ADSORPTIVE BIOLOGICAL TREATMENT OF PRETREATED LANDFILL LEACHATE BY FED – BATCH OPERATION

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M. Yunus PAMUKOĞLU

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We certify that we have read this thesis and **“Adsorptive Biological Treatment of Pretreated Landfill Leachate by Fed-Batch Operation”** completed by **M. Yunus PAMUKOĞLU** under supervision of **Prof.Dr. Fikret KARGI** and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Prof.Dr. Fikret KARGI

Supervisor

Prof.Dr.Azmi TELEFONCU

(Committee Member)

Yard.Doç.Dr.İlgi K. KAPDAN

(Committee Member)

Approved by the
Graduate School of Natural and Applied Sciences

Prof.Dr. Cahit HELVACI
Director

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Env.Eng
M. Yunus PAMUKOĞLU

ABSTRACT

Early biological treatment studies with the raw leachate did not yield high COD and nitrogen removals. In order to improve biological treatability, the landfill leachate was subjected to pretreatment by chemical coagulation-flocculation followed by air stripping of ammonia at pH =12. Three different chemical coagulants, alum ($Al_2(SO_4)_3$), $FeCl_3$ and lime (CaO) were used in different concentrations for COD and nitrogen removal by coagulation-flocculation. COD concentrations of the three coagulants at low doses (0.5-1.0 g/L) were comparable. Considering the problems associated with the use of high coagulant doses such as more sludge formation and high cost of coagulation, low doses of coagulants such as 1 g/L were preferred. Percent COD removals for the three coagulants at the dose of 1 g/L were almost the same as 45%. Supernatant solution after coagulation with 1g/L lime at pH =12 was subjected to air stripping at different pH levels to remove excess ammonia from the leachate. Ammonium concentration was reduced to nearly 700 mg/L from 1200 mg/L after 45 minutes of air stripping at pH=12.

The pretreated leachate was subjected to aerobic biological treatment in an aeration tank by fed-batch operation. The effects of the feed wastewater COD content and flow rate on COD and ammonium ions removal were investigated. Nearly 76% COD and 23% NH_4-N removals were obtained with a flow rate of 0.21

L/h and the feed COD content of 7,000 mgCOD/L. COD removal efficiency decreased with increasing COD loading rates. A kinetic model for COD removal was developed and the kinetic constants were determined by using the experimental data.

In order to improve the extent of COD and ammonium nitrogen removals, pretreated leachate was subjected to adsorbent supplemented biological treatment in an aeration tank operated in fed-batch mode by using powdered zeolite (PZ) and powdered activated carbon (PAC) as adsorbents. Adsorbent concentrations were varied between 0 g/L and 5 g/L. Percent COD and ammonium-N removals increased with increasing adsorbent concentrations. COD removals with PAC addition were significantly higher than those obtained with zeolite. However, zeolite performed better than the PAC in ammonium-N removal from the leachate. Nearly 87% and 77% COD removals were achieved with PAC and zeolite concentrations above 2 g/L, respectively. Ammonium-N removals were 30% and 40% with PAC and zeolite concentrations of 5 g/L, respectively at the end of 30 hours of fed-batch operation. An empirical equation was developed to describe the contribution of adsorption over biological treatment as a function of PAC and zeolite concentrations.

To further decrease effluent COD and ammonium concentrations, two sets of repeated fed-batch experiments with different operation times (3x10 h and 5x6 h) were performed with and without PAC addition. When the operation time was divided to 3x10 hours and 5x6 hours, better results were obtained than that of the 30 hours single cycle operation with and without PAC addition. The effluent COD and NH_4-N concentrations were 365 mg/L and 360 mg/L in the repeated fed-batch

operations of 5x6 hours with 2 g/L PAC addition. To observe system performance at longer operation times, a three-cycle operation with 30 hours durations was used (3x30 h) in repeated fed-batch mode in the presence of 2g/L PAC. At the end of 90 hours repeated fed-batch operation (3x30 h), the effluent COD and NH_4-N concentrations were 285 mg/L and 224 mg/L, respectively which are considerably lower than those obtained with 5x6h operation. Apparently, longer operation times in repeated fed-batch operation resulted in better effluent water quality.

Effects of N/COD ratio in the fed wastewater on COD and ammonium removal in PAC added biological treatment were investigated. Percent COD removals increased and the final COD contents decreased with increasing $L_{NH4\text{-}N}/L_{COD}$ ratio. $L_{NH4\text{-}N}/L_{COD}$=0.05-0.08 ratio was optimum resulting in 85% COD and 44 % NH_4-N removal. Percent COD removal decreased to 78%, when $L_{NH4\text{-}N}/L_{COD}$ was reduced to 0.03.

Chemical oxidation was used to further reduce COD content of landfill leachate after PAC added biological treatment. Three oxidizing agents (H_2O_2, Fenton's reagent, NaOCl) were used in different concentrations for chemical oxidation. Chemical oxidation by Fenton reagent resulted in higher COD removals as compared to H_2O_2 and NaOCl. Nearly, %68 COD removal, 95 mg/L effluent COD and 2 mg/L NH_4-N have been obtained with 150/250 mg/L $H_2O_2/FeSO_4$ ratio.

ÖZET

Yüksek miktarlarda KOI, amonyum azotu ve toksik madde varlığından dolayı, deponi alanları sızıntı suyunun biyolojik arıtımı önemli zorluklar arzeder ve düşük giderme verimi ile gerçekleşir. Sızıntı suyunun biyolojik olarak arıtılabilirliliğini arttırmak için ön arıtım olarak koagülasyon-flokülasyon ve pH=12 de amonyumun havalandırma ile giderimi uygulanmıştır. Koagülasyon-flokülasyon yöntemiyle KOI ve amonyum giderimini sağlamak için farklı dozlarda $Al_2(SO_4)_3$, $FeCl_3$ ve kireç (CaO)' den oluşan 3 kimyasal kogülant kullanılmıştır. Bu üç koagülantın KOI giderim verimleri düşük dozlarda karşılaştırılabilir (0.5 – 1 g/L). Yüksek miktarda kullanılan koagülantın daha fazla çamur oluşturması ve koagülantların yüksek fiyatları düşünüldüğünde, 1 g/L gibi düşük koagulant dozları tercih edilmiştir. Bu üç koagulantın 1 g/L derişiminde KOI giderme verimleri yaklaşık olarak %45 olarak bulunmuştur. 1 g/L kireç dozu ve pH=12' de uygulanan koagülasyondan sonra üst sıvıdaki aşırı amonyumu gidermek için farklı pH' larda havalandırma uygulanmıştır. pH=12' de 45 dakika sonrasında havalandırmayla amonyum konsantrasyonu 1200 mg/L' den yaklaşık 700 mg/L' ye düşürülmüştür.

Ön arıtılmış sızıntı suyu havalandırma tankında yarı sürekli (fed-batch) işletmeyle aerobik biyolojik arıtıma tabii tutulmuştur. Giriş suyundaki KOI derişimi ve debisinin KOI ve amonyum iyonlarının giderimleri üzerine etkisi araştırılmıştır. Girişteki 7000 mg KOI/L ve 0.21 L/sa debide yaklaşık olarak %76 KOI ve %23

NH_4-N giderim verimlerine ulaşılmıştır. KOI giderim verimleri KOI yükleme oranlarının artmasıyla azalmıştır. KOI giderimi için bir kinetik model geliştirilmiş ve deneysel veriler kullanılarak kinetik sabitler bulunmuştur.

KOI ve amonyum azotu giderimlerini arttırmak için ön arıtılmış sızıntı suyuna yarı sürekli (fed-batch) işletilen bir havalandırma tankında zeolit ve aktif karbon ilavesiyle adsorpsiyonlu biyolojik arıtım uygulanmıştır. Adsorban konsantrasyonları 0-5 g/L arasında değiştirilmiştir. KOI ve amonyum giderimleri adsorban konsantrasyonu artmasıyla birlikte artmıştır. PAC eklenmesiyle elde edilen KOI giderimleri zeolit eklenmesiyle elde edilenlerden daha yüksek çıkmıştır. Buna rağmen zeolit, sızıntı suyunda amonyum-N giderimleri açısından PAC' tan daha iyi sonuç vermiştir. 2 g/L' nin üzerindeki zeolit ve PAC ilavelerinde yaklaşık olarak sırasıyla %87 ve %77 KOI giderim verimlerine ulaşılmıştır. Yarı sürekli işletmede 30 saatin sonunda 5g/L PAC ve zeolit konsantrasyonlarında amonyum azotu giderim verimleri sırasıyla %30 ve %40 olarak bulunmuştur. PAC ve zeolit konsantrasyonlarının bir fonksiyonu olarak, biyolojik arıtımın üzerine adsorpsiyon etkilerini belirlemek amacıyla empirik bir eşitlik geliştirilmiştir.

Çıkıştaki KOI ve amonyum konsantrasyonlarını azaltmak için, ön arıtılmış sızıntı suyunun yarı sürekli biyolojik arıtımı ardışık olarak farklı operasyon zamanlarında (30 sa, 3x10 sa, 5x6 sa) PAC varlığında ve yokluğunda uygulanmıştır. Ardışık yarı sürekli işletmede işletme zamanı 6 saat olarak beş defa tekrarlandığında, 30 saatlik tek işletmeye gore daha yüksek KOI giderimleri sağlanmıştır. Ardışık yarı sürekli işletmede (PAC=2 g/L) işletme zamanı 6 saat olarak beş defa tekrarlandığında, toplam 30 saatlik peryodun sonunda çıkış KOI and NH_4-N konsantrasyonları 365 mg/L ve 360 mg/L olarak bulunmuştur. Sistemin uzun zamanda performansını görmek için ardışık yarı sürekli işletmede (PAC=2 g/L) işletme zamanı 30 saat olarak 3 kez tekrarlanmıştır. Toplam 90 saatlik sürenin sonunda çıkış KOI and NH_4-N konsantrasyonları 285 mg/L ve 224 mg/L olarak bulunmuştur. Bu değerler 5x6 saatlik işletmede elde edilenlerden daha düşüktür. Ardışık yarı sürekli işletmede işletme süresi artığında çıkış suyu kalitesi de yükselmektedir.

PAC ilaveli biyolojik arıtımda giriş suyundaki N/KOI oranının KOI ve amonyum giderme verimlerine etkisi araştırılmıştır. L_{NH4-N}/L_{KOI} oranının artmasıyla, KOI giderim verimleri artmış ve çıkış konsantrasyonları azalmıştır. Daha yüksek KOI giderim verimlerini sağlamak için optimum L_{NH4-N}/L_{KOI} oranı olan 0.05-0.08 arasında %85 COD ve %44 NH_4-N giderim verimlerine ulaşılmışltır. L_{NH4-N}/L_{KOI} oranı 0.03 olduğunda, KOI giderim verimi %78' e düşmektedir.

Çıkış suyu KOI derişimlerini kabul edilebilir seviyeye düşürmek için ileri arıtım olarak kimyasal oksidasyon kullanılmıştır. Bu amaçla biyolojik arıtımdan sonra toplanan sızıntı suyu üç değişik oksidant kullanılarak (H_2O_2, Fenton's oksidant, NaOCl) kimyasal oksidasyona tabii tutulmuştur. Fenton oksidasyon deneylerinde 150/250 mg/L $H_2O_2/FeSO_4$ oranında %68 giderim verimi, 95 mg/L çıkış KOI ve 2 mg/L NH_4-N derişimi ile H_2O_2 ve NaOCl deneylerinden daha iyi sonuçlar elde edilmiştir.

CONTENTS

Page

Chapter One
INTRODUCTION

Chapter Two
MATERIALS AND METHODS

Chapter Three
RESULTS AND DISCUSSION

Chapter Four
CONCLUSIONS

Chapter Five
REFERENCES

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

INTRODUCTION

1.1. INTRODUCTION

Because of high COD (6,000 – 15,000 mg/L) and ammonium ion (500 - 3000 mg/L) contents, high COD/BOD ratio and also due to the presence of toxic compounds such as metal ions, COD removals by direct biological treatment of municipal landfill leachates are usually low (Sletten et al., 1995; Amakrane et al.,1997; Irene and Lo, 1997; Chiang et al., 2001; Park et al., 2001).

Landfill leachate treatment has been given significant attention in recent years especially for municipal areas (Diamadopoulos et al., 1997; Bohdziewicz et al., 2001; Ding et al., 2001; Geenens et al., 2001; Ahn et al., 2002). Depending on the nature of the land-filled solid wastes, the active microbial flora, characteristics of the soil, the rainfall patterns and the age of the landfill the composition of the landfill leachates present variations (Chen, 1996). Young landfill leachates are usually treated more easily as compared to the old ones. For this reason, the treatment strategy mainly depends on the characteristics of the leachate.

Methods developed for treatment of landfill leachates can be classified as physical, chemical and biological methods. Since it is difficult to obtain satisfactory treatment efficiencies and effluent water quality by using anyone of those methods alone, usually a combination of physico-chemical and biological methods are used. Among the physical methods used for leachate treatment sedimentation, air-stripping, adsorption, membrane filtration are the major ones (Amakrene et al.,1997; Bohdziewicz et al., 2001; Morawe et al.,1995; Trebouet et al., 2001). These methods are usually used in combination with chemical and biological methods. Coagulation-flocculation (Amakrane et al.,1997; Ahn et al., 2002), chemical precipitation, chemical-electrochemical oxidations (Chiang et al., 2001; Lin and Chang, 2000;

Steensen, 1997; Marttinnen et al., 2002) have been the major chemical method used for the landfill leachate treatment. Biological treatment methods used for the leachate treatment can be classified as aerobic, anaerobic and anoxic processes which are widely used for the removal of biodegradable compounds. Physical-chemical methods are usually used along with the biological methods mainly to remove non-biodegradable compounds from the leachate (Bohdziewicz et al., 2001; Ahn et al., 2002; Geenens et al.,2001; Trebouet et al., 2001).

A number of physical-chemical methods such as nanofiltration, air-stripping and ozonation have been tested for their efficiency in COD, ammonium and toxicity removal by Martinnen et al. (2002). Nearly, 66% COD and 50% ammonia have been removed by nanofiltration. Air-stripping at pH =11 resulted in 89% ammonia removal at 20 °C within 24 hours. Ozonation increased the concentration of rapidly biodegradable COD. However, none of the tested methods were effective in toxicity removal. Physicochemical methods have been used in combination with nanofiltration for treatment of landfill leachate by Trebouet et al (2001). pH modifications and coagulation with $FeCl_3$ have been tested to remove foulants from the surface of the membranes. Nanofiltration has been found satisfactory for removal of refractory COD from the leachate used.

In ammonia stripping by 2 hours of aeration, ammonia removal was 72% at pH=12 while the removals were around 20% at pH=10 and pH=11. Ammonium nitrogen removals by air stripping were 45%, 80% and 85% for 6 hours, 12 hours and 17 hours aeration at pH = 11, respectively.(Öztürk I. et al.,2002)

Air stripping of landfill leachate has also been studied by Kabdaşlı et al.,(2002) Young leachate sample used in this study had COD and ammonia concentrations of 22,255 and 2,410 mg/L, respectively. Ammonia removal by stripping was found more effective at alkaline pH as expected. Air stripping of leachate provided COD removals over 80%.

Ammonium removal from landfill leachate by chemical precipitation was investigated by Li et al (Li et al.,1999; Li and Zhao, 2001). Ammonium ions were precipitated as magnesium ammonium phosphate (MAP) with the addition of $MgCl_2.6H_2O$ and $Na_2HPO_4.12\ H_2O$ with a $Mg/NH_4/\ PO_4$ ratio of 1/1/1 at pH of 8.5-9. Ammonium ion concentration was reduced from 5,600 mg/L to 110 mg/L within 15 minutes by this method.

Chemical oxidation methods have been applied to biologically pretreated landfill leachate by Steenson (1997). Non-biodegradable compounds were removed by H_2O_2/ UV, ozone and ozone/fixed bed catalyst methods to achieve desired effluent water quality.

Struvite (MAP) precipitation was investigated by Öztürk I. at al.(2002). Ammonium content of anaerobically pretreated raw landfill leachate effluent with an ammonium concentration of 2,240 mg/L was reduced to 250 mg/L by struvite (MAP) precipitation. Maximum ammonium removal observed was 89% at pH of 9.2 indicating high ammonium removals from anaerobically pre-treated leachate

Amokrane A. et al. used coagulation-flocculation as pretreatment of stabilized landfill leachates. Although their optimal doses were identical (0.035 mol/L of Fe or Al), Ferric chloride has produced better results than aluminium sulfate in the removal of turbidity (95% on 87%) and COD (55% on 42%). The optimal pH values obtained at the optimal coagulant dose were 5 for ferric chloride and 5.5 for aluminium sulphate(Amokrane A. et al., 1997)

The oxidation of organics resisting to biological decomposition process in leachate by means of hydrogen peroxide with ferrous ions in the medium (Fenton's reactions) was investigated experimentally. It is illustrated that some amount of non biodegradable organic substances in leachate can be removed by Fenton's reactions. (Kurt U. et al., 2002)

Pressure driven membrane techniques have been applied to biological treatment of landfill leachate (Bohdziewicz et al, 2001). Several hybrid processes such as activated sludge-chemical oxidation, activated sludge-ultrafiltration-chemical oxidation and activated sludge-ultrafiltration-reverse osmosis have been tested for landfill leachate treatment. Activated carbon adsorption process has been used along with biological treatment for effective treatment of landfill leachate (Morawe et al., 1995; Cecen et al., 2002). Non-biodegradable organics, inert COD and the colour have been reduced to acceptable levels by activated carbon column treatment of biologically treated landfill leachate.

Gülşen, H. et al. (2002) carried out studies on leachate treatment by combined anaerobic and chemical oxidation methods. Anaerobic treatability studies have been carried out, by an anaerobic fluidized bed reactor (AFBR). The effluents from the AFBR were additionally treated by Fenton's oxidation to remove inert COD. In the AFBR, COD removals of 88-90% were achieved for organic loading rates of 4-15 kg COD/m^3.d. Maximum COD removal by Fenton's oxidation was obtained at pH of 2.5. For the first sample containing 2 kg COD/ m^3, optimum H_2O_2 dosage maximizing the COD removal was found to be 1200 mg/L for 1800 mg/L Fe^{+2}. Under these conditions maximum COD removal of 85% was achieved.

Anaerobic treatment is usually more advantageous as compared to aerobic treatment due to high COD content and high COD/BOD ratio of the landfill leachate. Anaerobic biological treatment of landfill leachate has been investigated by many investigators (Timur and Ozturk, 1999; Im et al., 2001; Kennedy et al., 2000; Kettunen et al., 1996). Up to 92 % COD removals have been obtained by using upflow anaerobic sludge blanket reactors (Kennedy et al., 2000). Anaerobic and sequential anaerobic-aerobic reactors have been used for landfill leachate treatment at different temperatures such as 11 °C and 24 °C (Kettunen et al., 1996). Nearly 75% COD removals have been achieved by anaerobic treatment at 24 °C with a 10 hour HRT. Aerobic treatment following the anaerobic process removed 45-75% of the COD left after the anaerobic treatment resulting in effluent COD of less than 380 mg/L. The overall COD removal in the sequential process was 80-90% with nearly 80% ammonium removal.

Aerobic biological treatment of landfill leachate has been studied by using both suspension and biofilm cultures (Diamadopoulos et al., 1997; Loukidou and Zoubalis, 2001; Maehlum, 1995; Shiskowski and Mavinic, 1998). Maehlum (1995) used on site anaerobic-aerobic lagoons and constructed wetlands for biological treatment of landfill leachate. Overall N, P and Fe removals obtained in this system were above 70% for diluted leachate. Aerobic treatment of domestic leachates in a sequencing batch reactor (SBR) with a residence time of 20-40 days resulted in nearly 99% NH_4-N removal (Irene and Lo, 1997). Combined treatment of landfill leachate and domestic sewage was investigated by using an SBR consisting of filling, anoxic, oxic and settling phases (Diamadopoulos et al., 1997). When the ratio of sewage to leachate was 9/1, nearly 95% BOD and 50% nitrogen removals have been obtained at the end of the daily cycles. Loukidou & Zouboulis (Loukidou and Zoubalis, 2001) have used moving bed biofilm processes by using polyurethane and granular activated carbon (GAC) support particles in an SBR reactor. Nearly complete removal of nitrogen and satisfactory removals of COD, colour and turbidity have been achieved. A combination of anaerobic-aerobic and rotating biological contact (RBC) processes has been used for leachate treatment by Park et al (2001). The effluent of the RBC process was subjected to flocculation-sedimentation; adsorption and finally reverse osmosis processes and nearly 98% of the organic materials of low MW have been removed.

Autotrophic denitrification of landfill leachate by using elemental sulfur packed bed columns have been achieved by Koenig and Liu (1996). Nitrate ions produced in nitrification process have been removed effectively by using *Thibacillus denitrificans* in the column reactor. Imai et al (1993) used activated carbon fludized bed reactors for removal of refractory organics from landfill leachate. Nearly, 60% and 70% refractory organics and nitrogen have been removed by adsorption coupled biological treatment in activated carbon fluidized beds.

Zouboulis et al., (2001) used enzymatic degradation and optimized the performance, especially for the removal of nitrogen compounds and of biodegradable organic matter in leachate. It was found that the enzymatic process was able to remove organic matter effectively (expressed as BOD_5 and COD), nitrogen content, color and turbidity.

Combined chemical and biological treatment of landfill leachate has also been investigated. Geenens et al (2001) used ozone pre-treatment before biological treatment of landfill leachate in an activated sludge unit. COD/BOD ratio was decreased from 16 to 6 by ozonation which improved the efficiency of the activated sludge treatment. Coagulation by $FeCl_3$ and zeolite treatment for ammonium removal before biological treatment has been shown to improve biological treatability of landfill leachate by Ahn et al (2002). Chemical precipitation of ammonium present in landfill leachate by addition of $MgCl_2$ and Na_2HPO_4 and formation of magnesium ammonium phosphate (MAP) has also improved biological treatment efficiency (Li and Zhao, 2001).

In neither one of the aforementioned studies, different adsorbents were tested in adsorbent added biological treatment of pre-treated landfill leachate in a fed-batch operated aeration tank. Therefore, it is the major objective of this study to investigate the adsorbent added biological treatment of landfill leachate by using different adsorbents such as powdered activated carbon (PAC) and powdered zeolite (PZ). Flocculation-sedimentation of inert organic compounds by lime addition followed by ammonia stripping by air have been used as pretreatment to improve the biological treatability of the leachate. Pre-treated leachate was subjected to adsorbent added aerobic biological treatment by fed-batch operation in an aeration tank. Biological treatment of pretreated landfill leachate was investigated in the absence and presence of adsorbents. In biological treatment experiments feed COD content and flow rate were changed as variables. In adsorbent added biological treatment feed flow rate and COD content were kept constant while the type and concentration of adsorbents were changed. COD and ammonium-N removals were quantified as a function of the concentrations of the adsorbents. Control experiments devoid of organisms and adsorbents were carried out in order to quantify the rate and extent of COD and NH_4-N removal.

