

# COD fractions of leachate from aerobic and anaerobic pilot scale landfill reactors

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## Abstract

One of the most important problems with designing and maintaining a landfill is managing leachate that generated when water passes through the waste. In this study, leachate samples taken from aerobic and anaerobic landfill reactors operated with and without leachate recirculation are investigated in terms of biodegradable and non-biodegradable fractions of COD. The operation time is 600 days for anaerobic reactors and 250 days for aerobic reactors. Results of this study show that while the values of soluble inert COD to total COD in the leachate of aerobic landfill with leachate recirculation and aerobic dry reactors are determined around 40%, this rate was found around 30% in the leachate of anaerobic landfill with leachate recirculation and traditional landfill reactors. The reason for this difference is that the aerobic reactors generated much more microbial products. Because of this condition, it can be concluded that total inert COD/total COD ratios of the aerobic reactors were 60%, whereas those of anaerobic reactors were 50%. This study is important for modeling, design, and operation of landfill leachate treatment systems and determination of discharge limits.

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**Keywords:** Landfill; Leachate; Soluble substrate; COD fractions; Inert COD

## 1. Introduction

Sanitary landfilling plays an important role in solid waste management of various countries in the world. One of the main problems with regard to the operation of sanitary landfill is the difficulty in managing the resulting leachates, which are complex and highly contaminated wastewaters [1,2]. Landfill leachate is characterized by its generation rate and composition, both of which are affected by the age of the landfill site. In particular, leachate composition and characteristics strictly depend upon various factors such as waste type, climate, organic matter content, landfill hydrogeological structure, and operational conditions [3–7].

Leachate consists of many different organic and inorganic compounds that may be either dissolved or suspended and which are biodegradable and non-biodegradable [8]. In addition to this,

the characteristic of the leachate varies with regard to its composition and volume, and biodegradable matter present in the leachate with time [9–11]. For this reason, young and old landfill leachates have very different features. Calace et al. [12] reported that the young landfill leachate fractions have low molecular weight distributions (<500 Da) at the rate of 70%, while the high molecular weight distribution (>10,000 Da) is 18%. Besides, the low and high molecular weight distributions are 28 and 67%, respectively, in old landfill leachate samples. According to this result, easily biodegradable components of leachate reduce, and constituents having high molecular weights and that are non-biodegradable increase in the course of time. These factors make leachate treatment difficult and these factors needed to be taken into account when different treatment processes are considered. The treatment requirements for leachate from sanitary landfills can vary depending on the discharge limits and contaminants present. An effective method for the treatment of leachate is recirculation through the landfill. When leachate is recirculated, the constituents attenuated by biological activity and by other chemical and physical reactions occur within the landfill.

At present, collection and treatment of landfill leachates are issues surrounding the operation of landfill sites [13,14]. The

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### Nomenclature

A1	aerobic landfill reactor with leachate recirculation
A2	aerobic dry landfill reactor
AN1	anaerobic landfill with leachate recirculation
AN2	traditional landfill
F/M	food/mass ratio
MSW	municipal solid waste
$S_{bi}$	biodegradable COD (mg COD/L)
$S_{bpi}$	slowly biodegradable (particulate) COD (mg COD/L)
$S_{bsi}$	readily biodegradable (soluble) COD (mg COD/L)
$S_{ti}$	total/influent COD (mg COD/L)
$S_{ui}$	unbiodegradable COD (mg COD/L)
$S_{upi}$	unbiodegradable particulate COD (mg COD/L)
$S_{usi}$	unbiodegradable soluble COD (mg COD/L)
SMP	soluble microbial product
$T_bOD$	total biological oxygen demand (mg COD/L)
VSS	volatile suspended solid

biological leachate treatment by either aerobic or anaerobic processes is another option [15]. On the other hand, anaerobic treatment methods are more suitable for concentrated leachate streams [14,16–18]. After the biological treatment, wastewater can contain various compounds such as residual rapidly, slowly and non-biodegradable substrate, inter- and final-products, and soluble microbial products [19]. Inert COD components in wastewaters and soluble and particulate inert metabolic products occurred in the system must be determined in order to assess suitable operation conditions providing with correct modeling and design [20]. Similarly, leachate from landfill also includes same compounds. Hence, the capabilities of the present leachate treatment processes are quite limited due to the high contents of both initially present inert COD in influent and the inert COD produced by microbial activities. Therefore, fractions of COD play an important role in the design of leachate treatment plants. The determination of particulate and inert fractions of wastewaters is also important in order to regulate the discharge standards and operating conditions [20].

