous, G., Burton, F. L. and Stensel, D. H. (2003). Wastewater engineering treatment and reuse. 4th ed, The McGraw-Hill Companies, New York, USA.

Tsilogeorgis, J., Zouboulis, A., Samaras, P. and Zamboulis, D. (2008). Application of a membrane sequencing batch reactor for landfill leachate treatment. Desalination, 221, pp. 483–493.

Wang, X., Chen, S., Gu, X. and Wang, K. (2009). Pilot study on the advanced treatment of landfill leachate using a combined coagulation, fenton oxidation and biological aerated filter process. Waste Management, **29**, 1354-1358.

Wang, Z. and Banks, C. J. (2007). Treatment of a high strength sulfate rich alkaline leachate using an anaerobic filter. Waste Management, **27**, 359-366.

Wintgens, T., Gallenkemper, M. and Melin, T. (2003). Occurrence and removal of endocrine disrupters in landfill leachate treatment plants. Water Science and Technology, **48 (3)**, 127–134.

Zgajnar Gotvajna, A., Tisler, T. and Zagorc-Koncan, J. (2009). Comparison of different treatment strategies for industrial landfill leachate. Journal of Hazardous Materials, **162**, 1446-1456.

Zhang, H., Choi, H. J. and Huang, C. (2006). Treatment of landfill leachate by Fenton’s reagent in a continuous stirred tank reactor. Journal of Hazardous Materials, **33**, 124-132.