1.2. Theoretical Background

Fed-batch operation of an aeration tank involves slow addition of highly concentrated wastewater or nutrient media into aeration tank with no effluent removal until the tank is full. Aeration tank contains highly active and dense organisms at the beginning of operation. Concentrated or toxic wastewater is diluted inside the reactor by slow feeding resulting in low inhibition and relatively high COD removal rates as compared to classical continuous operations such as the activated sludge process.

Fed-batch operation is different from sequencing batch reactor (SBR) operation. Concentrated feed wastewater is added slowly or intermittently into the aeration tank without effluent removal in fed-batch operation. However, filling, aeration, sedimentation and effluent removal phases are applied in sequence in a batch operated reactor in sequencing batch operation. Certain amount of sludge was removed from the reactor everyday to adjust the sludge age. Theory of fed-batch operation is presented in many texts (Shuler and Kargi, 2002; Pirt, 1975) and is briefly summarized below.

As the feed wastewater is added slowly, the liquid volume in the reactor increases with time linearly according to the following equation since no effluent is removed.

$$V = V_0 + Q\,t \qquad (1.2.1.)$$

When the system was operated with feed-back controlled addition of the feed, the substrate (COD or BOD) concentration remains constant at a low level or nearly zero which is called the 'Quasi Steady-State' at which $dS/dt=0$ and $dX/dt = 0$
At quasi steady-state,

$$\mu = D = \frac{1}{\theta_H} = \frac{\mu_m S}{K_s + S} \qquad (1.2.2.)$$

$$\text{or} \quad S = \frac{K_S D}{\mu_m - D} \qquad (1.2.3.)$$

where D is the dilution rate ($Q/V = 1/\theta_H$).

As a result of increase in reaction volume, dilution rate ($D = Q/V$) decreases with time in this type of operation resulting in a decrease in specific growth rate (μ). Biomass concentration (X) remains almost constant; however, total amount of biomass ($X_T = X\ V$) in the reactor increases as a function of time according to the following equation.

$$X_T = X_{To} + Q\ Y\ (S_o - S)\ t \qquad (1.2.4.)$$

where Y is the growth yield coefficient (gX/gS), and S_o is the feed substrate (BOD or COD) concentration (gS/L) and Q is the flow rate (m^3/h).

1.2. Objectives and Scope

Major objectives of this thesis can be summarized as follows;

- to select an effective and low-cost adsorbent for use in landfill leachate treatment by adsorption
- to select an effective microbial culture for biological treatment of leachate.
- to enhance biological treatability of landfill leachate by pretreatment
- to investigate COD and ammonium removal performance of adsorptive biological treatment by fed-batch operation.
- to investigate the performance of repeated fed-batch experiments for COD and ammonium nitrogen removal
- to explore the effects of feed COD/N ratio on COD and ammonium removal in PAC added biological treatment

- to investigate COD removals from biologically treated leachate by chemical oxidation
- to determine kinetic constants by using experimental data.

In the first part of the thesis, compositions of the landfill leachate obtained from the Harmandalı Landfill area in Izmir, Turkey were determined. Adsorption capacity of low cost adsorbents like zeolite, bentonite, kaoline, clay, wood ash. and wood chip in addition to PAC (powdered activated carbon) were investigated. Activated sludge cultures obtained from Izmir Pak-Maya Yeast Industry, Izmir Domestic Wastewater Treatment Plant, Izmir Pınar Meat Industry were tested for biological treatment in order to select a suitable microbial culture. Early biological treatment studies with the raw leachate did not yield high COD and nitrogen removals, for this reason the leachate was subjected to pretreatment by chemical coagulation-flocculation followed by air stripping of ammonia at pH =12. Three different chemical coagulants, alum ($Al_2(SO_4)_3$), $FeCl_3$ and lime (CaO) were used in different concentrations for COD and nitrogen removal by coagulation-flocculation. COD and NH_4-N contents of the leachate were reduced to desired levels by pre-treatment.

In the second part of the thesis, two sets of experiments were performed for the fed-batch biological treatment of the pre-treated landfill leachate. In biological treatment studies, effects of different COD loading rates on the reactor performance were investigated. Kinetic constants were determined by using experimental data. In order to increase COD and ammonium removal rate, pretreated leachate was subjected to adsorbent supplemented biological treatment in an aeration tank operated in fed-batch mode by using powdered zeolite (PZ) and powdered activated carbon (PAC) as adsorbents. Empirical models were developed to quantify the contribution of adsorption.

In the third part, repeated fed-batch experiments were performed in order to decrease effluent COD and ammonium concentrations. Two sets of repeated fed-batch experiments were performed with and without PAC addition with different cycle times (3x10 h and 5x6 h) and total operation time of 30 hours. After these experiments, effects of the feed N/COD ratio on COD and ammonium removal in PAC added biological treatment by fed-batch operation were investigated.

In the final part of the thesis, chemical oxidation experiments were carried out after biological treatment by using H_2O_2, Fenton's reagent and NaOCl as oxidizing agents. Different dosages were used in chemical oxidation experiments to obtain low effluent COD and ammonium concentrations.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Experimental setup

Figure 2.1.1 depicts a schematic of the experimental setup. The system consists of a feed reservoir, a fed-batch aeration tank, pipes, wastewater and air pumps and diffusers. Feed reservoir was placed in a deep refrigerator to keep the temperature below 5 °C in order to avoid any decomposition. A plexiglass aeration tank of 20 cm diameter and 60 cm height with a total volume of 18.8 liter was used throughout the studies. Wastewater in the tank was aerated with the aid of an air pump and diffusers. Wastewater was fed to the reactor by using a peristaltic pump with adjusted flow rates varying between 0.05-0.6 L/h.

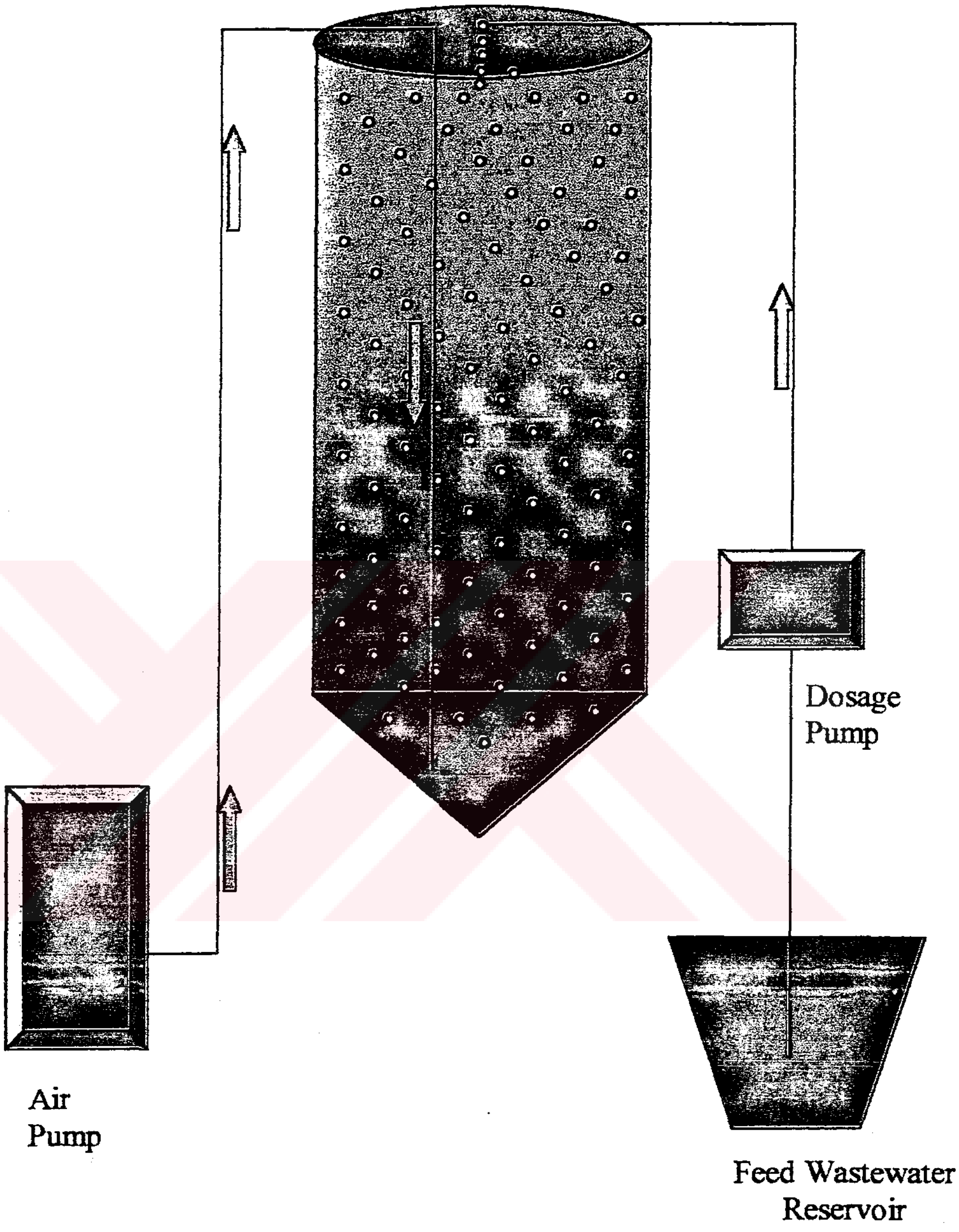

Figure 2.1.1. Schematic diagram of experimental setup.

2.2. Wastewater Composition

Synthetic wastewater used throughout the studies was composed of pre-treated leachate and KH_2PO_4. Total nitrogen and phosphorous concentrations in the feed wastewater were adjusted to yield COD/N/P ratio in the feed as 100/10/1.5. Powdered activated carbon (PAC) and zeolite (-200 mesh) were added to the tank every hour during the course of operation in desired amounts. Feed COD concentration was varied in biological treatment experiments. However, the feed COD content and the flow rate were kept constant at CODo = 7,000 mg/L and Q = 0.15 L/h during adsorptive biological treatment while the concentrations of the adsorbents were changed. Typical waste water composition after pre-treatment was COD = 7,000 mg/L and NH_4-N = 700 mg/L. KH_2PO_4 was added to the pre-treated leachate externally to adjust phosphate-P concentration to the desired level.

2.3. Organisms

Activated sludge culture was obtained from the wastewater treatment plant of PAK-MAYA Bakers Yeast Company (Izmir, TURKEY). The activated sludge culture was adapted to the leachate by cultivating the organisms in the diluted leachate in aeration tanks. Adaptation and cultivation medium had COD/N/P ratio of 100/10/1.5 with CODo = 4000 mg/L. Some stock cultures were preserved in the freezer in frozen form.

2.4. Experimental Procedure

2.4.1. Experiments with Erlenmeyer Flasks

2.4.1.1. Selection of Adsorbent

The adsorbents used for adsorption were powdered activated carbon (PAC), zeolite, bentonite, kaoline, clay, wood ash, wood chips. The particle diameters of adsorbents were -200 mesh (D_p<74 μm).

Experiments were carried out on a gyratory shaker in 250 mL flasks with 200 mL reaction volume at T=25±1 °C, pH=7±0.5 and 200 rpm. Adsorbent concentration was kept constant at 1 g/200 mL. Control flasks contained only landfill leachate without any adsorbent. Samples withdrawn were centrifuged at 6000 rpm for 30 minutes.

2.4.1.2. Selection of Microbial Culture

Activated sludge cultures were obtained from Izmir Pak-Maya Yeast Industry, Izmir Domestic Wastewater Treatment Plant and Izmir Pınar Meat Industry. The flasks contained with 180 mL wastewater and 20 mL culture and were incubated in an incubator shaker for 54 hours at T=25±1 °C and rotational speed of 200 rpm. A control flask with no inoculation was also used. Samples were removed and centrifuged at 6000 rpm for 30 minutes to remove organisms.

2.4.2. Pretreatment Experiments

Pre-treatment of the landfill leachate consisted of coagulation-sedimentation followed by air stripping of ammonia at pH=12. Coagulation-sedimentation experiments were carried out by using a jar-test apparatus. Different coagulants ($FeCl_3$, lime and alum) were added in desired concentrations onto the raw leachate in 1 liter beakers. The contents were mixed fast at 200 rpm for 2 minutes followed by a slow mixing at 20 rpm for about 30 minutes and were sedimented for about 1 hour. The effluent of the flocculation step was subjected to air stripping at different pH for a desired period to remove ammonia.

2.4.3. Experiments with Fed – Batch Operation

Biological treatment experiments were started batch wise. About 5 liter of pretreated leachate was placed in the aeration tank and inoculated with the activated sludge culture pre-adapted to the leachate. Reactor content was aerated for several days to obtain a dense culture. At the end of batch operation, reactor contents were sedimented and two liters of the supernatant was withdrawn before continuous feeding of the medium was started without any effluent removal.

Powdered activated carbon (PAC) and powdered zeolite (PZ) of -200 mesh were added manually to the aeration tank every hour to adjust the adsorbent concentrations to the desired level. Temperature, pH and dissolved oxygen of the medium during operation were T = 20 ± 2 C, pH = 8.0 ± 0.5 and DO = 3 ± 0.5 mg/L. The reactor liquid volume increased linearly with time depending on the flow rate. Experiments continued for thirty hours and were run twice to test the reproducibility of the results. Since the results of the replicates were almost the same, no further triplicates were run. A control experiment devoid of organisms and adsorbent (C) was run under the same conditions for each experiment and COD concentrations were quantified. Simultaneous experiments were conducted by using only adsorbents without the organisms for adsorption alone (A) and only with the organisms without any adsorbents for biological oxidation alone (B) under the same conditions along with the adsorbent added biological treatment (AB). Sludge age (Θ_c) was arranged as 10 days in all fed-batch experiments.

2.4.4. Chemical Oxidation Experiments

Post-treatment of the landfill leachate was accomplished by chemical oxidation. Different oxidizing agents (H_2O_2, Fenton's Reagent and NaOCl) were used in desired concentrations for chemical oxidation of biologically treated landfill leachate. COD measurements were made to quantify the extent of COD removals.

2.4.4.1. Chemical Oxidation Experiments using H_2O_2

The efficiency of this oxidizing agent was examined for further treatment of biologically treated landfill leachate. 250 mL volume wastewater sample was prepared in beakers; pH value of leachate was adjusted to 3 with the addition of H_2SO_4. Calculated H_2O_2 dosages were added into each beaker. H_2O_2 oxidation experiments were carried out by aeration using an air pump. Different aeration times were tested. Finally, COD concentrations of treated leachate were determined and percent COD removals were calculated.

2.4.4.2. Chemical Oxidation Experiments using Fenton's Reagent

250 ml leachate samples were placed in the jar test apparatus and pH's were adjusted to 3 with the addition of H_2SO_4. Proper amounts of hydrogen peroxide (35%) and ferrous sulfate ($FeSO_4.7H_2O$) were added to the wastewater samples. The contents were mixed fast at 200 rpm for 2 minutes followed by a slow mixing at 20 rpm for about 30 minutes and were sedimented for about 1 hour. The upper liquid was removed and pH adjusted to 7 with the addition of NaOH solution and stood still for 4 hours. The supernatant was removed and COD content was measured.

2.4.4.3. Chemical Oxidation Experiments using NaOCl

pH values of leachate was adjusted to 9 with the addition of 0.1 N NaOH and samples (250 mL) were placed in the jar test apparatus. Proper amounts of NaOCl (50%) were added to the wastewater samples. The contents were mixed fast at 200 rpm for 2 minutes followed by a slow mixing at 20 rpm for about 30 minutes and were sedimented for about 2 hours. The supernatant was removed and COD contents were measured.

2.5. Analytical Methods

Samples were removed from the experimental and the control reactor every hour and were centrifuged at 6000 rpm for 0.5 hour to remove the organisms. The supernatant was analyzed for COD and ammonium nitrogen. Samples were preserved at refrigerator.

2.5.1. Chemical Oxygen Demand (COD) Analysis

COD measurements were carried out according to Standard methods (APHA, 1989). Closed reflux colorimetric methods were used.

In closed reflux colorimetric method, borosilicate culture tubes with 10 ml capacity were used. A visible spectrophotometer was used to measure absorbance at 600 nm. Digestion solution was prepared by adding 10.216 g $K_2Cr_2O_7$, 167 ml concentrated H_2SO_4 and 33.3 g $HgSO_4$ into distilled water to be 1000 ml and the solution was cooled to room temperature. Sulfuric acid reagent and potassium hydrogen phthalate (KHP) standard were used. KHP was used for preparation of the calibration curve. KHP was lightly crushed and then dried to constant weight at 120 ^{0}C. Then different initial KHP concentrations were dissolved in distilled water for different concentrations. KHP solution had a theoretical COD of 900 mg/L for 0.765 g KHP/L. 16 standards of KHP were prepared to obtain COD concentration of 10 – 900 mg COD/L. The calibration curve was used for determination of COD contents of samples. The absorbencies of samples are placed to the equation for calculating the COD concentration. (Greenberg A.E, 1989, pp.5, 9-10).

2.5.2. Ammonium nitrogen analysis (NH_4-N^+)

Ammonium ion concentrations were determined by using the test kits (Merck No 14572 and Aqualytic spectroquant No 500) and a spectrometer. Samples were diluted properly before measurements.

2.5.3. Mixed Liquor Suspended Solid Measurements (MLSS)

Biomass (MLSS) concentrations were determinated by filtering the samples through milipore filters (45 μm) and drying until constant weight in an oven at 105 ^{0}C. The calculations were made by using the following equation (Greenberg A.E, 1989).

$$M = (A - B) \times 1000/V$$

Where, (A) is the weight of filter and residue after drying; (B) is the weight of filter after drying and (V) is the volume (ml) of sample.

2.5.4. Dissolved Oxygen Measurements

Dissolved oxygen (DO) measurements were made by using a WTW DO Analyzer and a DO probe. The analyzer was calibrated properly before use.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1. Characterization of the Landfill Leachate

Composition of the landfill leachate obtained from the Harmandalı Landfill area in Izmir, Turkey is presented in Table 3.1.1.

Table 3.1.1. Composition of the landfill leachate obtained from the Harmandalı Landfill area in Izmir, Turkey

Parameters	**Values**
PH	8.15-8.65
COD (mg / L)	9500-14000
TOC (mg / L)	3750-5500
TN (mg / L)	1450
$NH_4 - N$ (mg / L)	1270-2780
$NO_3 - N$ (mg / L)	7.3
TP (mg / L)	33-121
$PO_4 - P$ (mg / L)	31-110
T – Sulfur (mg / L)	160
SO_4^{-2} (mg / L)	140
TS (mg / L)	20400-21000
SS (mg / L)	1350
Salinity (%00)	0.0105
Conductivity (µMhos / cm)	21000
Mn (mg / L)	0.079
Ni (mg / L)	0.066
Zn (mg / L)	0.160
Cu (mg / L)	0.665
Cd (mg / L)	Non – Detectable
Cr (mg / L)	0.191

Table 3.1.2. Composition of the landfill leachate obtained from the Harmandalı Landfill area in Izmir, Turkey as used in experiments

Parameters	**Values**
PH	8.15
COD (mg / L)	9500
TOC (mg / L)	3750
TN (mg / L)	1450
NH_4 – N (mg / L)	1270
NO_3 – N (mg / L)	7.3
TP (mg / L)	33
PO_4 – P (mg / L)	31
T – Sulfur (mg / L)	160
SO_4^{-2} (mg / L)	140
TS (mg / L)	21000
Ni (mg / L)	0.066
Zn (mg / L)	0.160
Cu (mg / L)	0.665
Cr (mg / L)	0.191

The landfill leachate has a typical high COD and NH_4-N content and is also phosphate deficient. Ammonium-N content should be reduced and phosphate-P content should be increased to satisfy COD/N/P ratio of 100/6/1 for effective biological treatment. Heavy metal concentrations are not at toxic levels; however, may be inhibitory. Heavy metal removal is also recommended before biological treatment.

3.2. Selection of Adsorbent

In the selection of adsorbent material, in addition to powdered activated carbon (PAC), several low cost adsorbents such as zeolite, bentonite, kaoline, klay, wood ash and wood chips were used. Adsorption experiments were conducted in shake flasks at 150 rpm, pH = 7.0 ± 0.5 and at room temperature (20 °C). Initial COD concentration was adjusted to 7500 mg/L. The experiments were conducted for 24 hours until adsorption reached equilibrium.

Figure 3.2.1 depicts variations of COD concentrations with time in adsorption experiments for different adsorbents. COD concentration decreased from 7500 mg/L to 4800 mg/L within 1 hour when PAC was used as adsorbent. At the end of the 24 hours, adsorption was completed with the effluent COD concentration of 3980 mg/L. When zeolite was used as adsorbent, COD concentration decreased from 7500 mg/L to 6450 mg/L at the end of four hours. No adsorption was observed afterwards.

Wood chips resulted in low adsorption capacity in adsorption of COD compounds of landfill leachate. Bentonite, kaoline, clay and wood ash did not result in satisfactory COD removals by adsorption.

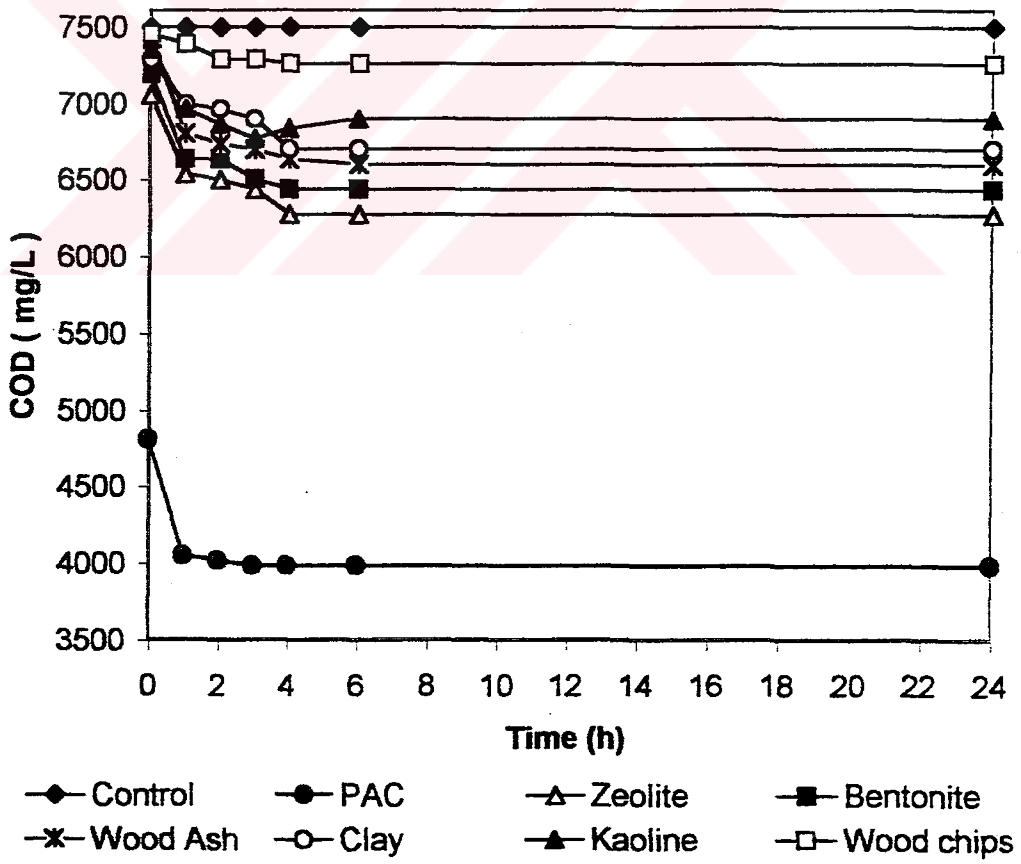

Figure 3.2.1 Variation of COD concentration with time in adsorption experiments.