The aim of the present study is to determine COD fractions of the leachate samples obtained from aerobic and anaerobic pilot scale landfill reactors. For this aim, biodegradable and non-biodegradable fractions of COD are evaluated using the total biological oxygen demand ( $T_bOD$ ) method [21]. The operation time is 600 days for anaerobic reactors and 250 days for aerobic reactors.

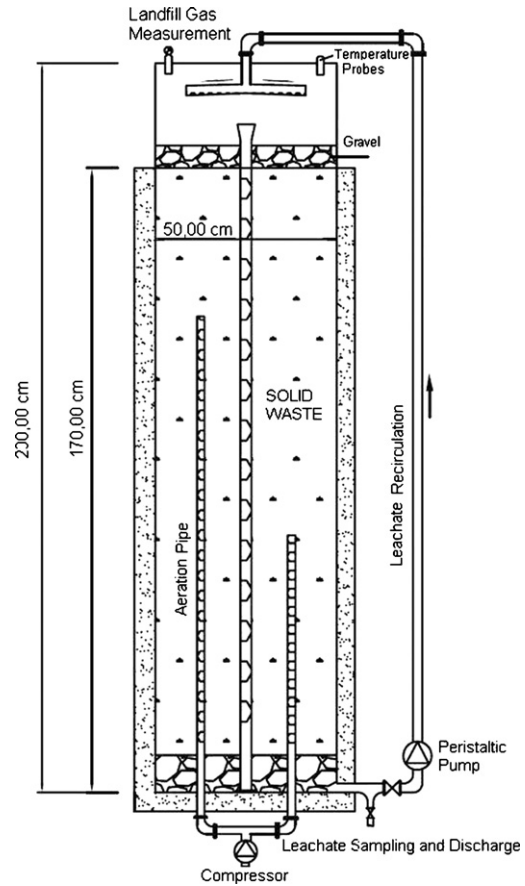


Fig. 1. Aerobic and anaerobic landfill reactors.

## 2. Materials and methods

### 2.1. Aerobic and anaerobic reactors

Four polypropylene columns are constructed to simulate different landfill operational conditions which are summarized in Table 1 [22]. Thickness, inner diameter and height of these polypropylene columns are 0.5, 50 and 200 cm, respectively. Fig. 1 shows the similar structure of the columns.

The fresh solid waste added to the landfill reactors obtained from Odayeri Sanitary Landfill (Istanbul, Turkey), and the average composition of solid wastes removed at Odayeri Landfill is 44% organic, 8% paper, 6% glass, 6% metals, 5% plastic, 5% textile, 9% nylon, 8% diaper, and 9% ash and others [22]. A1, A2, AN1, and AN2 reactors were filled with 179, 174, 173, and 175 kg of fresh solid waste, respectively, with the waste representing the bulk composition of MSW determined by waste composition analysis [23]. Leachate collection was realized by

Table 1  
Operational conditions used in the reactors to simulate different landfill concepts

Column	Operating condition	Refuse (kg)	Air flow (L/(min kg waste))	Water flow (L/(day m <sup>3</sup> waste))
A1	Aerobic with leachate recirculation	179	0.084	0.35
A2	Aerobic dry	174	0.086	–
AN1	Anaerobic with leachate recirculation	173	–	0.21
AN2	Traditional landfill	175	–	–

opening the discharge valve on a daily basis at the beginning of the experiment, and at 1- or 2-week intervals for the following period. Leachate samples were collected while discharging leachate from the landfill reactors and kept at 4 °C in plastic bottles. The quality and quantity of leachate observed for 250 days in aerobic reactors and for 600 days in anaerobic reactors are given in a previous paper [23] and summarized in Table 2.

2.2. Experimental methods

The COD is divided into two main fractions biodegradable and unbiodegradable which are subdivided to particulate and soluble fractions [24]. Fig. 2 shows the subdivisions presented by Park et al. [21].

The total COD has two major components named as biodegradable ( $S_{bi}$ ) and non-biodegradable or inert COD ( $S_{ui}$ ). The non-biodegradable fraction may be further divided into soluble ( $S_{usi}$ ) and particulate ( $S_{upi}$ ) fractions. The biodegradable fraction is also subdivided into soluble readily biodegradable ( $S_{bsi}$ ) and particulate slowly biodegradable ( $S_{bpi}$ ) fractions.