Variations of percent COD removals with time for different adsorbents are shown in Figure 3.2.2. Percent COD removal within 1 hour was 36% when PAC was used as adsorbent. At the end of the 24 hours, adsorption was completed with the 47% COD removal efficiency. When zeolite was used as adsorbent, percent COD removal was found 16% at the end of 4 hours. No adsorption was observed afterwards.

Wood chips resulted in low adsorption capacity in adsorption of COD compounds of landfill leachate. Bentonite, kaoline, clay and wood ash did not perform well in adsorption experiments. These adsorbents were found inefficient and therefore, were not used in the further experiments.

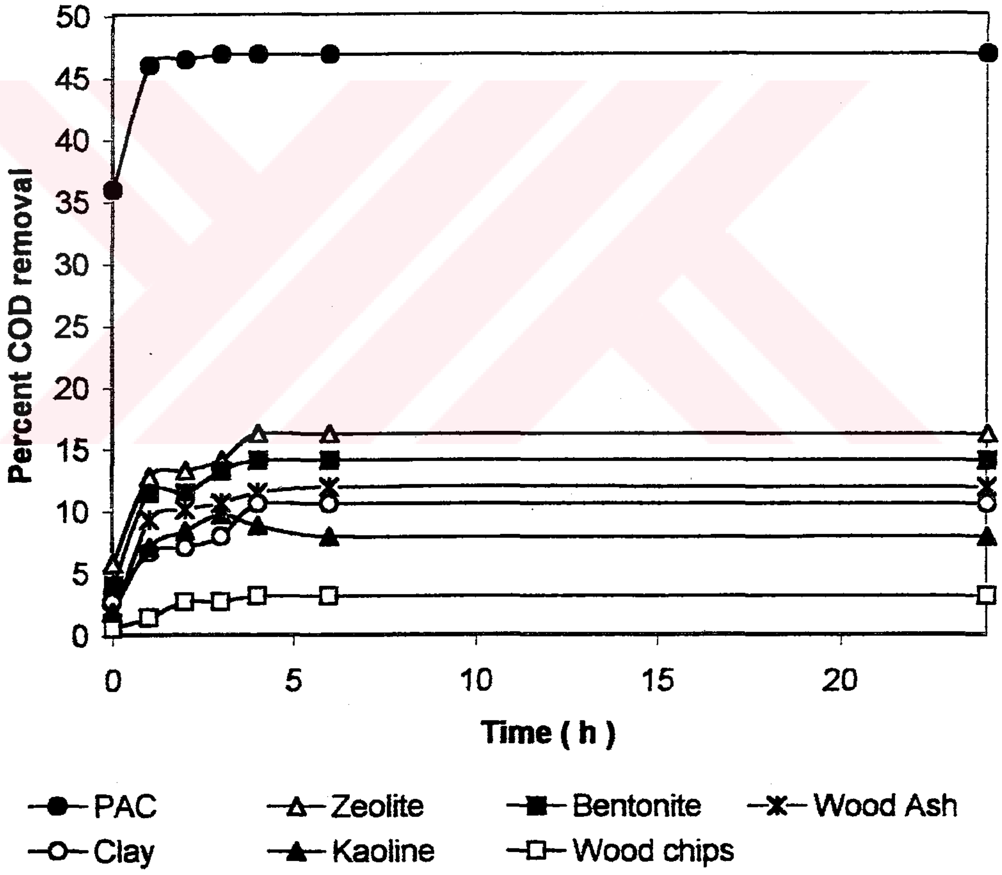

Figure 3.2.2 Variation of percent COD removals with time for different adsorbents

In summery, PAC and zeolite were the most efficient adsorbents among the tested adsorbents resulting in 47% and 16% COD removal efficiency within 24 hours, respectively. PAC and zeolite were used in further experiments.

3.3. Selection of Microbial Culture

Biotreatment efficiencies of different activated sludge cultures such as Izmir Pak-Maya Yeast Industry, Pınar Meat Industry and Cigli Domestic Wastewater Treatment activated sludges were examined in this study. The experiments were carried out in a gyratory shaker. To prevent shock loadings, landfill leachate was diluted with tap water and COD content was adjusted to 2200 mg/L. Control flasks contained landfill leachate without microbial culture.

Figure 3.3.1. depicts biodegradation of COD concentration of landfill leachate for different activated sludge cultures. As seen from the figure, COD concentration decreased from 2200 mg/L to 775 mg/L with a removal efficiency of 65% at the end of 54 hours, when Pak-Maya activated sludge culture were used.. There was no biodegradation in the control flasks. When Pınar-Meat activated sludge culture was used, COD concentration decreased from 2200 mg/L to 825 mg/L with a removal efficiency of 62 % at the end of 54 hours. COD concentration decreased from 2200 mg/L to 990 mg/L with a removal efficiency of 55% at the end of 54 hours, when Cigli Domestic Wastewater Treatment activated sludge was used.

When the mixed activated sludge culture was used, COD concentration decreased from 2200 mg/L to 1700 mg/L at the end of 24 hours. The resulting COD removal efficiency was 65%. No significant COD removal was observed in the control flasks.

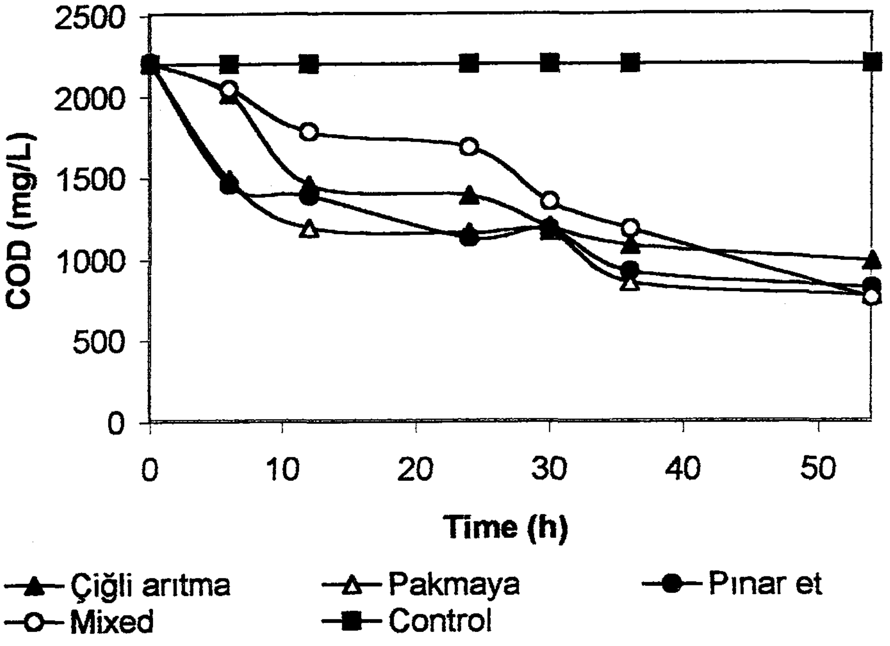

Figure 3.3.1. Variation of COD concentration with time for different activated sludge cultures.

In summary, Pak-Maya activated sludge was the most effective activated sludge culture among the tested cultures resulting in 65 % COD removal efficiency within 54 hours. Pak-Maya activated sludge culture was used in further experiments.

3.4. Pretreatment of Landfill Leachate

Early biological treatment studies with the raw leachate did not yield high COD and nitrogen removals, for this reason the leachate was subjected to pretreatment by chemical coagulation-flocculation followed by air stripping of ammonia at pH =12. Three different chemical coagulants, alum ($Al_2(SO_4)_3$), $FeCl_3$ and lime (CaO) were used in different concentrations for COD and nitrogen removal by coagulation-flocculation.

3.4.1. Coagulation and Flocculation

Coagulation-flocculation experiments were conducted in a jar-test apparatus using 1 liter beakers. The pH of the leachate was adjusted by sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) to pH=6 for alum and ferric chloride and to pH=12 for lime addition, respectively. Concentrations of the coagulants varied between 0 and 3.5 g/L. The contents of the jars were mixed fast at 200 rpm for 2 minutes, then slowly at 20 rpm for 30 minutes and then allowed for settling for one hour. Samples were removed from the clear supernatant after settling and were analyzed for COD contents.

Figure 3.4.1. shows that COD concentration as a function of coagulant doses for the three coagulants tested. COD concentrations decreased with increasing coagulant doses for alum and ferric chloride. However, COD concentration with lime addition increased with the increasing lime dose. High lime dosages may cause dissolution of some COD compounds. Final COD concentrations of 2140 mg/L, 2620 mg/L and 3670 mg/L were obtained with 3 g/L ferric chloride, alum and lime additions, respectively. As clearly seen from the figure, COD concentrations of the three coagulants at low doses (0.5-1.0 g/L) are comparable. Considering the problems associated with the use of high coagulant doses such as more sludge formation and higher cost of coagulation, low doses of coagulants such as 1 g/L were preferred.

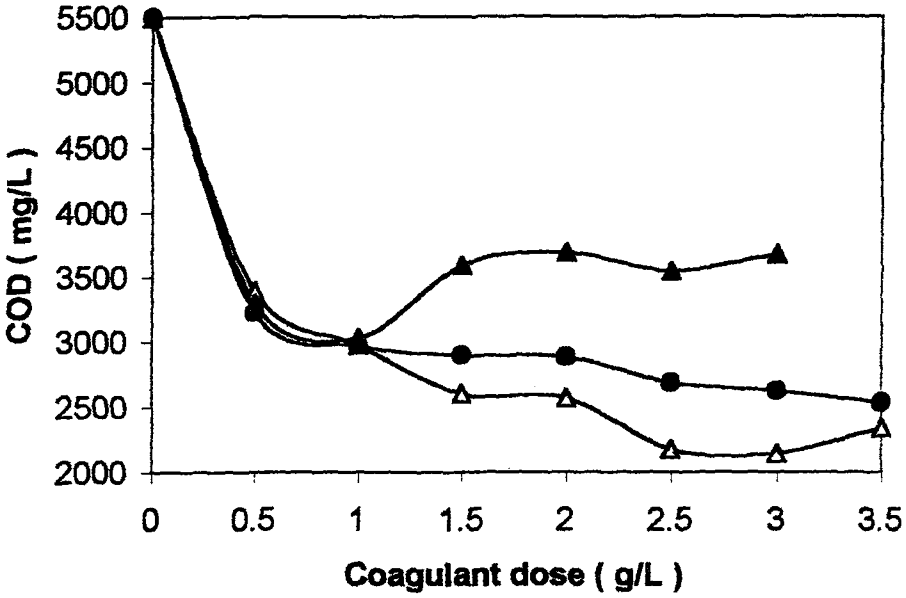

Figure 3.4.1. Variation of COD concentration with coagulant dose for different coagulating agents.

Δ $FeCl_3$ ● Alum ▲ Lime

Figure 3.4.2. depicts COD removal efficiency as a function of coagulant doses for the three coagulants tested. Percent COD removals increased with increasing coagulant doses for alum and ferric chloride. However, COD removal with lime addition decreased with the increasing lime dose. High lime dosages may cause dissolution of some COD compounds. The highest COD removal (60%) was obtained with 3 g/L ferric chloride addition. COD removal performances of the three coagulants at low doses (0.5-1.0 g/L) were comparable. Considering the problems associated with the use of high coagulant doses such as more sludge formation and higher cost of coagulation, low doses of coagulants such as 1 g/L were preferred. Percent COD removals for the three coagulants at the dose of 1 g/L were almost the same as 45%. Since lime coagulation was realized at pH =12 which was the most suitable pH for air stripping of ammonia used after the coagulation and also because of lime's disinfection affects, lime was selected as the most suitable coagulant for use in further studies.

COD and ammonium-N contents of the leachate dropped from COD_o = 9500 mg/L and NH_4-N_o = 1270 mg/L to COD = 7250 mg/L and NH_4-N = 1200 mg/L, respectively after coagulation with 1 g/L lime.

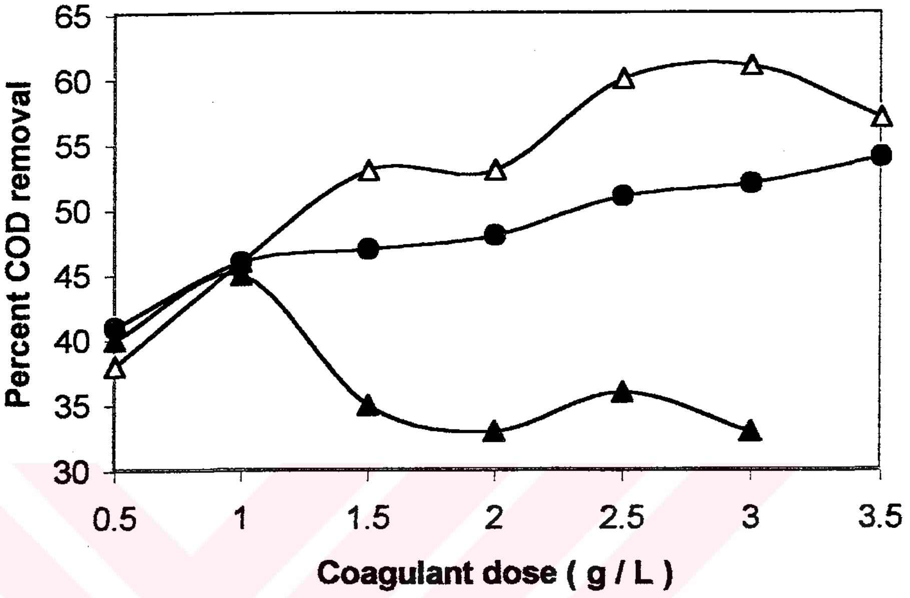

Figure 3.4.2. Variation of COD removal efficiency with coagulant dose for different coagulating agents.

Δ $FeCl_3$ ● Alum ▲ Lime

3.4.2. Air Stripping of Ammonia

Figure 3.4.3 depicts variation of NH_4-N concentration of landfill leachate with time at different pH values during air stripping. Supernatant solution after coagulation at pH =12 with lime of 1g/L dose was subjected to air stripping at different pH to remove excess ammonia from the leachate. Ammonium concentration after 45 minutes of air stripping at pH=12 was reduced to nearly 700 mg/L from 1200 mg/L. Ammonium concentration decreased to 820 mg/L, 410 mg/L and 400 mg/L at pH values of 9, 10 and 11, respectively.

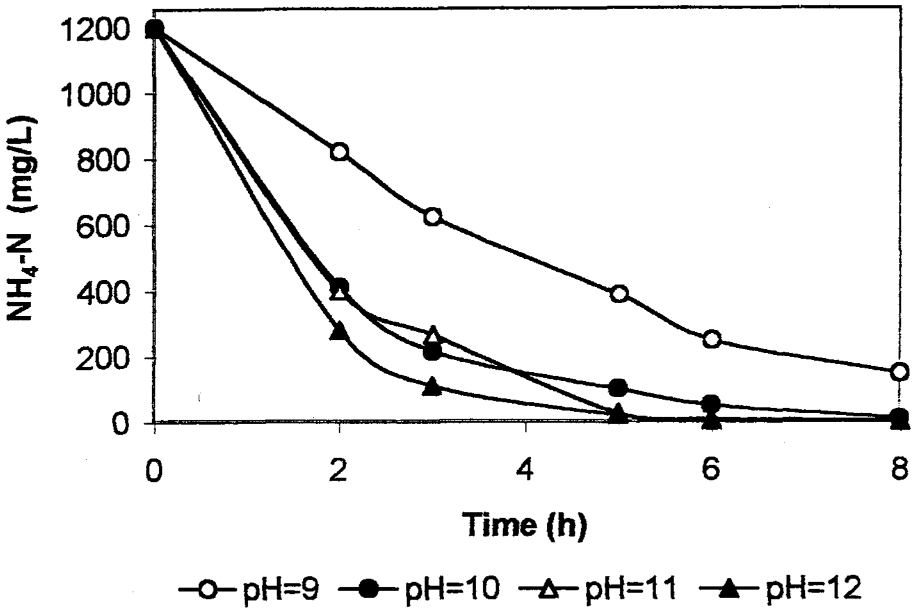

Figure 3.4.3. Variation of NH_4-N concentration with time as a function of pH during air stripping of ammonia.

Variation of percent NH_4-N removal with time as a function of pH is depicted in Figure 3.4.4. Percent COD removals for pH= 9, 10, 11 and 12 were nearly 32%, 66%, 67% and 77% at the end of the 2 hours, respectively. Ammonium concentration in air stripping at pH=12 was reduced to nearly 5 mg/L from 1200 mg/L with a removal efficiency of 99% at the end of 6 hours.

The pH of the leachate was adjusted to pH=7 by alkaline addition (1 M NaOH) after air stripping of ammonia and was used for biological treatment in an aeration tank operated in fed-batch mode. COD and NH_4-N contents of the pretreated leachate after air stripping was approximately, COD = 7,000 mg/L and NH_4-N = 700 mg/L, respectively. Required amount of KH_2PO_4 was added to the pretreated leachate to adjust COD/N/P ratio to 100/10/1.5 before biological treatment.

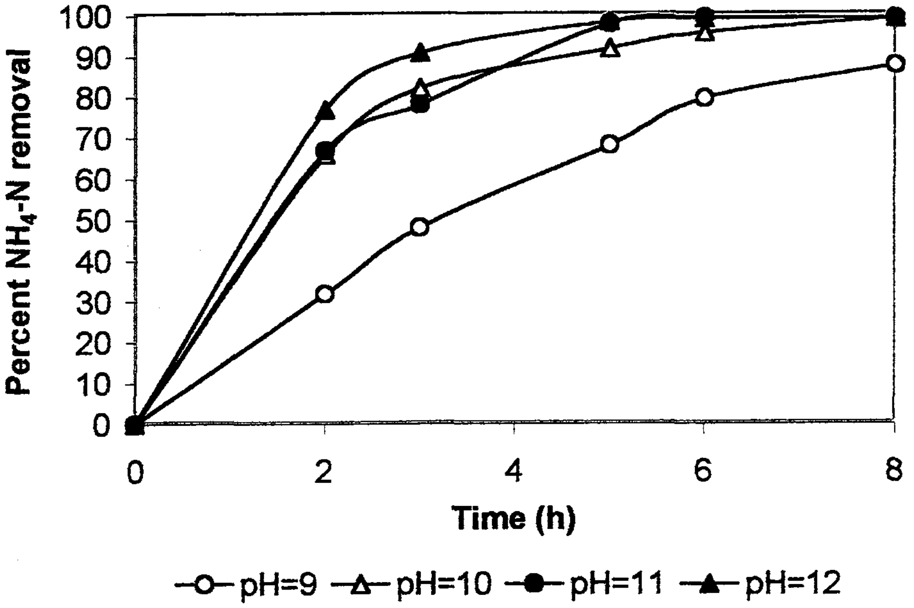

Figure 3.4.4. Variation of percent NH_4-N removal with time as a function of pH in air stripping of ammonia.

3.5. Biological Treatment of Landfill Leachate by Fed–Batch Operation

3.5.1. Experiments with Different Feed COD Concentrations

In the first set of experiments, the feed flow rate was kept constant at Q = 0.18 L/h and COD contents of the feed were varied between 1,000 mg/L and 7,000 mg/L. The COD loading rate (L_{COD}) varied between 180 mg COD/h and 1260 mg COD/h with 30 hours of operation time, in this set of experiments. The landfill leachate was diluted with tap water to reduce the COD contents to the desired level.

The initial COD content in the aeration tank was nearly 300 mg/L and the initial biomass concentration was nearly 4200±200 mg biomass/L, on dry weight basis. Temperature and pH were 20 °C and pH=8-8.5, throughout the experiments. Vigorous aeration was supplied to the aeration tank to keep the dissolved oxygen (DO) above 2 mg/L. Temperature, pH and DO were monitored and manually controlled during the experiments. A control experiment devoid of microorganisms was run in parallel to the biological treatment experiment for every experimental condition. Percent COD removals in control experiments were considered to be zero and COD content of the control experiments were used as the base in calculation of COD removal efficiencies.

Variation of COD concentration and percent COD removal with time ($Q=0.18$ L/h, $S_i=978$ mg/L, $V_o=3$ L) is depicted in Figure 3.5.1. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank remained constant around 300 mg/L, because of low loading rate, throughout the experiment as a result of bio-oxidation. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 58% at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.2. COD content in the aeration tank increased while percent COD removals (E) decreased with the increasing COD loading rates.

Variation of wastewater volume with time is depicted in Figure 3.5.3. Starting from a 3.0 L of initial volume, wastewater volume in the tank increased linearly with time as expected.

In Figure 3.5.4 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

Variation of COD removal rate with COD loading rate (QSi/V) is depicted in Figure 3.5.5. COD removal rate decreased with increasing COD loading rate because of high COD levels in the tank at high loading rates.

Variation of COD removal rate ($R_s = Q (S_c\text{-}S)/ V$) with COD concentration is presented in Figure 3.5.6. COD removal rate decreased with increasing COD concentration.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.60 gX/gS for 978 mg/L feed COD concentration.

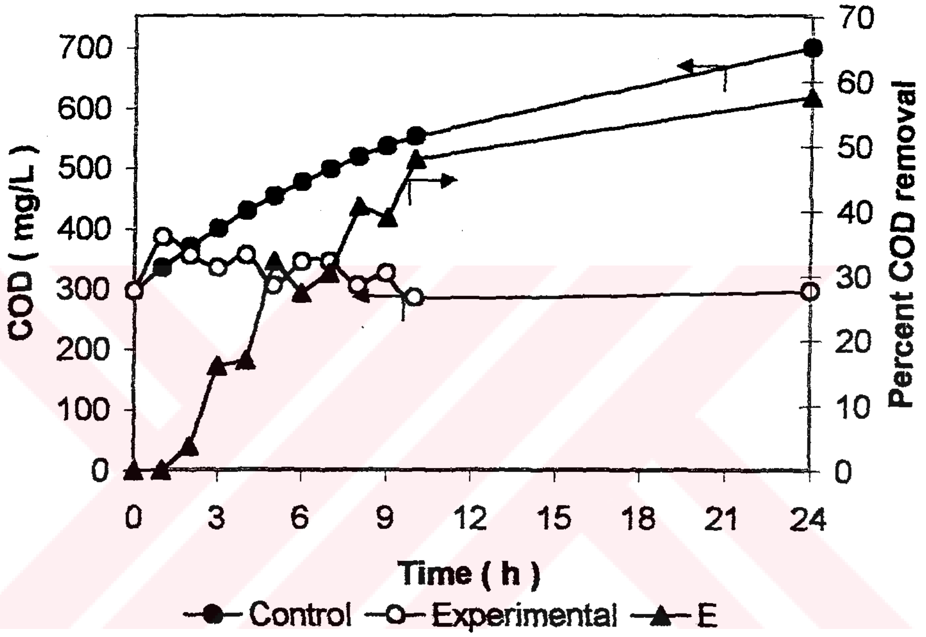

Figure 3.5.1. Variation of COD concentration and percent COD removal with time (S_i=978 mg/L, Q=0.18 L/h, V_o=3L)

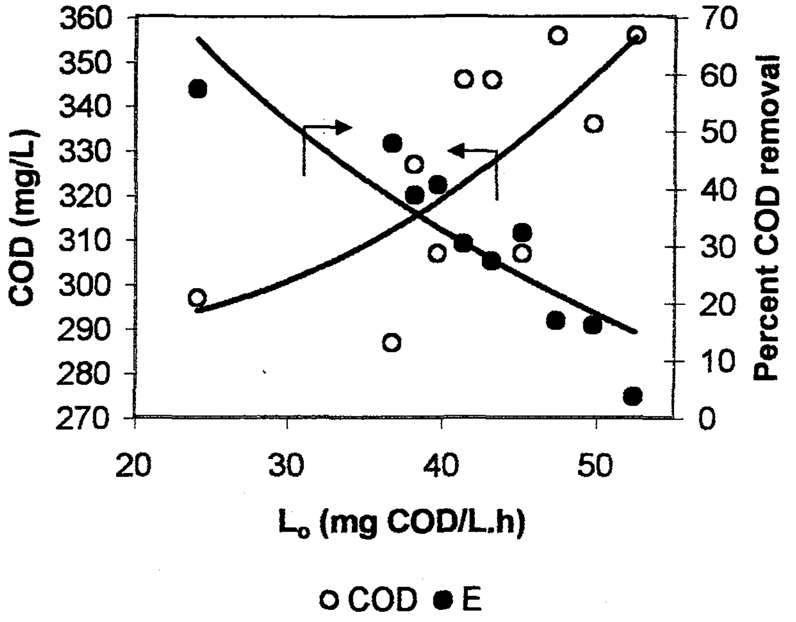

Figure 3.5.2. Variation of COD concentration and percent COD removal with COD loading rate (S_i=978 mg/L, Q=0.18 L/h, V_o=3 L)

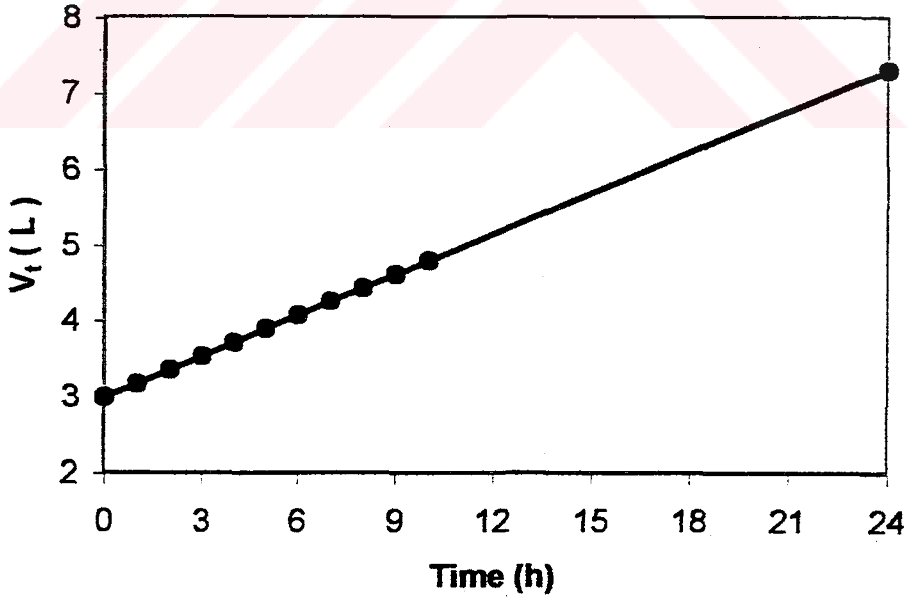

Figure 3.5.3. Variation of reactor volume with time (S_i=978 mg/L, Q=0,18 L/h, V_o=3 L)

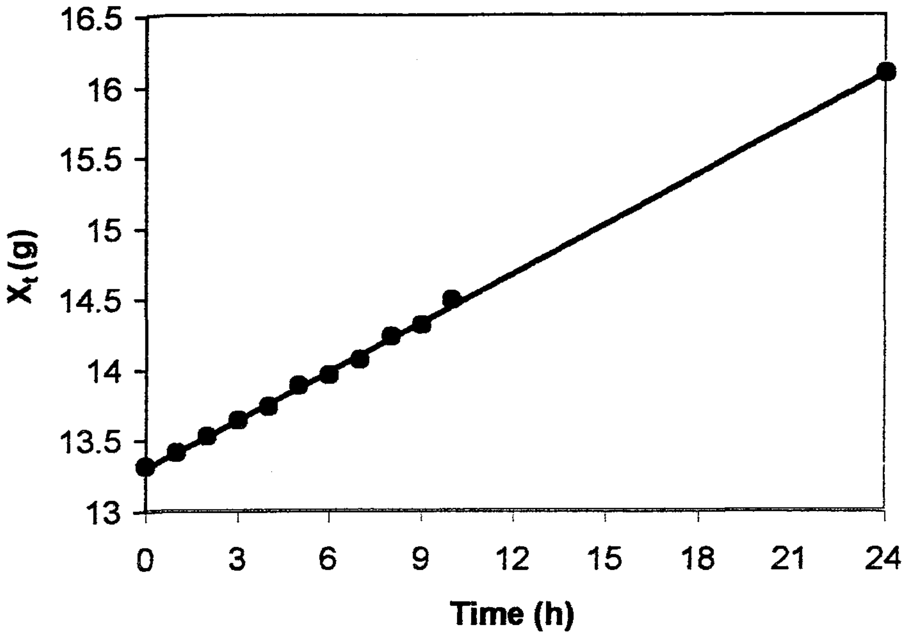

Figure 3.5.4. Variation of total amount of biomass with time
(S_i=978 mg/L, Q=0.18 L/h, V_o=3 L)

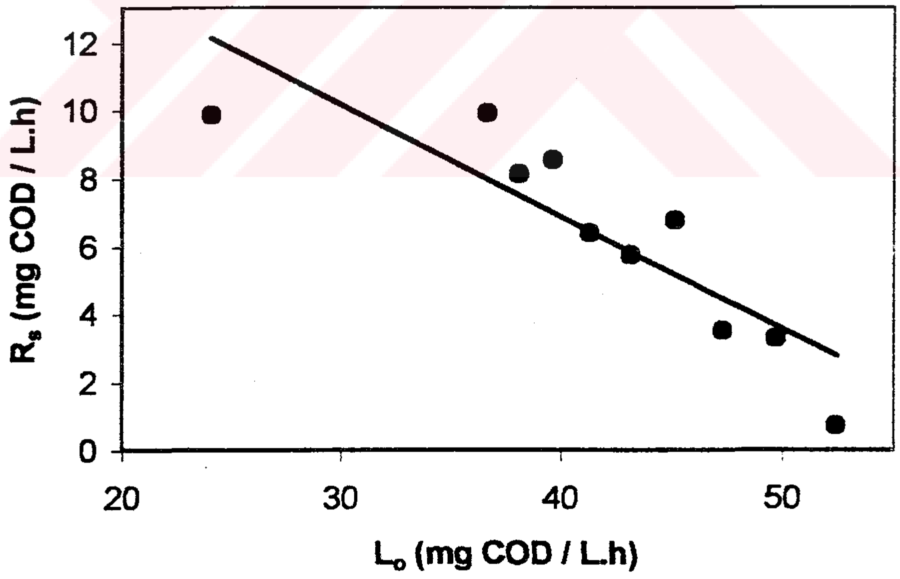

Figure 3.5.5. Variation of COD removal rate with COD loading rate
(S_i=978 mg/L. Q=0.18 L/h, V_o=3 L)

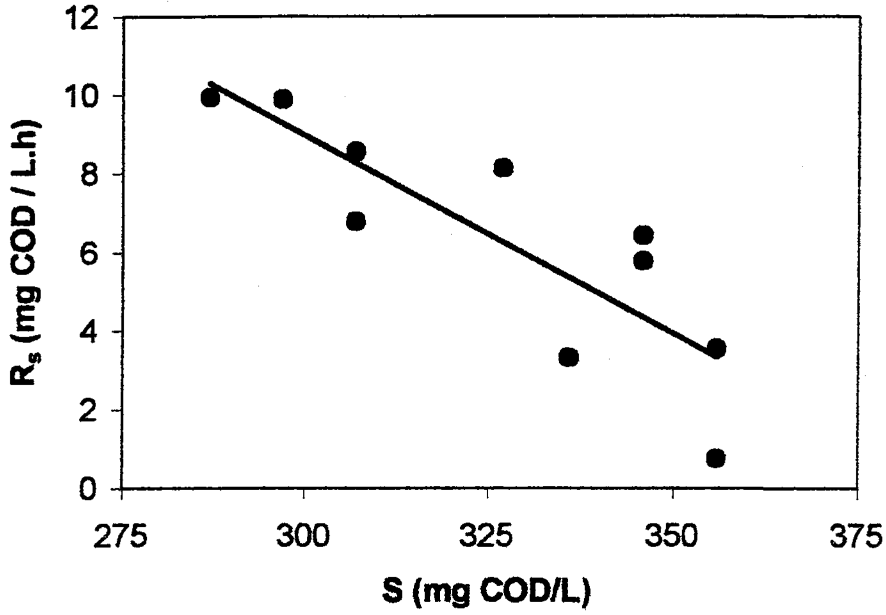

Figure 3.5.6. Variation of COD removal rate with COD concentration (S_i=978 mg/L, Q=0.18 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time (Q=0.18 L/h, S_i=1840 mg/L, V_o=3 L) is shown in Figure 3.5.7. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank remained constant around 340 mg/L throughout the experiment as a result of bio-oxidation. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 73% at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.8. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.9 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time. Wastewater volume in the tank increased with time linearly as expected.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.49 gX/gS for 1840 mg/L feed COD concentration.

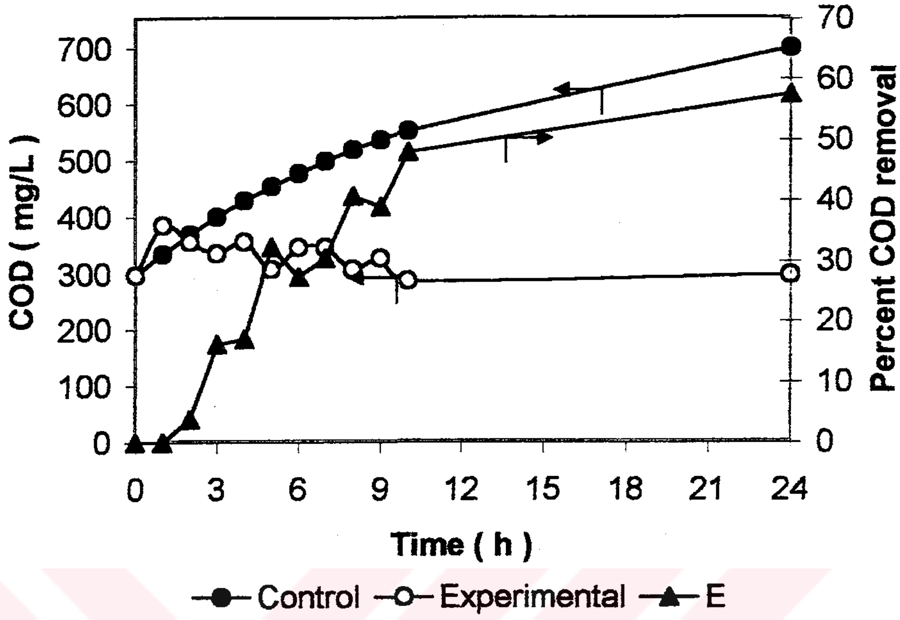

Figure 3.5.7. Variation of COD concentration and percent COD removal with time (S_i=1840 mg/L, Q=0.18 L/h, V_o=3 L)

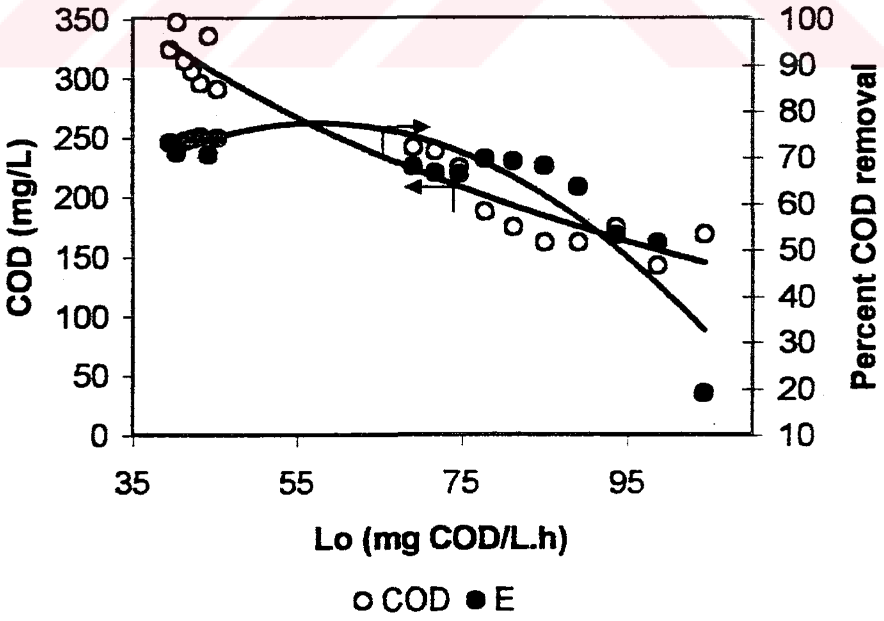

Figure 3.5.8. Variation of COD concentration and percent COD removal with COD loading rate (S_i=1840 mg/L, Q=0.18 L/h, V_o=3 L)

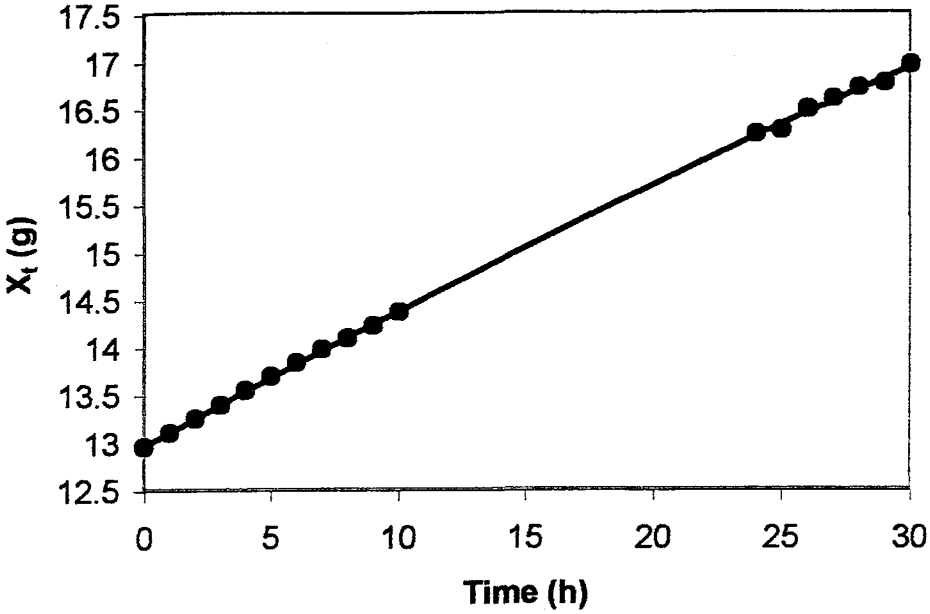

Figure 3.5.9. Variation of total amount of biomass with time (S_i=1840 mg/L, Q=0.18 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time (Q=0.18 L/h, S_i=2815 mg/L, V_o=3 L) is depicted in Figure 3.5.10. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank remained constant around 500 mg/L throughout the experiment because of bio-oxidation. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time as a result of increased total biomass in the aeration tank. Percent COD removal was 73 % at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.11. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.12 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time. Wastewater volume in the tank increased with time linearly as expected.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.58 gX/gS for 2815 mg/L feed COD concentration.

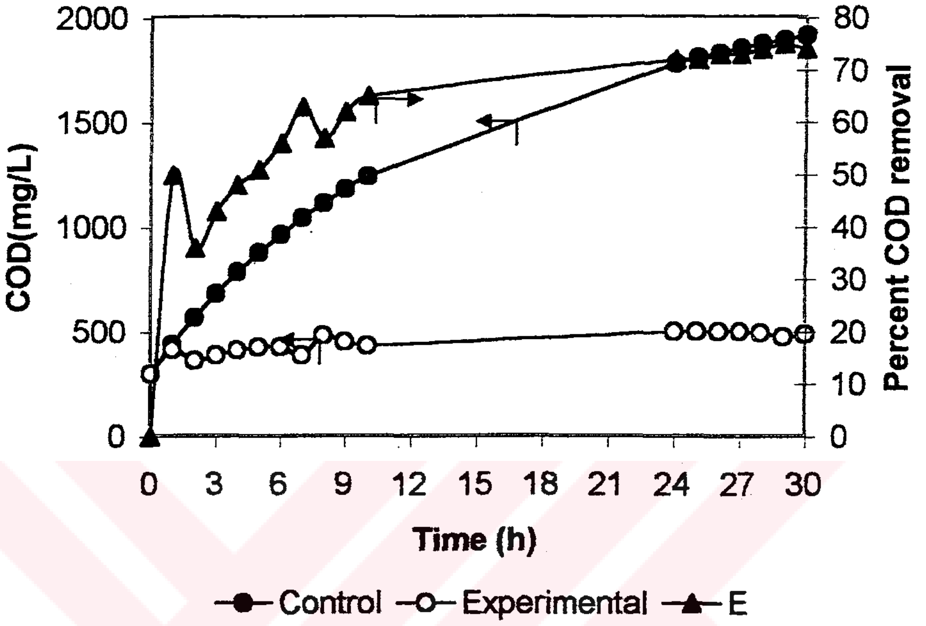

Figure 3.5.10. Variation of COD concentration and percent COD removal with time (S_i=2815 mg/L, Q=0.18 L/h, V_o=3 L)

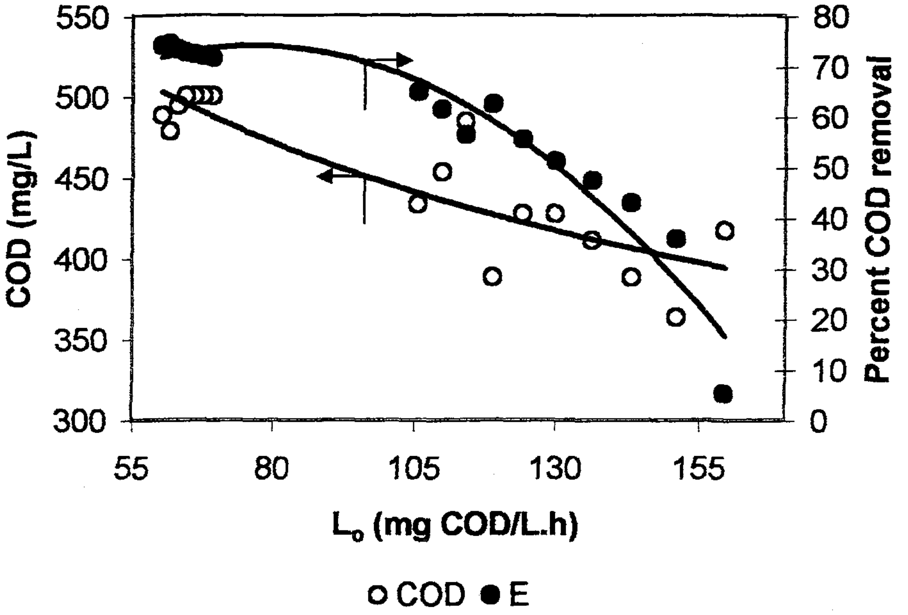

Figure 3.5.11. Variation of COD concentration and percent COD removal with COD loading rate (S_i=2815 mg/L, Q=0.18 L/h, V_o=3 L)

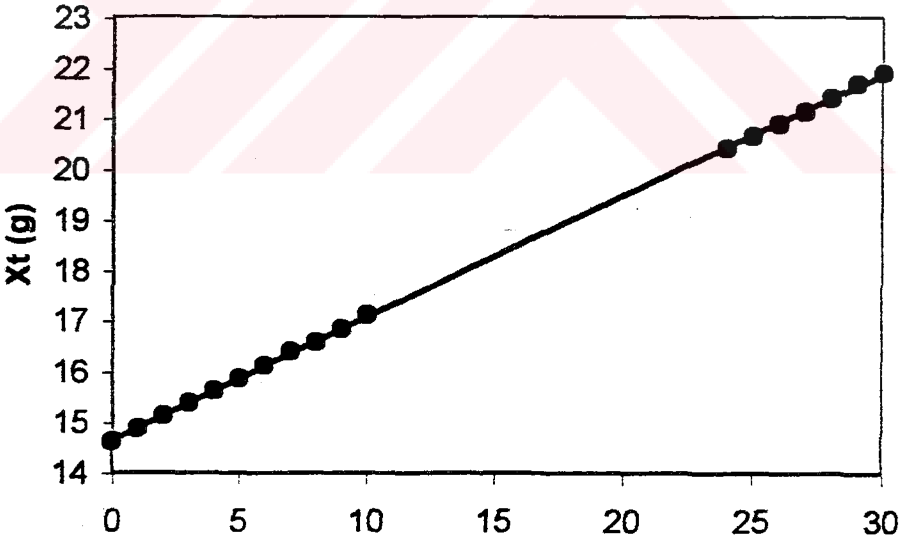

Figure 3.5.12. Variation of total amount of biomass with time (S_i=2815 mg/L, Q=0.18 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time (Q=0.18 L/h, S_i=4171 mg/L, V_o=3 L) is depicted in Figure 3.5.13. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank was nearly 675 mg/L at the end of 30 hours. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 76 % at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.14. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.15 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly as a result of increasing reactor volume with time. Wastewater volume in the tank increased with time linearly as expected.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.55 gX/gS for 4171 mg/L feed COD concentration.