The soluble COD in the effluent from a process treating leachate includes biodegradable and non-biodegradable compounds from the raw leachate and microbial activities in the treatment system itself [6]. This assessment has been discussed previously in the literature [25–27].

In this study four different landfill reactors were used to determine the change of COD profiles in landfill leachate. Experimental method suggested by Park et al. [21] used in order to determine directly influent COD fractions. The measurement of COD was based on the “closed reflux, colorimetric method” described in section 5220-D of APHA [28]. The following section gives detailed explanation of the experimental procedures.

2.2.1. Biodegradable COD ( $S_{bi}$ )

Biodegradable COD ( $S_{bi}$ ) may be determined using the total biological demand ( $T_bOD$ ) method which assumes that particulate organic materials are hydrolyzed when the biological oxidation process is completed. Thus, the  $T_bOD$  is conceptually equal to the biodegradable COD including soluble ( $S_{bsi}$ ) and particulate ( $S_{bpi}$ ) degradable COD.

The initial total COD ( $S_{ti}$ ) and initial soluble COD (filtrated with 0.45- $\mu$ m membrane filters) of the leachate samples are measured. The particulate COD is the difference between the total COD and the soluble COD values. 1 L of an acclimated activated sludge and leachate mixture is obtained to have F/M ratio between 0.5 and 0.8. This ratio is obtained by different dilution rates which is calculated with  $BOD_5$  of the leachate sample and VSS of the activated sludge for each sample. COD of the mixture and the filtrate passing through 0.45- $\mu$ m filter are measured and the particulate COD of the mixture is calculated by subtracting soluble COD from total COD. Then, the mixture is aerated to reach a dissolved oxygen level of approximately 2 mg/L. The aeration period is 24 h for each sample. After these procedures, the  $T_bOD$  values can be calculated as

Table 2  
Leachate characteristics of aerobic and anaerobic landfill reactors

Parameter	A1			A2			AN1			AN2		
	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average	Minimum	Maximum	Average
pH	4.5	9.1	6.7	4.4	8.9	6.5	4.4	7.7	6.3	4.4	7.5	6.0
Alkalinity (mg/L)	6750	16,000	11,980	4600	16,000	10,320	1800	25,000	9390	1200	22,830	7040
ORP (mV)	12	243	140	24	240	137	-320	75	-156	-315	60	-125
TDS (ppt)	11.9	27.7	17.5	10.9	25.5	16.7	2.7	16.6	12.3	7.2	19.7	12.7
Conductivity (mS/cm)	15.5	38.6	26.5	16.4	38.2	24.8	4.0	24.8	17.2	10.7	23.9	17.3
Chloride (mg/L)	2080	6600	3770	2300	6920	3775	2250	4700	3075	2600	5280	3390
COD (mg/L)	5120	68,515	37,630	8260	63,685	37,760	1600	94,800	46,845	2400	98,000	52,120
TKN (mg/L)	284	2128	1255	357	2128	1356	986	3326	2424	918	3260	2310
Ammonia (mg/L)	123	1758	721	206	1770	758	280	2184	1383	202	1974	1290

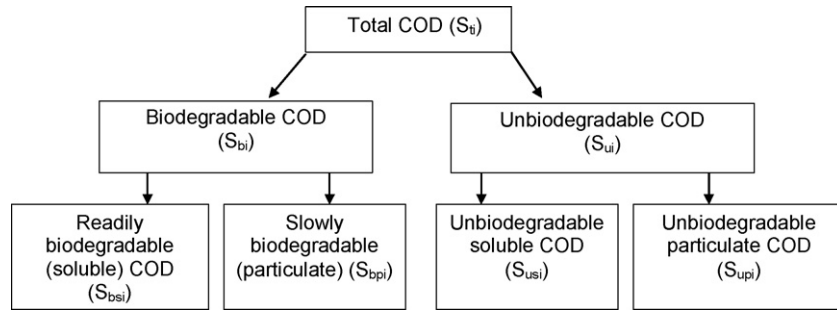


Fig. 2. Division of influent COD into its constituent fractions.

follows:

$$T_{bOD} = S_{bi} = \text{initial substrate COD} - \text{final substrate soluble COD} \quad (1)$$

where

$$\text{initial substrate COD} = \text{initial mixture COD} - \text{initial biomass COD} \quad (2)$$

and

$$\text{initial biomass COD} = \text{initial mixture particulate COD} - \text{raw leachate particulate COD} \quad (3)$$

With these results, we can distinguish  $S_{bi}$  and  $S_{ui}$  fractions of the leachate samples.