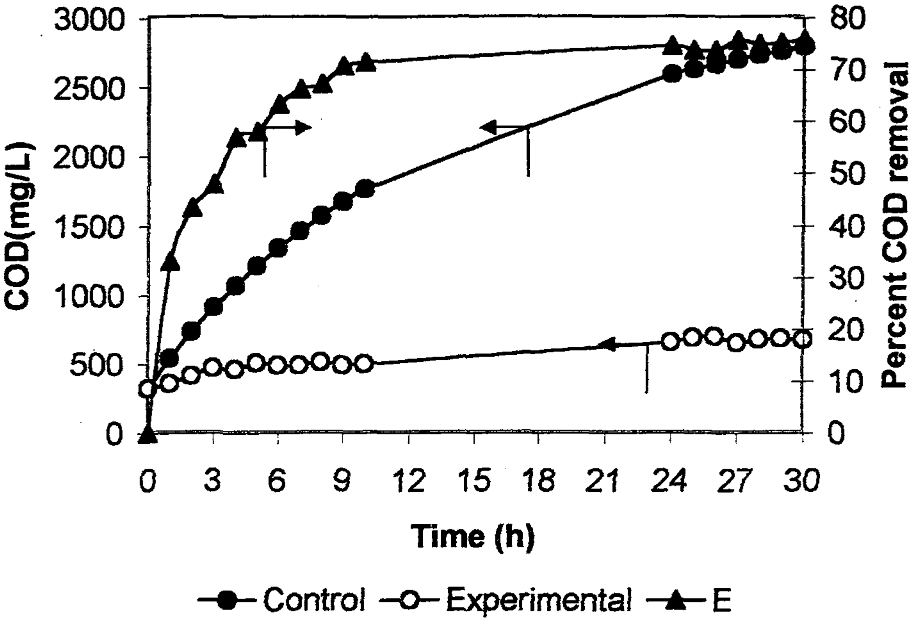

Figure 3.5.13. Variation of COD concentration and percent COD removal with time (S_i=4171 mg/L, Q=0.18 L/h, V_o=3 L)

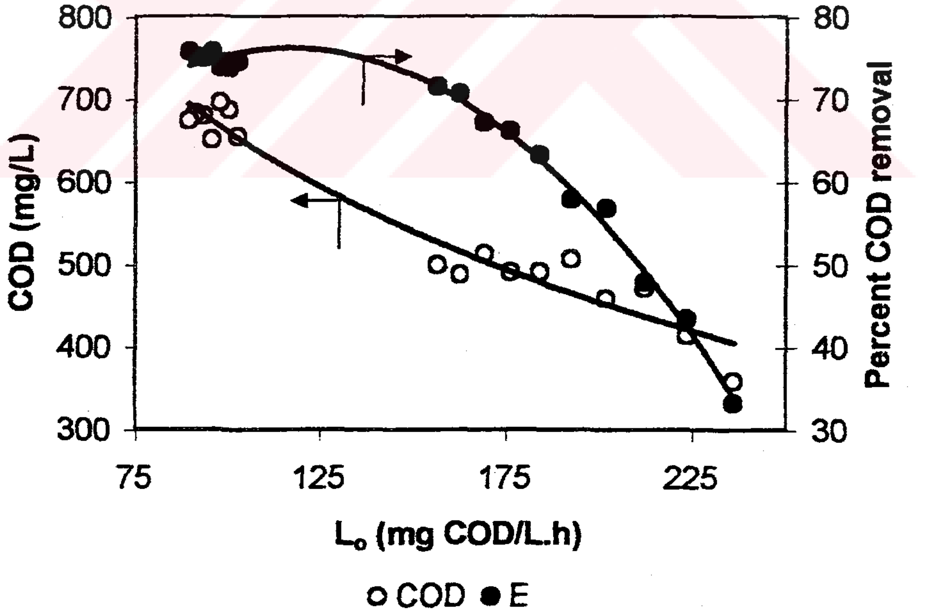

Figure 3.5.14. Variation of COD concentration and percent COD removal with COD loading rate (S_i=4171 mg/L, Q=0.18 L/h, V_o=3 L)

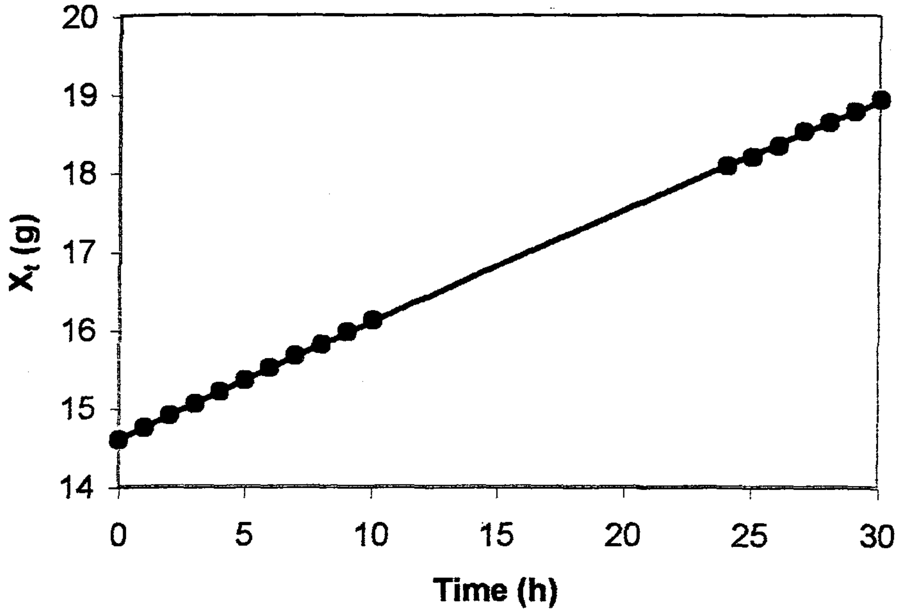

Figure 3.5.15. Variation of total amount of biomass with time (S_i=4171 mg/L, Q=0.18 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time (Q=0.18 L/h, S_i=5115 mg/L, V_o=3 L) is depicted in Figure 3.5.16. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank was 970 mg/L at the end of the operation time. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time as a result of increased total biomass in the aeration tank. Percent COD removal was 73% at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is depicted in Figure 3.5.17. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.18 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time. Wastewater volume in the tank increased with time linearly as expected.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.37 gX/gS for 5115 mg/L feed COD concentration.

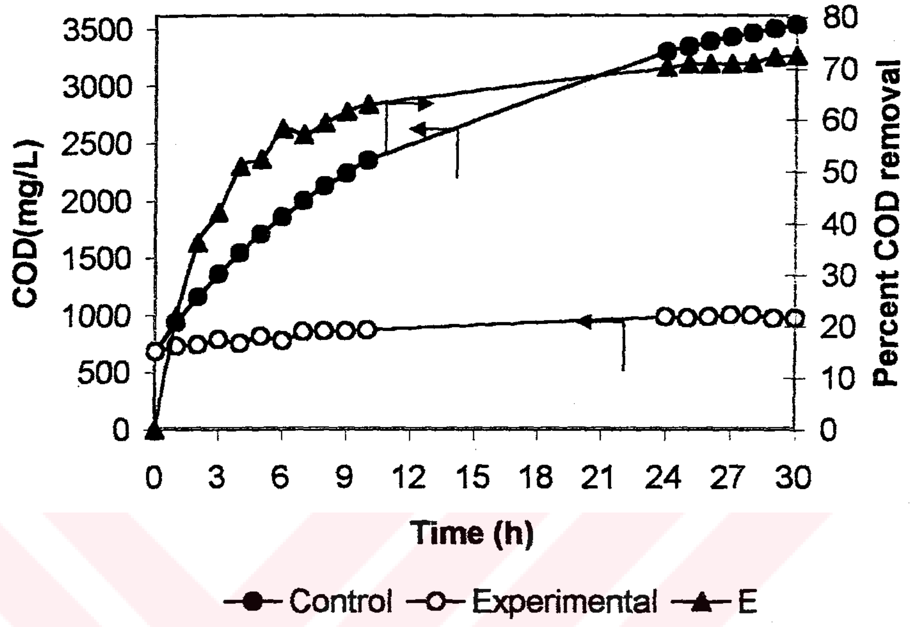

Figure 3.5.16. Variation of COD concentration and percent COD removal with time (S_i=5115 mg/L, Q=0.18 L/h, V_o=3 L)

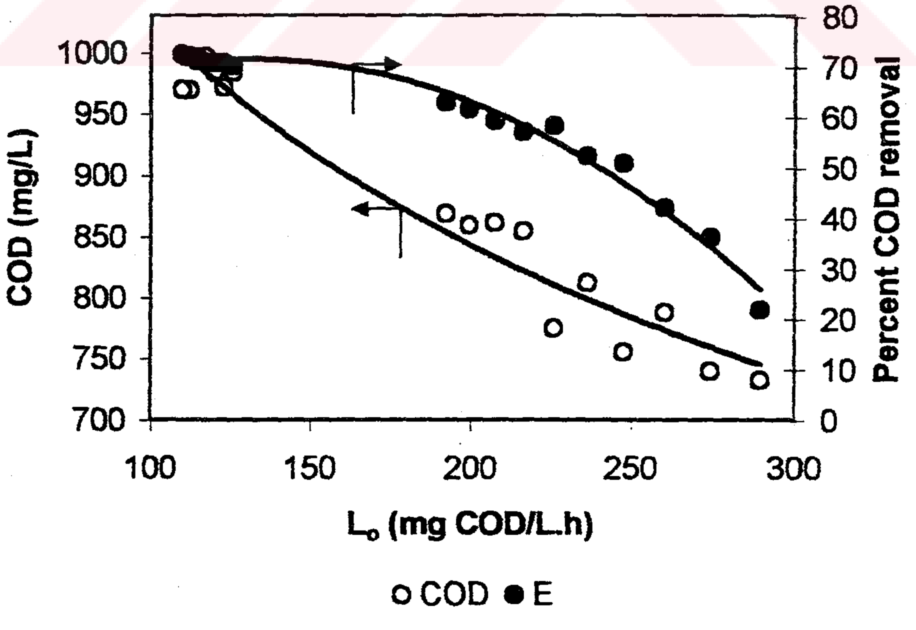

Figure 3.5.17. Variation of COD concentration and percent COD removal with COD loading rate (S_i=5115 mg/L, Q=0.18 L/h, V_o=3 L)

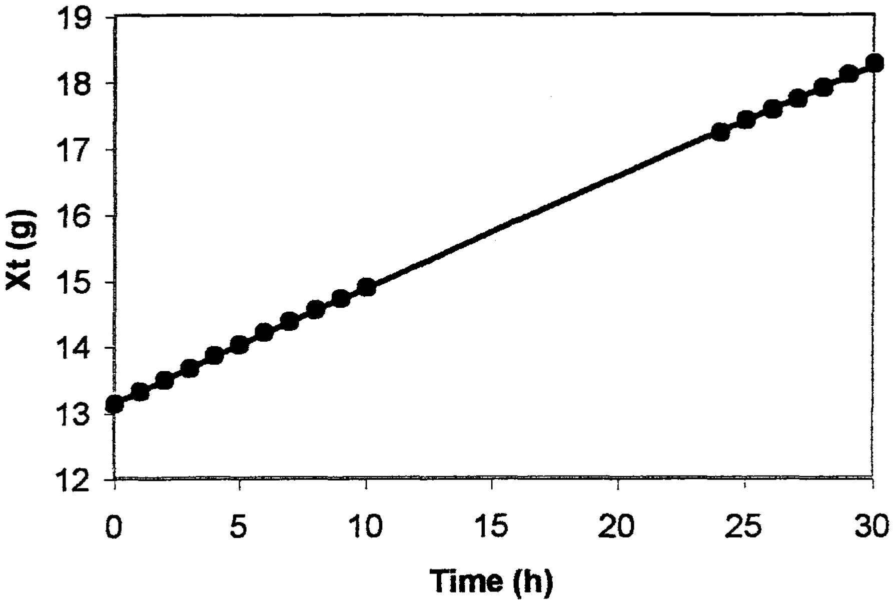

Figure 3.5.18. Variation of total amount of biomass with time (S_i=5115 mg/L, Q=0.18 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time (Q=0.18 L/h, S_i=5980 mg/L, V_o=3 L) is depicted in Figure 3.5.19. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank was nearly 1025 mg/L at the end of t=30 hours. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 74% at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.20. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.21 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly as a result of increasing reactor volume with time. Wastewater volume in the tank increased with time linearly as expected.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.39 gX/gS for 5980 mg/L feed COD concentration.

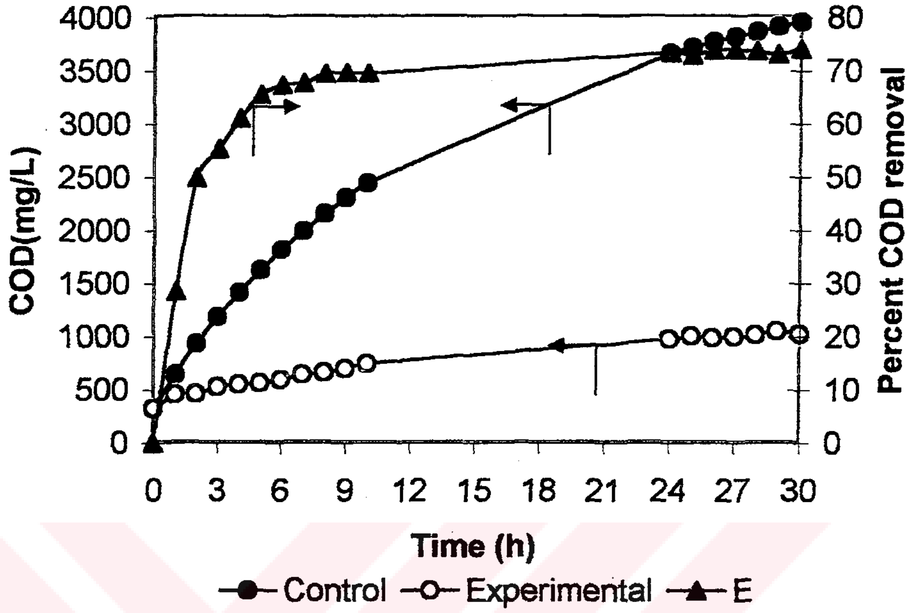

Figure 3.5.19. Variation of COD concentration and percent COD removal with time (S_i=5980 mg/L, Q=0.18 L/h, V_o=3 L)

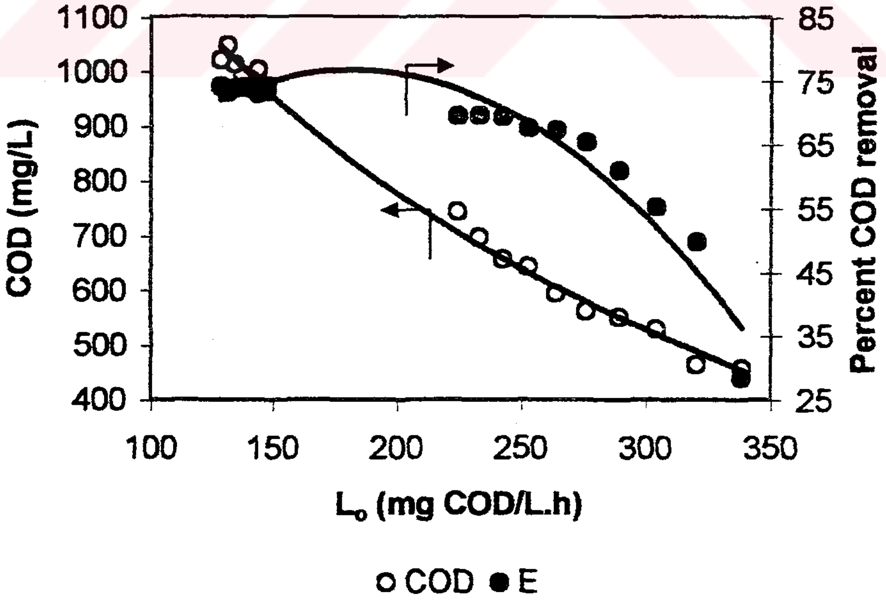

Figure 3.5.20. Variation of COD concentration and percent COD removal with COD loading rate (S_i=5980 mg/L, Q=0.18 L/h, V_o=3 L)

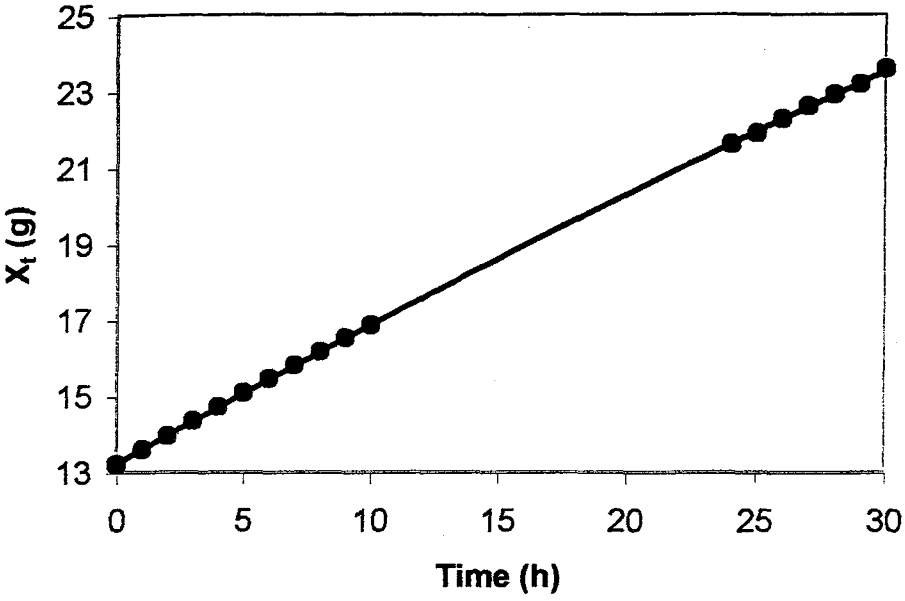

Figure 3.5.21. Variation of total amount of biomass with time (S_i=5980 mg/L, Q=0.18 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time (Q=0.18 L/h, S_i=7050 mg/L, V_o=3 L) is depicted in Figure 3.5.22. COD concentration in the control tank increased with time due to accumulation of COD. COD concentration in the experimental tank was nearly 1250 mg/L at the end of the operation time. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 73% at the end of the operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.23. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.24 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time. Wastewater volume in the tank increased with time linearly as expected.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.51 gX/gS for 7050 mg/L feed COD concentration.

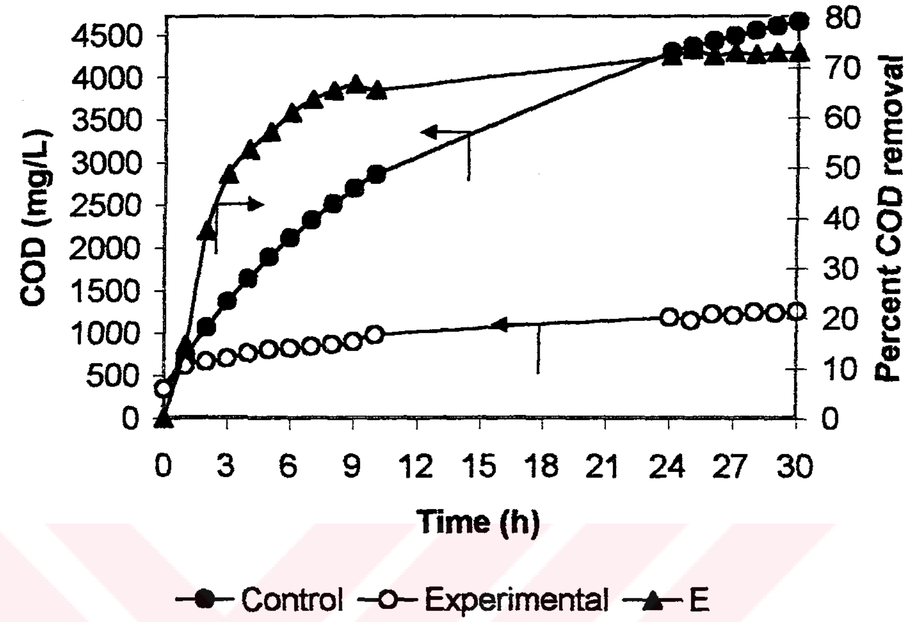

Figure 3.5.22. Variation of COD concentration and percent COD removal with time (S_i=7050 mg/L, Q=0.18 L/h, V_o=3 L)

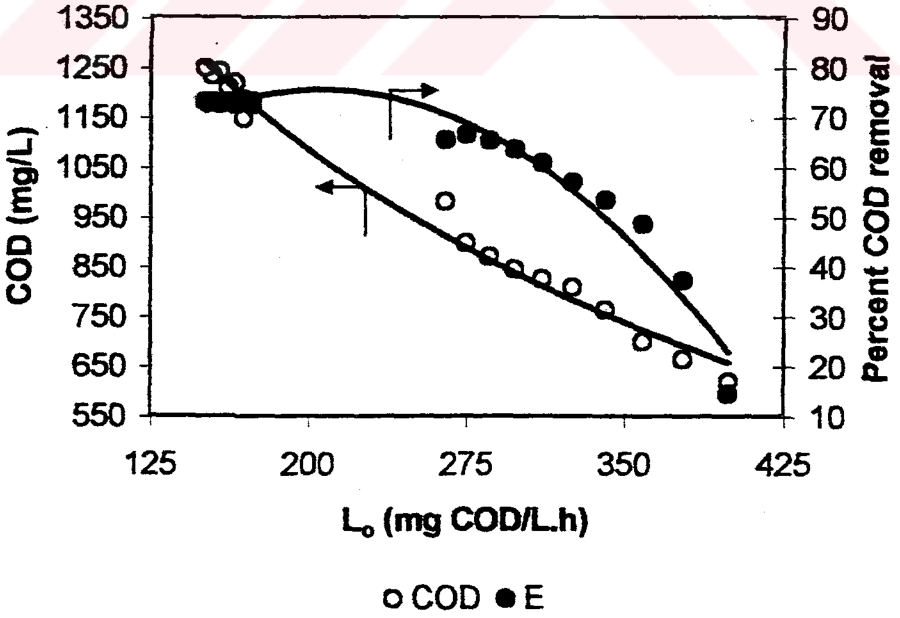

Figure 3.5.23. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7050 mg/L, Q=0.18 L/h, V_o=3 L)

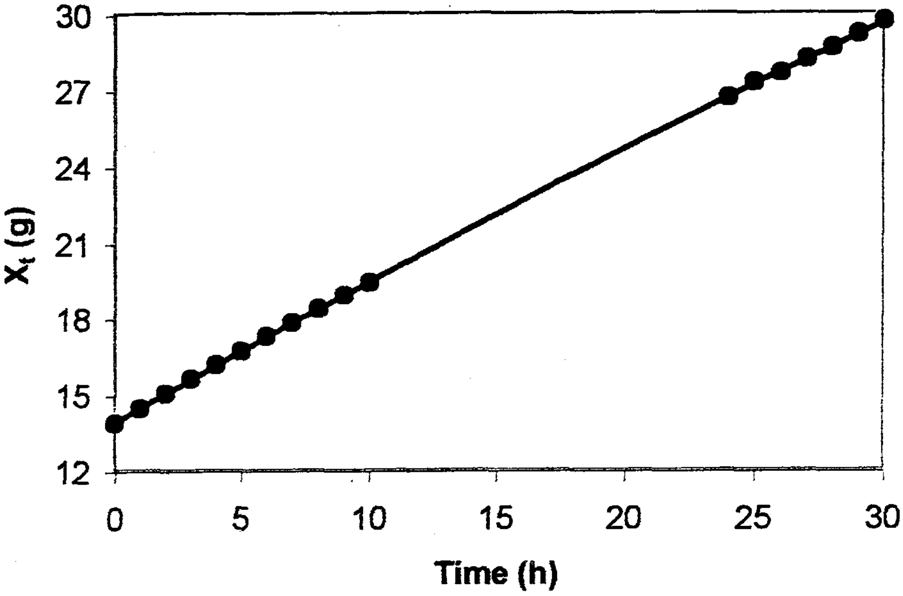

Figure 3.5.24. Variation of total amount of biomass with time
(S_i=7050 mg/L, Q=0.18 L/h, V_o=3 L)

3.5.2. Experiments with Different Feed Flow Rates

The COD content of the feed wastewater was kept constant at 7,000 mg/L, while the flow rate of the feed was varied between 0.05 L/h and 0.6 L/h, in the second set of experiments. The COD loading rate varied between 350 mg COD/h and 4200 mg COD/h with 10 hours of operation time.

The initial COD content in the aeration tank was nearly 300 mg/L and the initial biomass concentration was nearly 4200±200 mg biomass/L on dry weight basis. Temperature and pH were 20°C and pH=8-8.5, throughout the experiments. Vigorous aeration was supplied to the aeration tank to keep the dissolved oxygen (DO) above 2 mg/L. Temperature, pH and DO were monitored and manually controlled during the experiments. A control experiment devoid of microorganisms was run in parallel to the biological treatment experiment for every experimental condition. Percent COD removals in control experiments were considered to be zero and COD content of the control experiments were used as the base in calculation of COD removal efficiencies.

Variation of COD concentration and percent COD removal with time for Q=0.05 L/h and S_i=7000 mg/L is depicted in Figure 3.5.25. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank remained constant around 720 mg/L, because of balanced loading rate and bio-oxidation, throughout the experiment. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 73% at the end of 10h fed-batch operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.26. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

Variation of wastewater volume with time is shown in Figure 3.5.27. Starting from a 3.0 L of initial volume, wastewater volume in the tank increased linearly with time as expected.

In Figure 3.5.28 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

Variation of COD removal rate with COD loading rate is depicted in Figure 3.5.29. COD removal rate decreased with increasing COD loading rate.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.32 gX/gS for 0.05 L/h feed flow rate.

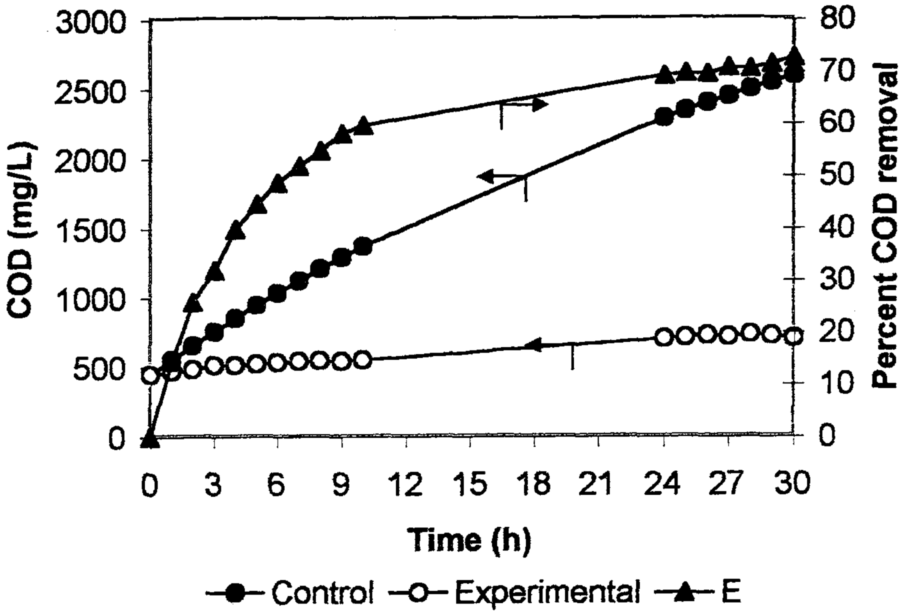

Figure 3.5.25. Variation of COD concentration and percent COD removal with time (S_i=7000 mg/L, Q=0.05 L/h, V_o=3 L)

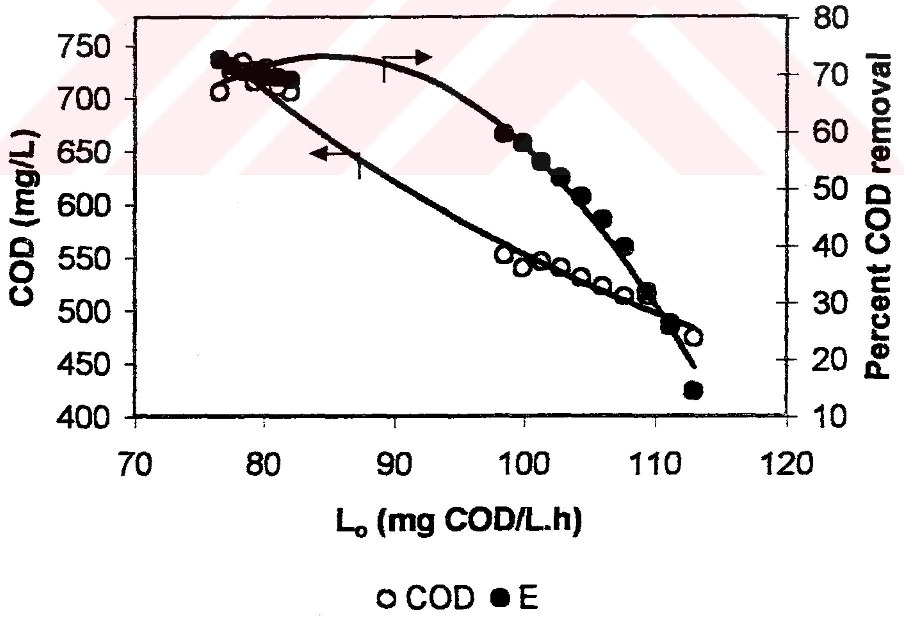

Figure 3.5.26. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7,000 mg/L, Q= 0.05 L/h, V_o=3 L)

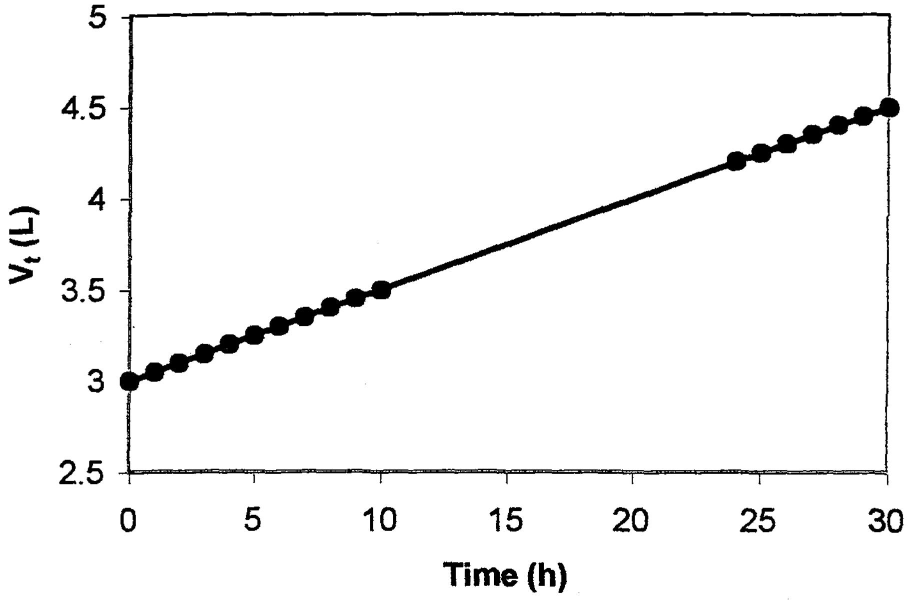

Figure 3.5.27. Variation of reactor volume with time (S_i=7000 mg/L, Q=0.05 L/h, V_o=3 L)

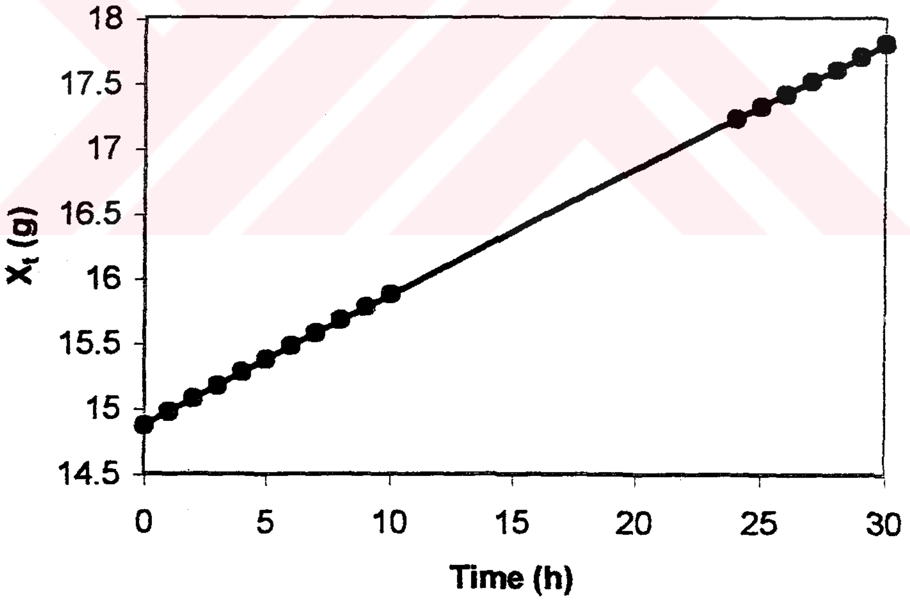

Figure 3.5.28. Variation of total amount of biomass with time

(S_i=7000 mg/L, Q=0.05 L/h, V_o=3 L)

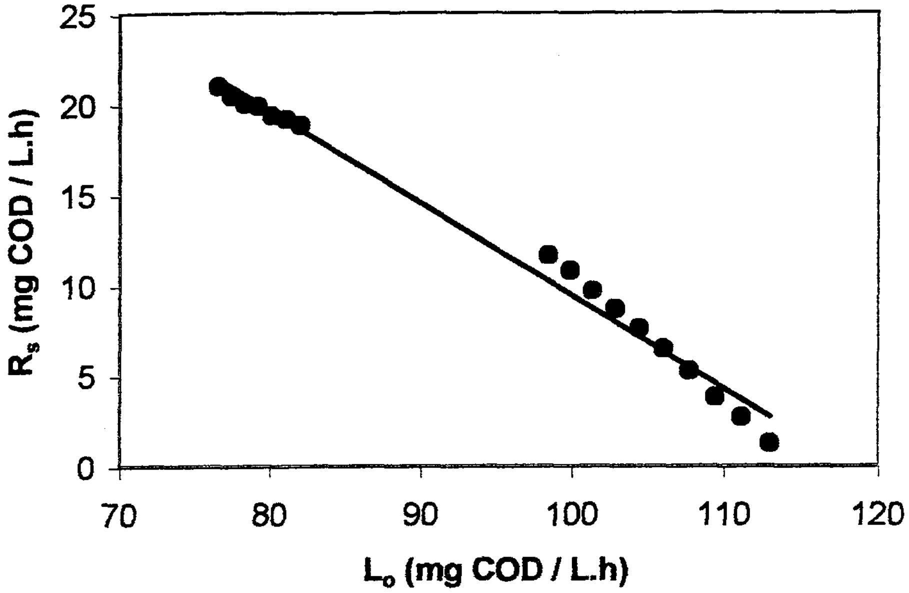

Figure 3.5.29. Variation of COD removal rate with COD loading rate (S_i=7000 mg/L, Q=0.05 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time for Q=0.10 L/h and S_i=7000 mg/L is depicted in Figure 3.5.30. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank remained constant around 520 mg/L, because of balanced COD removal and loading rates throughout the experiment. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 72 % at the end of the 10 h fed-batch operation.

Variation of COD concentration and percent COD removal with COD loading rate are shown in Figure 3.5.31. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.32 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.39 gX/gS for 0.10 L/h feed flow rate.

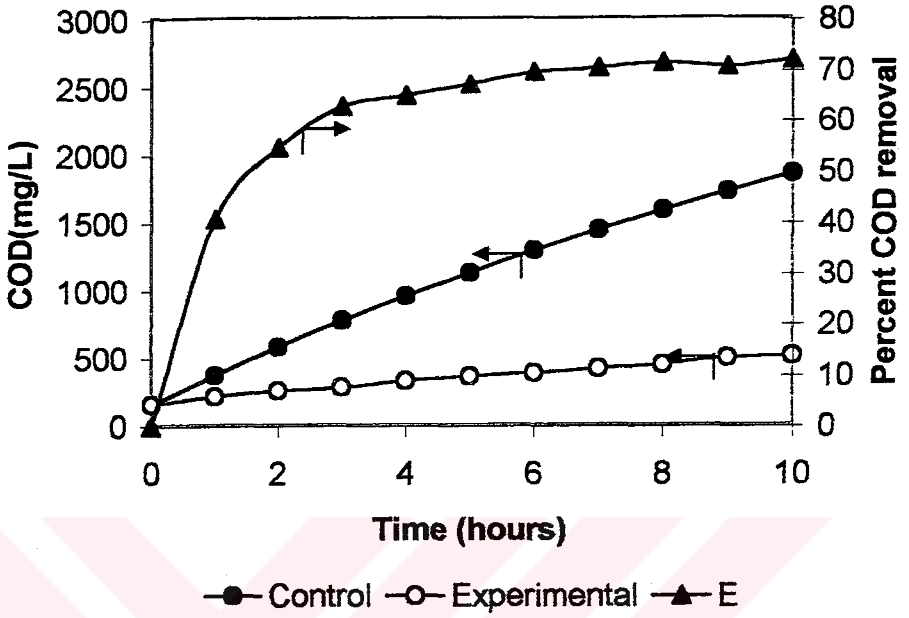

Figure 3.5.30. Variation of COD concentration and percent COD removal with time (S_i=7000 mg/L, Q=0.10 L/h, V_o=3 L)

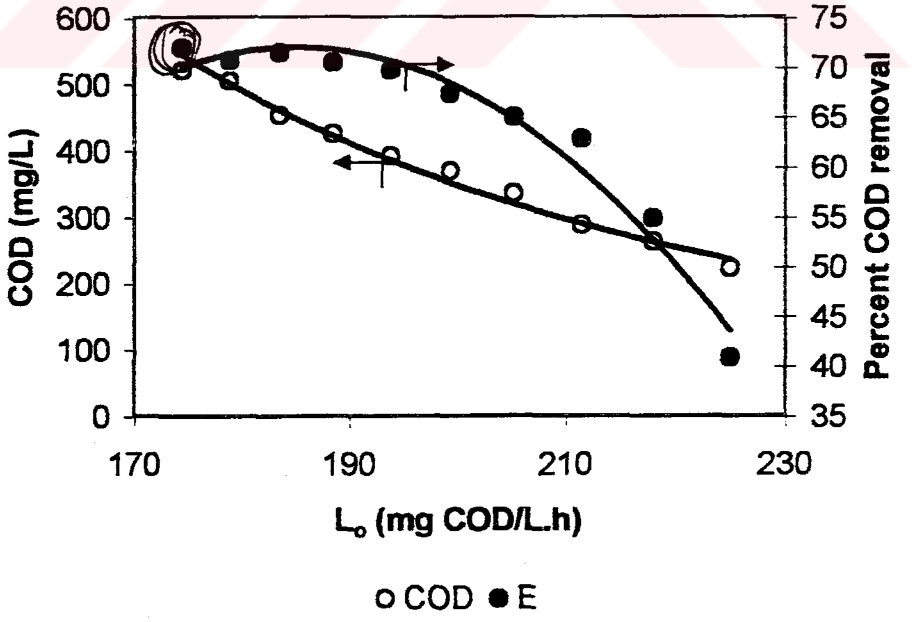

Figure 3.5.31. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7000 mg/L, Q=0.10 L/h, V_o=3 L)

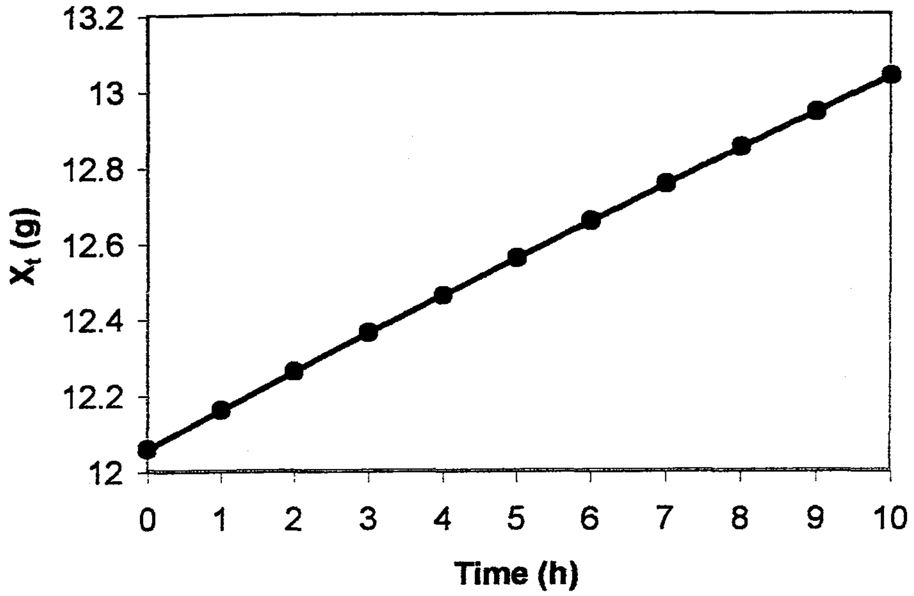

Figure 3.5.32. Variation of total amount of biomass with time
(S_i=7000 mg/L, Q=0.10 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time for Q=0.21 L/h and S_i=7000 mg/L are depicted in Figure 3.5.33. COD concentration in the control tank increased with time due to accumulation of COD in the absence of organisms. COD in the experimental tank was nearly 710 mg/L at the end of ten hours. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 76 % at the end of 10 h operation.

Variation of COD concentration and percent COD removal with COD loading rate are shown in Figure 3.5.34. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.35 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.26 gX/gS for 0.21 L/h feed flow rate.

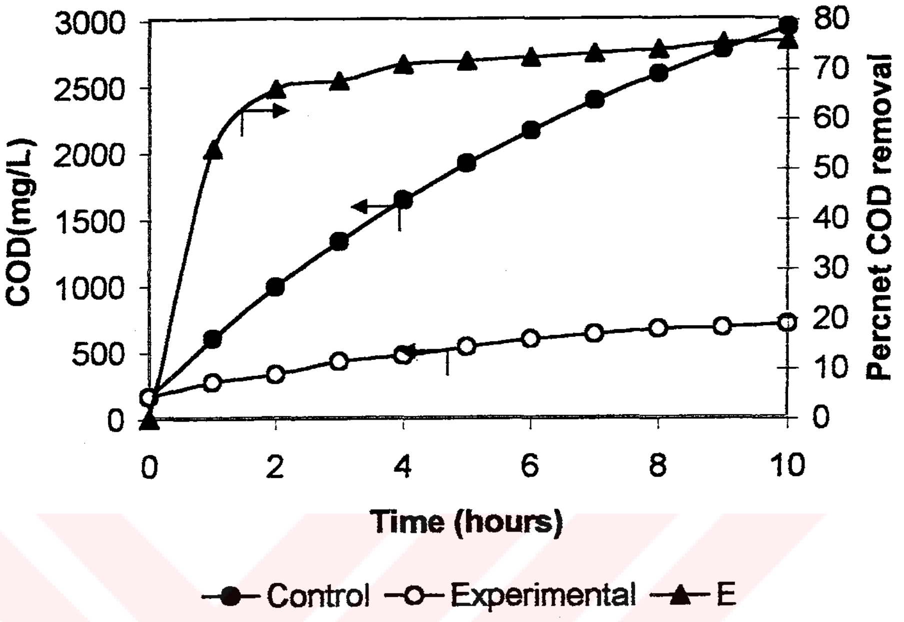

Figure 3.5.33. Variation of COD concentration and percent COD removal with time (S_i=7000 mg/L, Q=0.21 L/h, V_o=3 L)

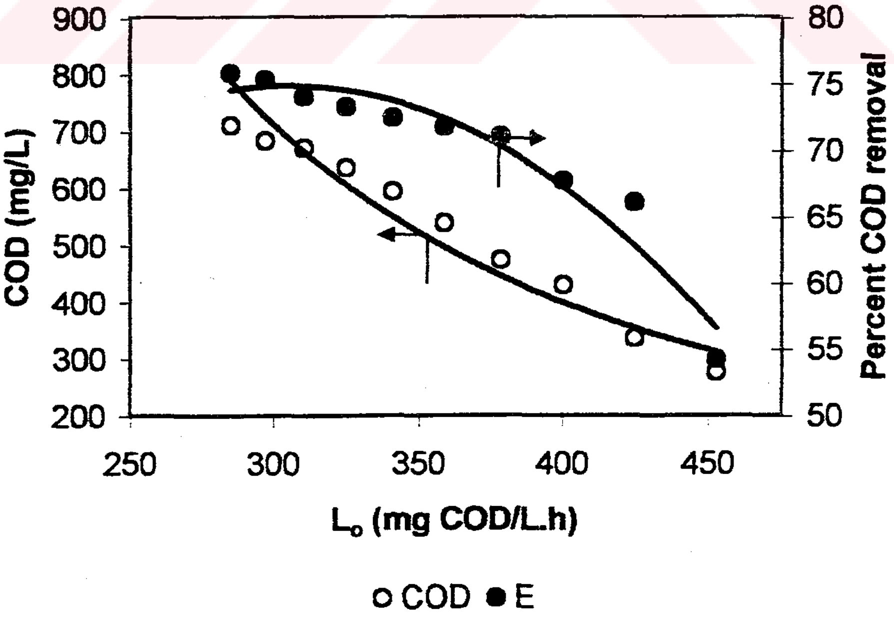

Figure 3.5.34. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7000 mg/L, Q=0.21 L/h, V_o=3 L)

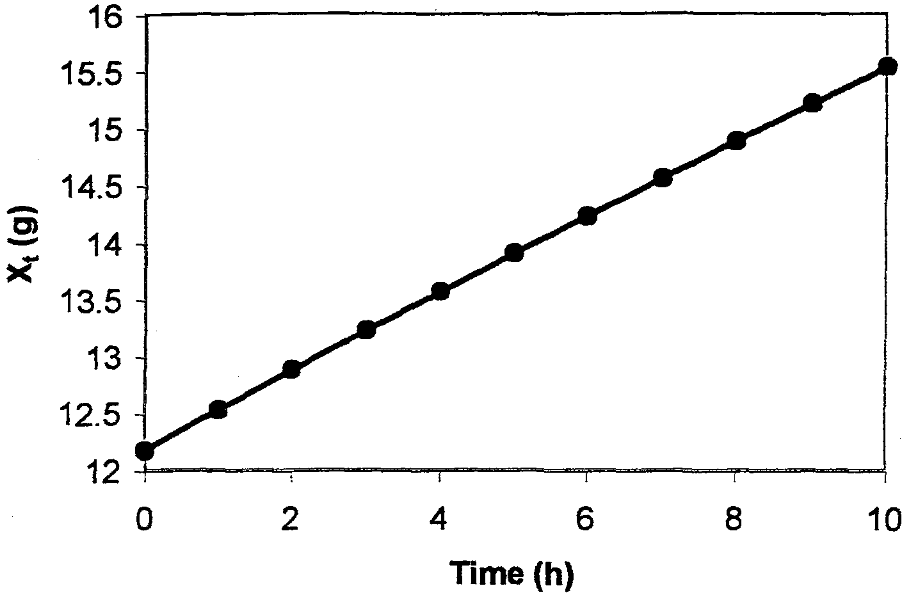

Figure 3.5.35. Variation of total amount of biomass with time
(S_i=7000 mg/L, Q=0.21 L/h, V_o=3 L)

Variation of COD concentration and percent COD removal with time for Q=0.36 L/h and S_i=7000 mg/L are depicted in Figure 3.5.36. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank was 1225 mg/L at the end of the operation time. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 69% at the end of 10 h operation.