#### 2.2.2. Soluble readily biodegradable COD ( $S_{bsi}$ ) and soluble unbiodegradable COD ( $S_{usi}$ ) determination

A rapid physical–chemical method for determining the soluble readily biodegradable COD ( $S_{bsi}$ ) and the soluble unbiodegradable COD ( $S_{usi}$ ) was developed by Mamais et al. [29]. Flocculation, precipitation, and filtration of wastewater samples allow for the direct measurement of  $S_{bsi}$  and  $S_{usi}$ . The analyzing procedure is determined below.

1 mL of a 100-g/L zinc sulfate solution is added to 100 mL leachate sample and mixed with magnetic stirrer for 1 min. Then the pH is adjusted to 10.5 with 6 M sodium hydroxide solution and the mixture is precipitated. 20–30 mL of sample from clear supernatant was taken, after that passed through a 0.45- $\mu\text{m}$  filter, and the COD of the filtrate was measured. The calculation method is given in the following equation:

$$(S_{bsi}) = \text{total soluble COD} - \text{unbiodegradable soluble COD (} S_{usi} \text{)} \quad (4)$$

#### 2.2.3. Particulate slowly biodegradable COD ( $S_{bpi}$ ) and particulate unbiodegradable COD ( $S_{upi}$ ) determination

After the determination of soluble COD fractions, particulate COD fractions can be calculated easily.  $S_{bpi}$  and  $S_{upi}$  can be determined as follows:

$$S_{bi} = S_{bsi} + S_{bpi} \quad (5)$$

Then  $S_{upi}$  is obtained by

$$S_{upi} = S_{ti} - S_{bi} - S_{usi} \quad (6)$$

### 3. Results and discussion

#### 3.1. COD concentrations

Fig. 3 gives the change of COD concentrations in aerobic and anaerobic landfill reactors within time. It can be seen that COD values have been increased to 70,000 mg/L after first 15 days of storage in the aerobic reactors. For initial 50 days, COD was around 40,000–70,000 mg/L for aerobic reactors. Afterwards, it has decreased to 8000 mg/L in A1 reactor and 15,000 mg/L in A2 reactor after 120 days of operation. After 250 days of operation, it is determined that the COD values of the aerobic reactors were 5000 and 8000 mg/L.

COD concentrations increased to maximum values of 94,000 and 98,000 mg/L for AN1 and AN2 reactors after 65 and 85 days of operation, respectively. It means that high organic compounds of leachate on primary phase (acidic phase) decomposed to organic acids. After reaching to maximum values, because of methanogenic phase, COD concentrations began to decrease rapidly, and the concentrations on day 250 were determined as 17,400 and 24,500 for AN1 and AN2 reactors, respectively. The last concentrations determined in AN1 and AN2 reactors on day 600 were 1200 and 1800 mg/L, respectively. According to the results of Fig. 3, it can be concluded that aerobic stabilization and decomposition of solid wastes is more rapid than anaerobic stabilization.

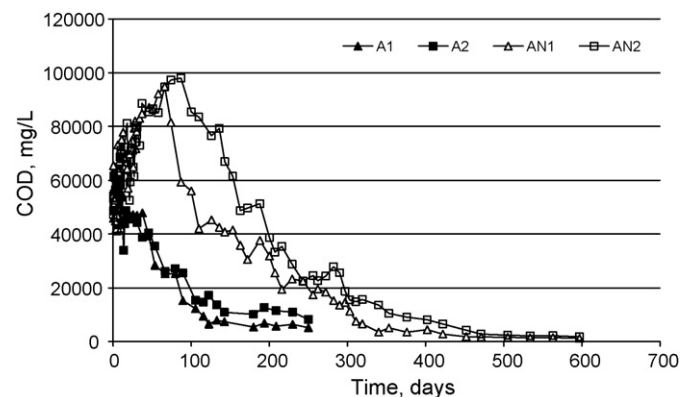


Fig. 3. COD concentrations in aerobic and anaerobic landfill reactors.



Cossu et al. [30] found in their column study that the COD values of leachate from aerobic dry and wet reactors were lower than an anaerobic reactor. They found that after 120 days of operation the COD value of the anaerobic landfill reactor was approximately 20,000 mg/L, while equivalent values were 3000 and 800 mg/L in the aerobic dry and wet reactors, respectively.

The results of the present study are similar to those of Cossu et al. [30] and clearly show that aeration and leachate recirculation have a positive effect on the rate of solid waste degradation in landfills.