Variations of COD concentration and percent COD removal with COD loading rate are shown in Figure 3.5.37. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.38, variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.44 gX/gS for 0.36 L/h feed flow rate.

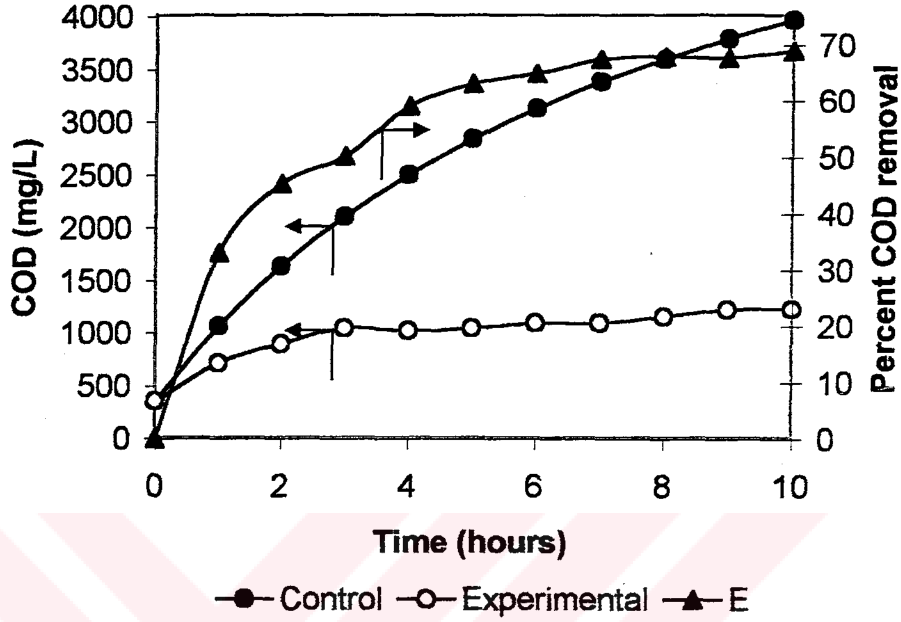

Figure 3.5.36. Variation of COD concentration and percent COD removal with time (S_i=7000 mg/L, Q=0.36 L/h, V_o=3 L)

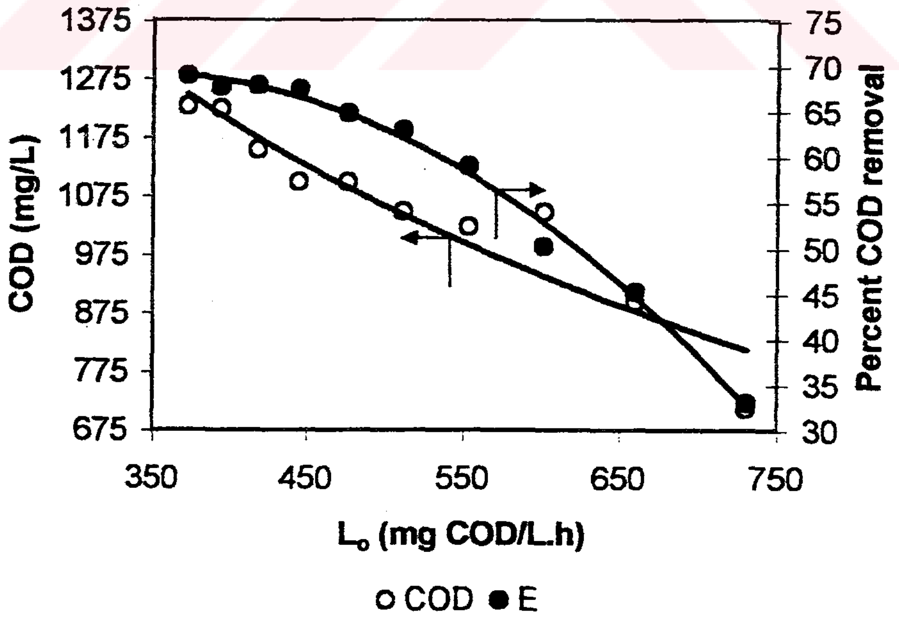

Figure 3.5.37. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7000 mg/L, Q=0.36 L/h, V_o=3 L)

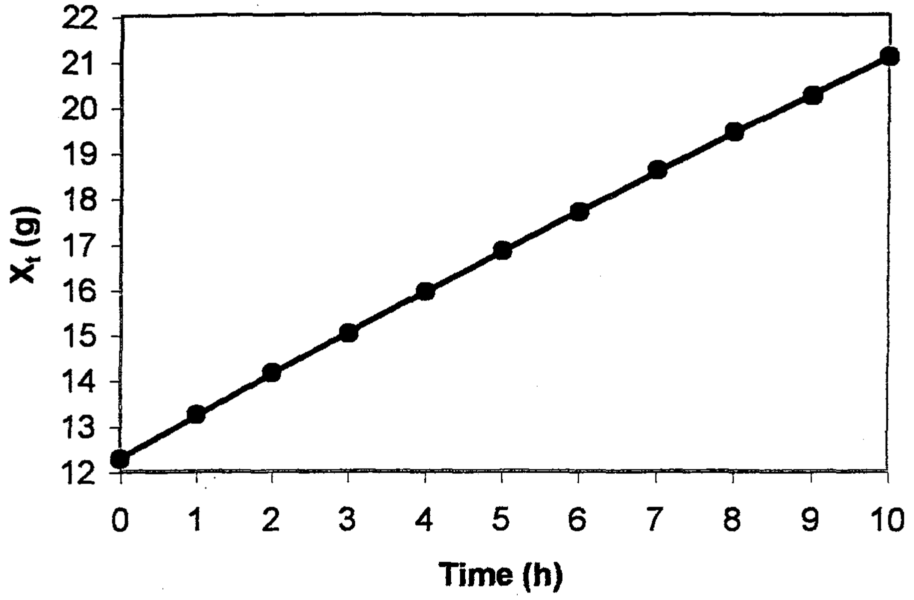

Figure 3.5.38. Variation of total amount of biomass with time (S_i=7000 mg/L, Q=0.36 L/h, V_o=3 L)

Variations of COD concentration and percent COD removal with time for Q=0.45 L/h and S_i=7000 mg/L are depicted in Figure 3.5.39. COD concentration in the control tank increased with time due to accumulation of COD. COD in the experimental tank was nearly 1300 mg/L at the end of 10 hours operation time. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 70 % at the end of the operation time.

Variations of COD concentration and percent COD removal with COD loading rate are depicted in Figure 3.5.40. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.41, variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.58 gX/gS for 0.45 L/h feed flow rate.

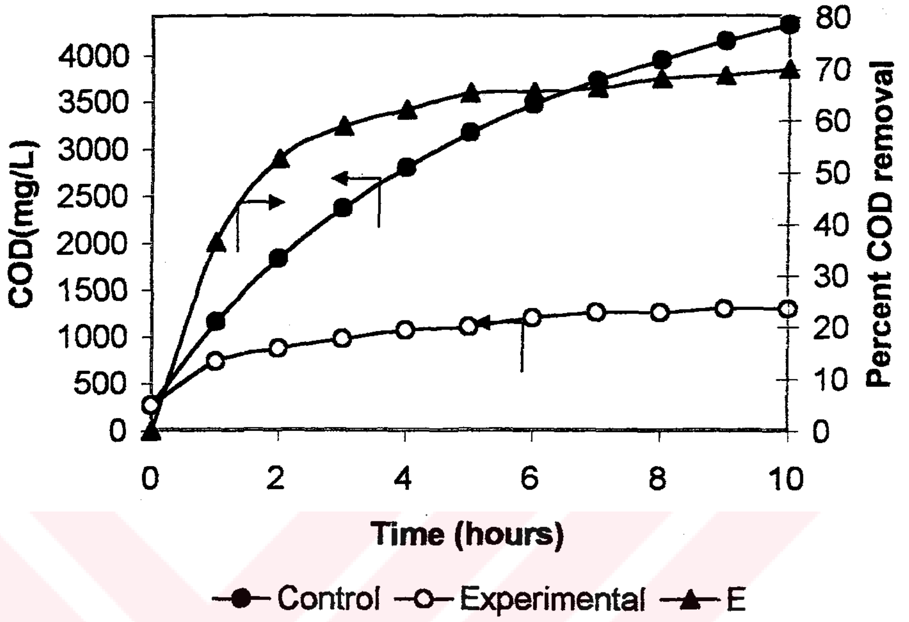

Figure 3.5.39. Variation of COD concentration and percent COD removal with time (S_i=7000 mg/L, Q=0.45 L/h, V_o=3 L)

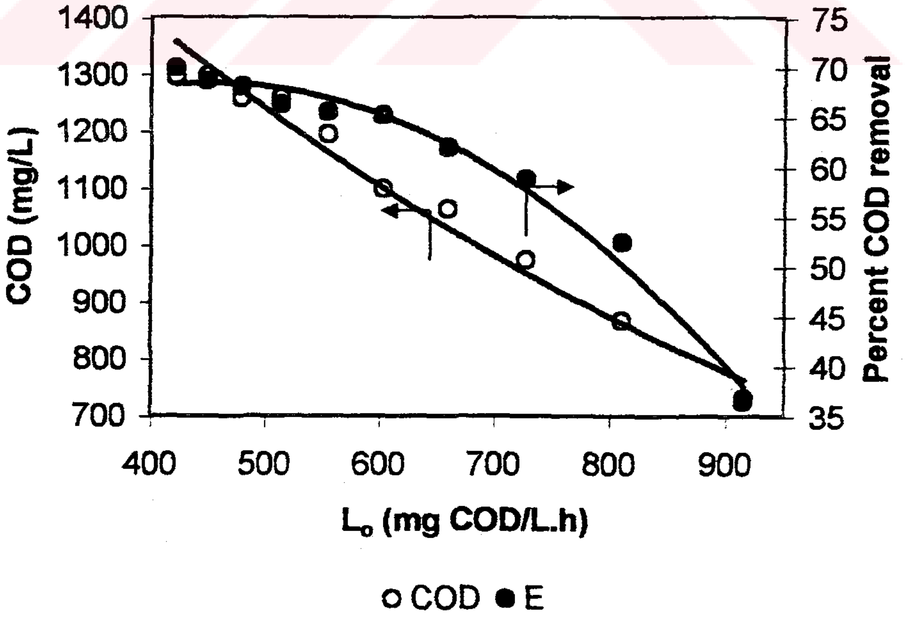

Figure 3.5.40. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7000 mg/L, Q=0.45 L/h, V_o=3 L)

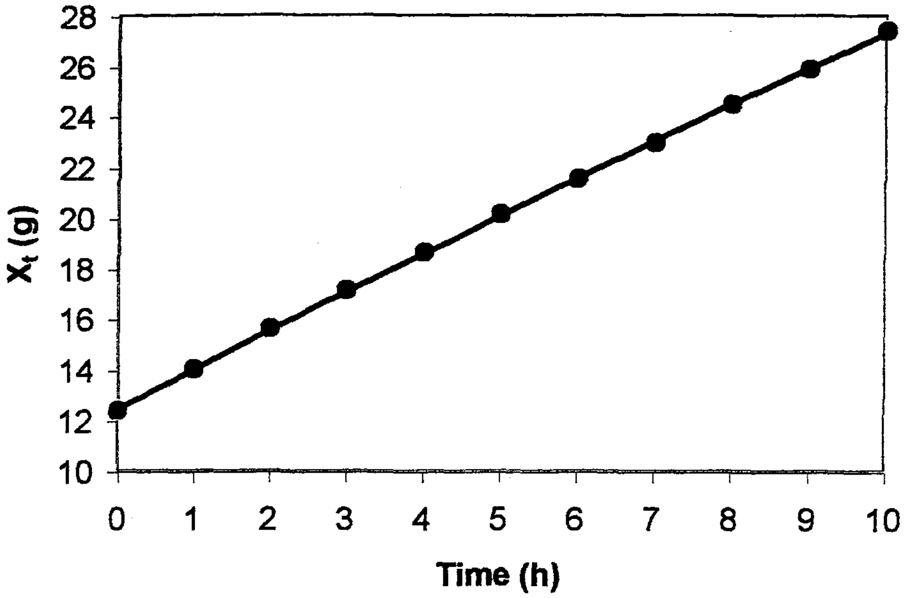

Figure 3.5.41. Variation of total amount of biomass with time
(S_i=7000 mg/L, Q=0.45 L/h, V_o=3 L)

Variations of COD concentration and percent COD removal with time for Q=0.60 L/h and S_i=7000 mg/L are depicted in Figure 3.5.42. COD concentration in the control tank increased with time due to accumulation of COD in the absence of organisms. COD in the experimental tank at the end of the operation was around 1500 mg/L, because of high COD loading and relatively low removal rate. Percent COD removal based on the difference in COD concentrations in the control and the experimental tanks increased with time because of increased total biomass in the aeration tank. Percent COD removal was 68% at the end of 10h operation.

Variation of COD concentration and percent COD removal with COD loading rate is shown in Figure 3.5.43. Both COD content in the aeration tank and percent COD removals (E) decreased with the increasing COD loading rates.

In Figure 3.5.44 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.52 gX/gS for 0.60 L/h feed flow rate.

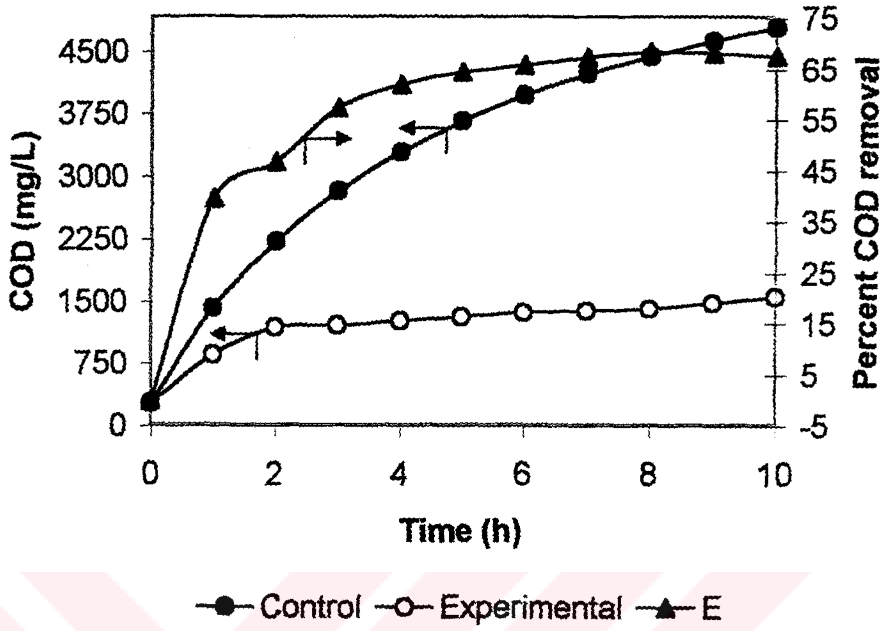

Figure 3.5.42. Variation of COD concentration and percent COD removal with time (S_i=7000 mg/L, Q=0.60 L/h, V_o=3 L)

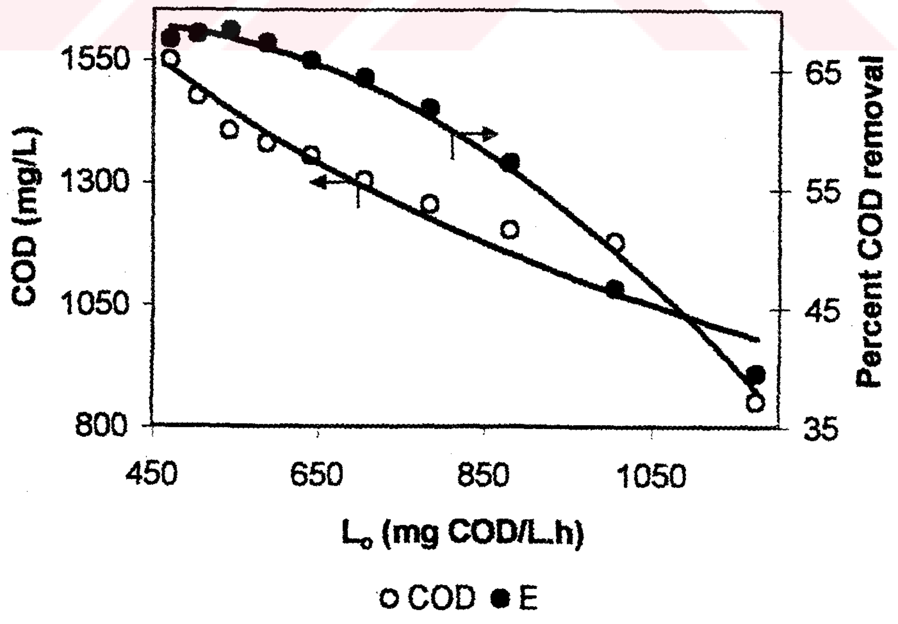

Figure 3.5.43. Variation of COD concentration and percent COD removal with COD loading rate (S_i=7000 mg/L, Q=0.60 L/h, V_o=3 L)

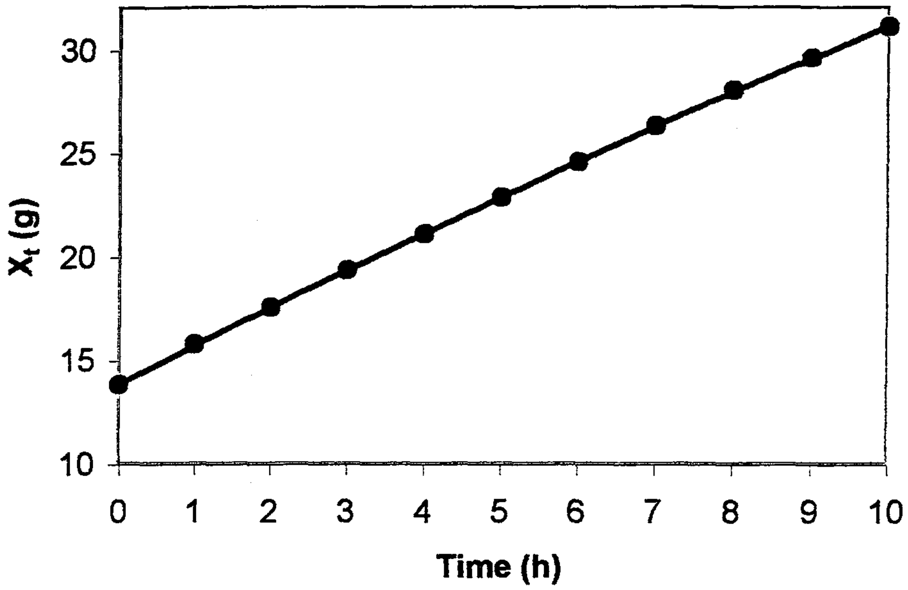

Figure 3.5.44. Variation of total amount of biomass with time
(S_i=7000 mg/L, Q=0.60 L/h, V_o=3 L)

3.5.3. Effect of COD Loading Rate on the Reactor Performance

COD loading rate was varied by varying both the feed COD and the feed flow rate. The effects of COD loading rates (L_s = Q Si) on the final COD levels and COD removal efficiencies are depicted in Figure 3.5.45. Final COD content in the aeration tank at the end of operation increased while percent COD removals (E) decreased with the increasing COD loading rates. At low COD loading rates, the effluent COD levels increased and percent COD removals decreased more steeply. However, changes in both parameters slowed down at high COD loadings and levelled off at COD loadings above 3.5 g COD/h. In order to achieve high COD removal efficiencies the COD loading rate should be kept below 1 gCOD/h.

The effects of ammonium loading rates (L_s = Q S_o) on the final ammonium levels and ammonium removal efficiencies are depicted in Figure 3.5.46. Similarly, effluent ammonium-N concentrations at the end of operation increased and percent removals decreased with increasing NH_4-N loading rate. Changes in those parameters with the

NH_4-N loading rate were steeper at low loading rates and slowed down as the loading rate increased. Percent NH_4-N removals decreased from 26% to 18 % as the ammonium-N loading rate increased from 35 mg N/h to 420 mg N/h.