The ratio of measured COD to the maximum COD determined in each reactor is given in Fig. 4. It can be seen from the figure that COD removal in A1 reactor is realized more rapidly than other reactors. The maximum output for getting rid of COD is 93% on day 250 in aerobic reactor. Additionally, COD removal for A2, AN1, and AN2 are 87, 82, and 75%, respectively. On the other hand, COD reached to lower concentrations in anaerobic reactors at following days. However, in aerobic reactors leachate generation is completed after 250 days, which means an important advantage. Final COD concentrations (Figs. 3 and 4) show the positive effects of leachate recirculation obviously on aerobic and anaerobic degradation of municipal solid wastes.

### 3.2. Biodegradable and non-biodegradable COD

In this study, the concentrations of the biodegradable and non-biodegradable COD of leachate samples are determined. The results are given as the ratio of total inert COD ( $S_{usi} + S_{upi}$ ) to total COD ( $S_{ti}$ ) in Fig. 5. Initial ratios of inert COD are at very low levels in all reactors. The increasing rate of the inert COD has changed according to organic material decomposition process and rate. Inert COD has increased after 20 days and ( $S_{usi} + S_{upi}$ )/ $S_{ti}$  ratio reached to 60% at the end of 120 days in A1 reactor. After this day, it has been steady in A1 reactor. Similarly, in A2 reactor this ratio was 10% on day 70. After that, it started to increase and reached to 60% on day 200. The same variations are observed in AN1 and AN2 reactors. However, the increasing period of ( $S_{usi} + S_{upi}$ )/ $S_{ti}$  ratio began on day 100 in AN1, and on

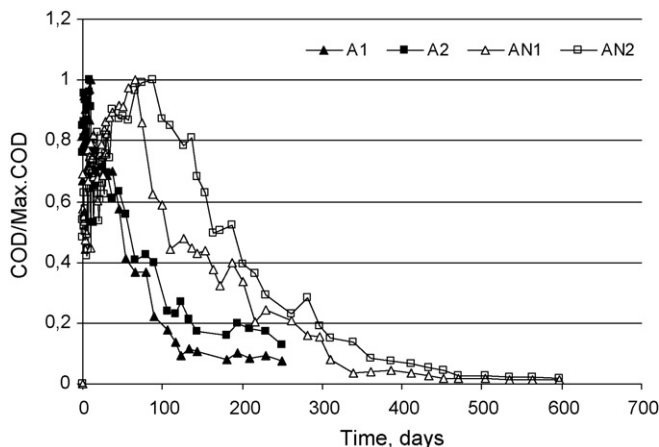


Fig. 4. COD/max. COD in aerobic and anaerobic landfill reactors.

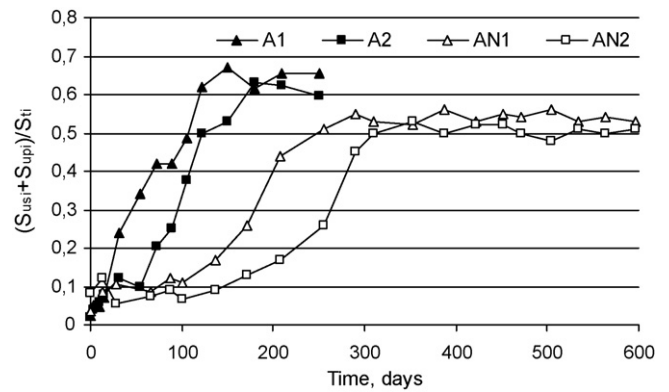


Fig. 5.  $(S_{usi} + S_{upi})/S_{ti}$  variation in aerobic and anaerobic landfill reactors.

day 150 in AN2 reactor. The stable rates of  $(S_{usi} + S_{upi})/S_{ti}$  are around 50% in these reactors.

The increasing values consist of the SMP and complex organic materials of leachate. It can be concluded that the total inert COD increases as landfill stabilizes in both aerobic and anaerobic landfills. This increase can be seen more rapidly in aerobic landfills. Furthermore, the enhanced stabilization with leachate recirculation results with rapid increase in inert COD fraction of both aerobic and anaerobic leachate samples.

Sometimes, pollutant concentrations of biologically treated leachate exceed discharge standards due to inappropriate estimation or consideration of  $S_{usi}$  and SMP. Since  $S_{usi}$  by-passes the treatment system without any change, careful consideration of  $S_{usi}$  and SMP is very important in the process design of biological leachate treatment to optimize process structure and operating parameters and to estimate effluent residual COD [6]. Furthermore,  $S_{usi}$  of leachate gradually increases as a landfill stabilizes, therefore, it should be considered carefully to design the leachate treatment plant with respect to refuse age. Therefore, the objective of this work is to determine the change of present  $S_{usi}$  in leachate from aerobic and anaerobic landfill leachate with various refuse ages.

The stabilized value of inert COD to total COD is higher in aerobic reactors (60%) than anaerobic reactors (50%). This is the result of more soluble microbial product formation because of microbial activities during the waste degradation.

### 3.3. Soluble and particulate COD fractions

The ratio of the soluble and particulate inert COD fractions to total COD concentration increased within time. The ratio of soluble inert COD to total COD ( $S_{usi}/S_{ti}$ ) is given in Fig. 6. As can be seen from the figure,  $S_{usi}/S_{ti}$  ratio is determined as 40 and 30% for aerobic and anaerobic landfill reactors, respectively, at the end of the operation. In the same way, the ratio of particulate inert COD to total COD ( $S_{upi}/S_{ti}$ ) is increased in time and reached to 25% values for all reactors at the end of the operation (Fig. 7).

Although  $S_{upi}/S_{ti}$  ratio is at the same levels in all reactors, as a result of aerobic degradation constitutes more microbial products, this situation caused and the  $(S_{usi} + S_{upi})/S_{ti}$  ratio determined higher in aerobic reactors when compared with anaerobic reactors.

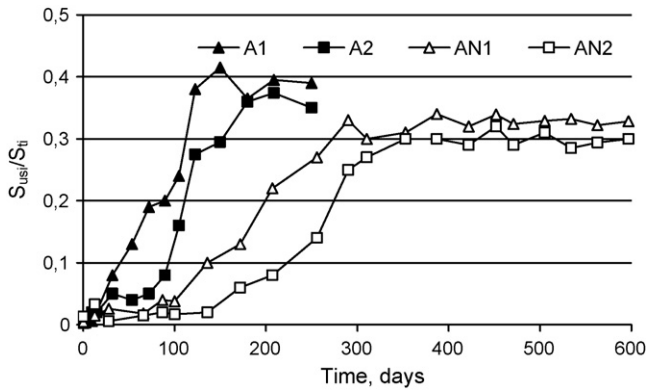


Fig. 6.  $S_{usi}/S_{ti}$  variation in aerobic and anaerobic landfill reactors.

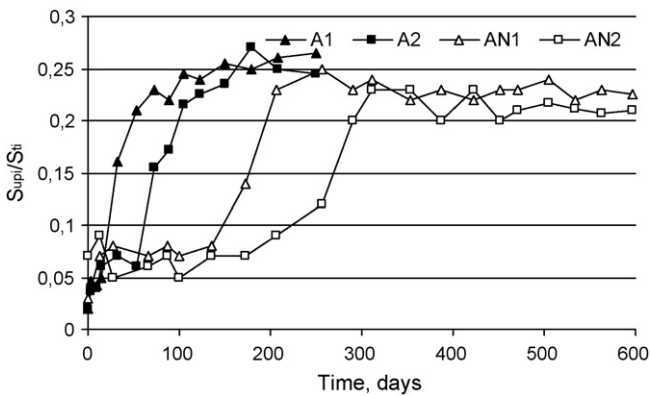


Fig. 7.  $S_{upi}/S_{ti}$  variation in aerobic and anaerobic landfill reactors.

#### 4. Conclusion

The experimental study investigated the change of inert COD concentrations of leachate depending on landfill operational methods (A1, A2, AN1 and AN2). Evaluation of this experimental study indicated that when COD values considered, aerobic decomposition of organic substance generates considerably faster than that of anaerobic decomposition. When the ratio of COD to maximum COD values in the leachate taken into account, it was determined that COD removals for A1, A2, AN1 and AN2 were 93, 87, 82 and 75%, respectively. Although the values of soluble inert COD to total COD in the leachates of A1 and A2 reactors were determined around 40%, this rate was found around 30% in the leachates of AN1 and AN2 reactors. The reason of this difference is that the aerobic reactors generated much more microbial products. Because of this condition, it can be concluded that total inert COD/total COD ratios of the aerobic reactors were 60%, whereas those of anaerobic reactors were 50%. This study is important for modeling, design, and operation of landfill leachate treatment systems and determination of discharge limits.

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