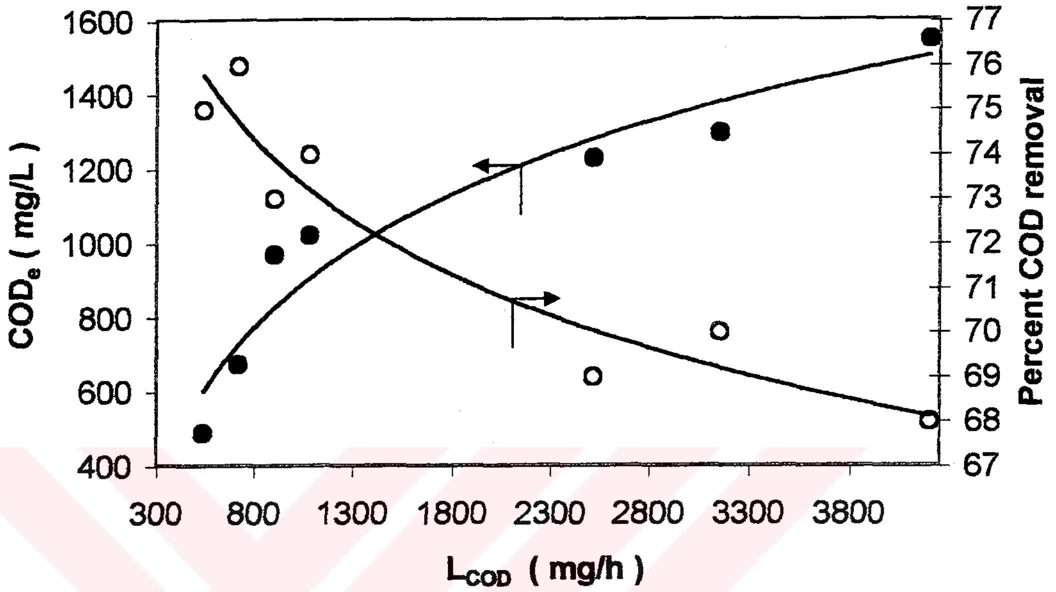

Figure 3.5.45. Variations of the effluent concentrations and percent removals for COD with COD loading rates at the end of the operation

● Effluent COD ○ E

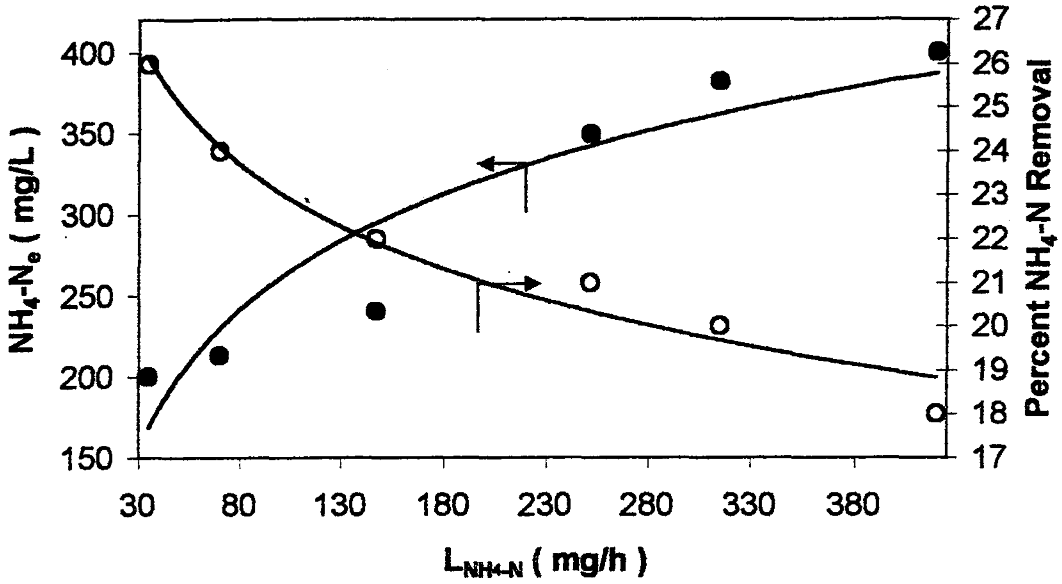

Figure 3.5.46. Variations of the effluent concentrations and percent removals for NH_4-N with NH_4-N loading rates at the end of the operation
● Effluent NH_4-N ○ E

3.5.4. Kinetic Analysis and Determination of Kinetic Constants

The following kinetic model was used in the analysis of data obtained at the end of 30 hours of operation. The system was assumed to be at quasi steady-state at the end of operation as seen from the previous figures.

$$R_s = \frac{Q\,(S_c - S)}{V_o + Q\,t} = \frac{k\,X\,S}{K_s + S} = \frac{R_m\,S}{K_s + S} \qquad (3.5.1.)$$

where, Q is the feed flow rate (L/h); S_c is the control COD concentration (mg/L); S is the actual COD content in the tank after 30 hours of operation (mg/L); V_o is the initial wastewater volume in the tank (3 liter); t is the operating time (h); k is the maximum COD removal rate constant (h^{-1}); X is the biomass concentration in the aeration tank at any time during operation (mg/L); K_s is the saturation constant (mg/L) and R_m is the maximum rate of COD removal (mg COD/L.h) which is equal to k X.

In double reciprocal form, the eqn.3.5.1. takes the following form,

$$\frac{1}{R_s} = \frac{(V_o + Q\,t)}{Q\,(S_c - S)} = \frac{1}{R_m} + \frac{K_s}{R_m}\;\frac{1}{S} \qquad (3.5.2.)$$

A double reciprocal plot of $1/R_s$ versus 1/S yields a line with a slope of K_s/R_m and intercept of $1/\,R_m$.

Experimental data with variable feed COD obtained at the end of 30 hours of operation (i.e., at the quasi steady-state) were plotted in form of $1/R_s$ versus 1/S as shown in Figure 3.5.47. From the slope and the intercept of the best-fit line, the following values found for the kinetic constants.

R_m=81.7 mg COD/L h, K_s=377 mg/L ($r^2 = 0.90$)

By using the equation of R_m=kX and considering the average biomass concentration in the aeration tank as X=2200 mg/L, the rate constant was found to be in the order of k =0.037 h^{-1} = 0.89 d^{-1} for the biological system used.

The rate constant (k) was found to be lower and the saturation constant (K_s) higher than those of the conventional activated sludge systems probably due to the presence of inhibitory compounds in the leachate used.

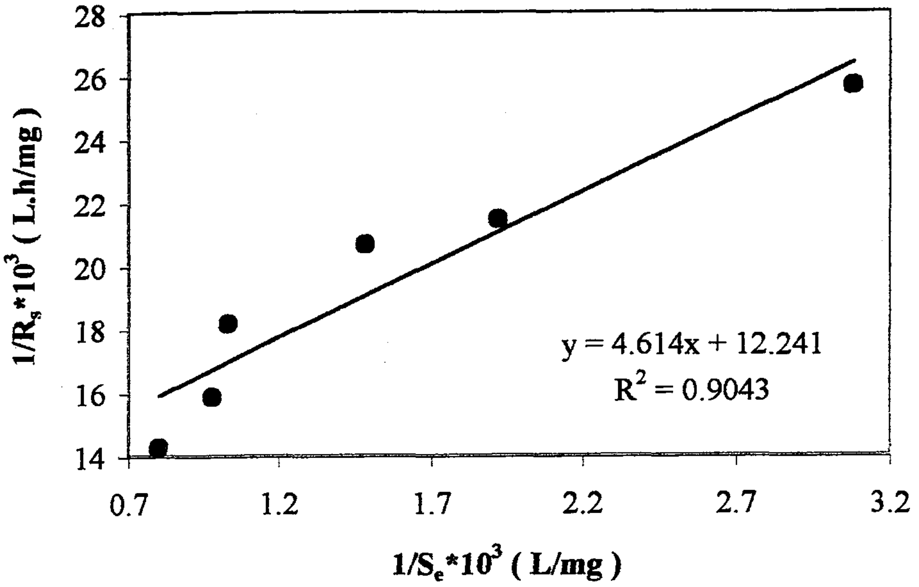

Figure 3.5.47. Double reciprocal plot of $1/R_s$ versus $1/S_e$ at the quasi steady-state for determination of kinetic constants for COD removal.

3.6. Adsorbent Added Biological Treatment of Landfill Leachate by Fed-Batch Operation

In this set of experiments, pre-treated landfill leachate was subjected to adsorbent supplemented biological treatment in an aeration tank operated in fed-batch mode by using powdered activated carbon (PAC) and powdered zeolite (PZ) as adsorbents.

3.6.1. Powdered Activated Carbon (PAC) added Biological Treatment

A set of experiments with different activated carbon concentrations (0-5 g/L) were carried out in an aeration tank operated in fed-batch mode by using the pretreated leachate. Each set of experiments consisted of four simultaneous experiments. Control (C) experiments were performed without any microorganisms and any adsorbent. Biological treatment (B) experiments were performed only by using the activated sludge culture without any adsorbent addition. Only adsorbent

(PAC) was added to the aeration tank devoid of microorganisms in adsorption experiments(A). Simultaneous adsorption and biological treatment (AB) experiments were performed by addition of adsorbent to the aeration tank containing activated sludge organisms. Four simultaneous experiments were performed under the same initial and operating conditions. Percent COD removals were based on control experiment's COD contents, since no COD removal was realized in the control tank.

Variation of COD concentration with time for the activated carbon concentration of 0.25 g/L is depicted in Figure 3.6.1. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4300 mg/L at the end of 30 h operation period. Similar trend was observed in the adsorption experiment (Δ) where COD in the aeration tank increased steadily with time. However, COD levels were lower than those of the control experiments because of COD removal by adsorption resulting in a COD content of nearly 3550 mg/L at the end of 30 h of operation. COD profiles in biological oxidation (B) and adsorbent added biological treatment (AB) were almost the same, slightly increasing within the first 10 hours and levelling off afterwards. The final COD contents in those experiments were nearly 1100 mg/L for only biological treatment (B) and 1050 mg/L for adsorptive biological treatment (AB). Because of low activated carbon concentration (0.25 g/L), adsorption was not significant and the major mechanism for COD removal was biological oxidation in this case.

Variations of percent COD removal with time in fed-batch operation when PAC is 0.25 g/L is presented in Figure 3.6.2. Percent COD removals in adsorption experiment was nearly 17%; whereas, nearly 74% and 76% COD removals were obtained with the biological treatment (B) and adsorptive-biological treatment (AB), respectively at the end of operation. COD removals in the control experiment were assumed to be zero by definition. Again, due to low activated carbon concentration, the difference in COD removal performances of the bio-treatment (B) and adsorption-biodegradation (AB) experiments was negligible.

Variation of wastewater volume with time is shown in Figure 3.6.3. Starting from a 3.0 L of initial volume, wastewater volume in the tank increased with time linearly as expected.

In Figure 3.6.4 variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

Variation of COD removal rate with COD loading rate is depicted in Figure 3.6.5. COD removal rate decreased with increasing COD loading rate.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.57 gX/gS for 0.25 g/L PAC concentration.

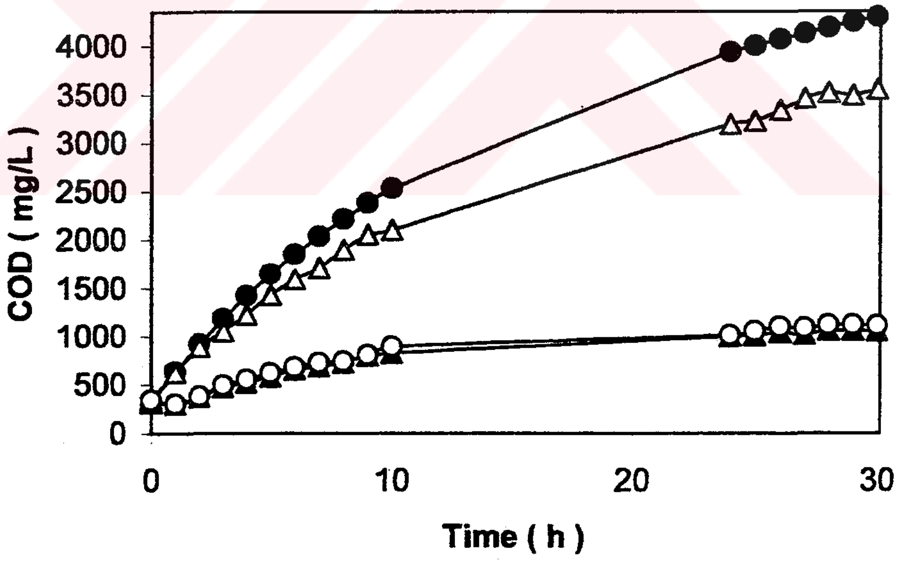

Figure 3.6.1. Variations of COD with time in fed-batch operation (0.25 g/L PAC)

● control (C), Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

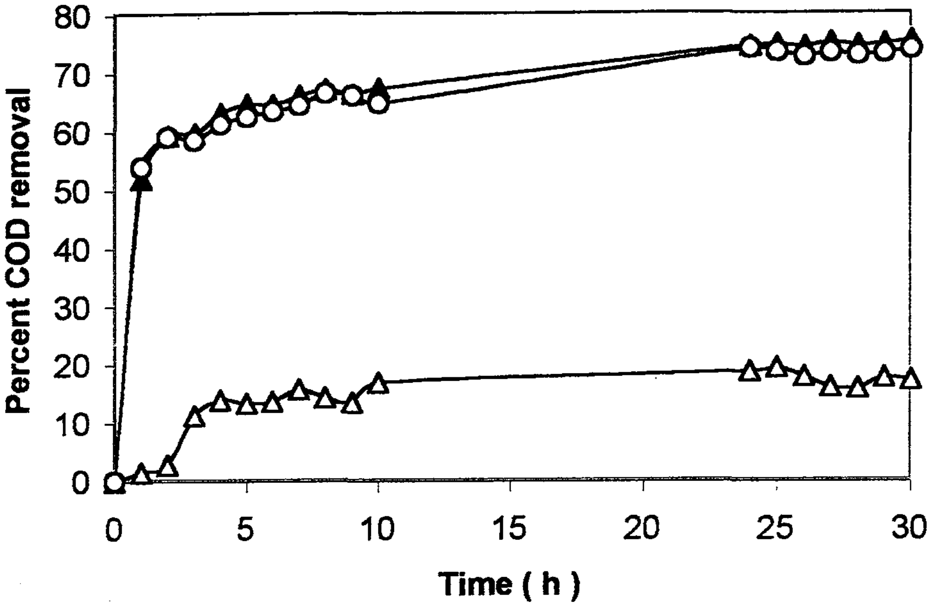

Figure 3.6.2. Variations of percent COD removal with time in fed-batch operation (0.25 g/L PAC) Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

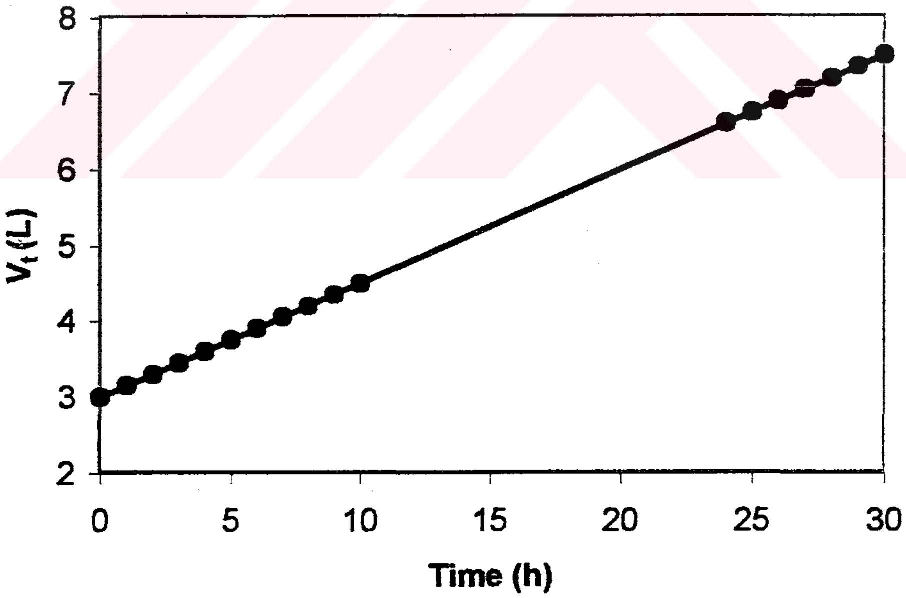

Figure 3.6.3. Variations of reactor volume with time (0.25 g/L PAC)

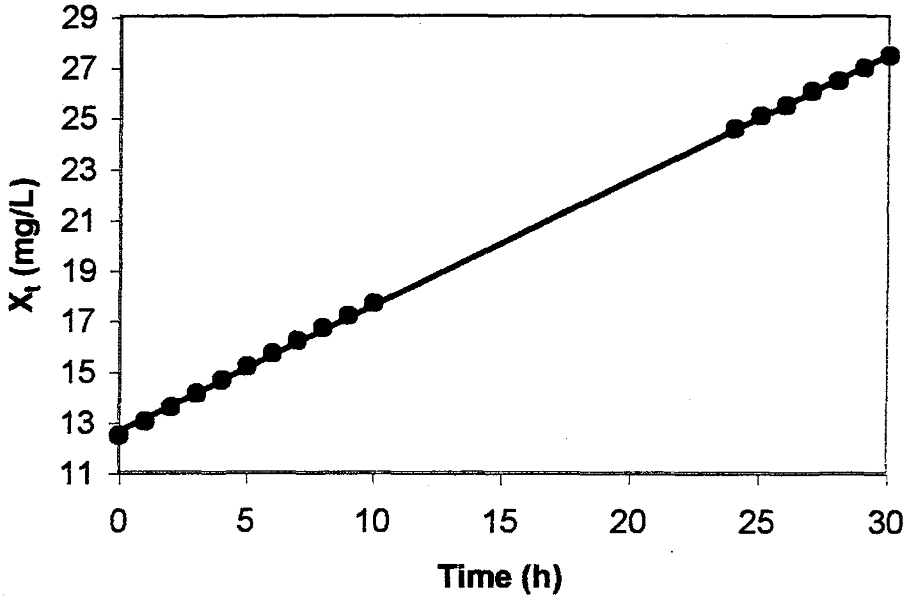

Figure 3.6.4. Variations of total amount of biomass with time (0.25 g/L PAC)

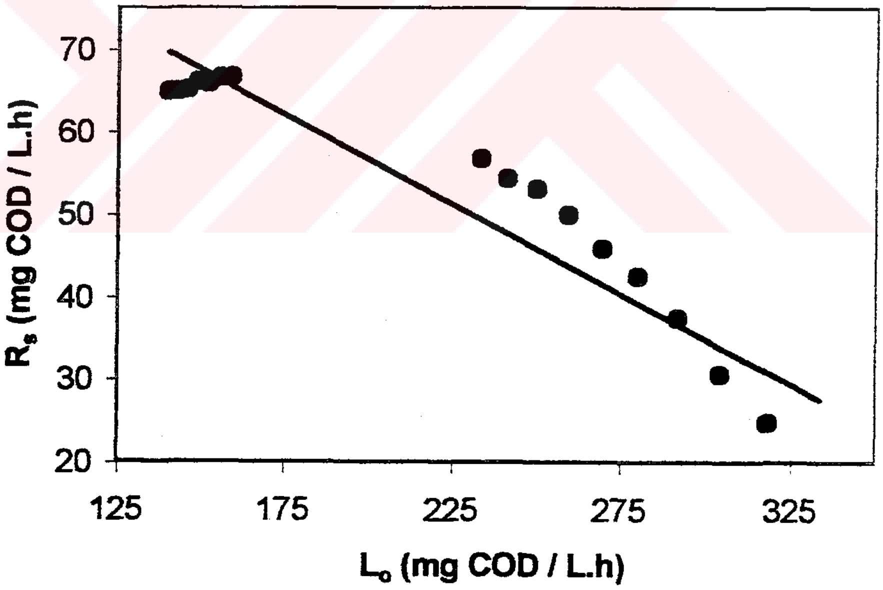

Figure 3.6.5. Variations of COD removal rate with COD loading rate (0.25 g/L PAC)

In Figure 3.6.6 variation of COD concentration with time for the activated carbon concentration of 0.50 g/L is depicted. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4200 mg/L at the end of 30 h operation period. Similar trend was observed in the adsorption experiment (Δ) where COD in the aeration tank increased steadily with time. However, COD levels were lower than those of the control experiments because of COD removal by adsorption resulting in a COD content of nearly 3300 mg/L at the end of 30 h of operation. COD profiles in biological oxidation (B) and adsorbent added biological treatment (AB) showed a slightly increasing trend within the first 10 hours and levelling off afterwards. The final COD contents in those experiments were nearly 935 mg/L for only biological treatment (B) and 1050 mg/L for adsorptive biological treatment (AB). Because of low activated carbon concentration (0.50 g/L), adsorption was not significant and the major mechanism for COD removal was biological oxidation in this case.

Variation of percent COD removal with time in fed-batch operation when PAC is 0.50 g/L is presented in Figure 3.6.7. Percent COD removals in adsorption experiment was nearly 21%; whereas, nearly 74% and 78% COD removals were obtained with the biological treatment (B) and adsorptive biological treatment (AB), respectively at the end of operation. COD removals in the control experiment were assumed to be zero by definition. Again, due to low activated carbon concentration the difference in COD removal performances of the biodegradation (B) and adsorption-biodegradation (AB) experiments was negligible.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.46 gX/gS for 0.50 g/L PAC concentration.

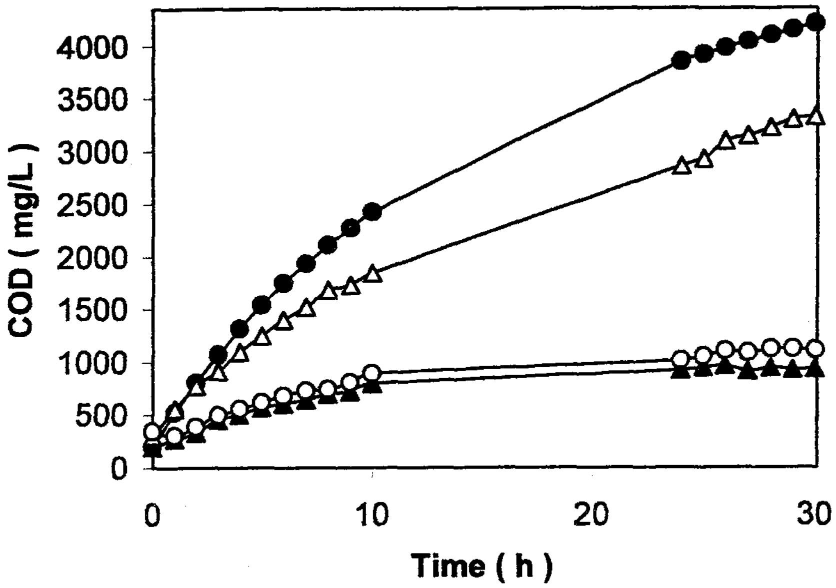

Figure 3.6.6. Variation of COD concentration with time in fed-batch operation (0.50 g/L PAC) ● control (C), Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

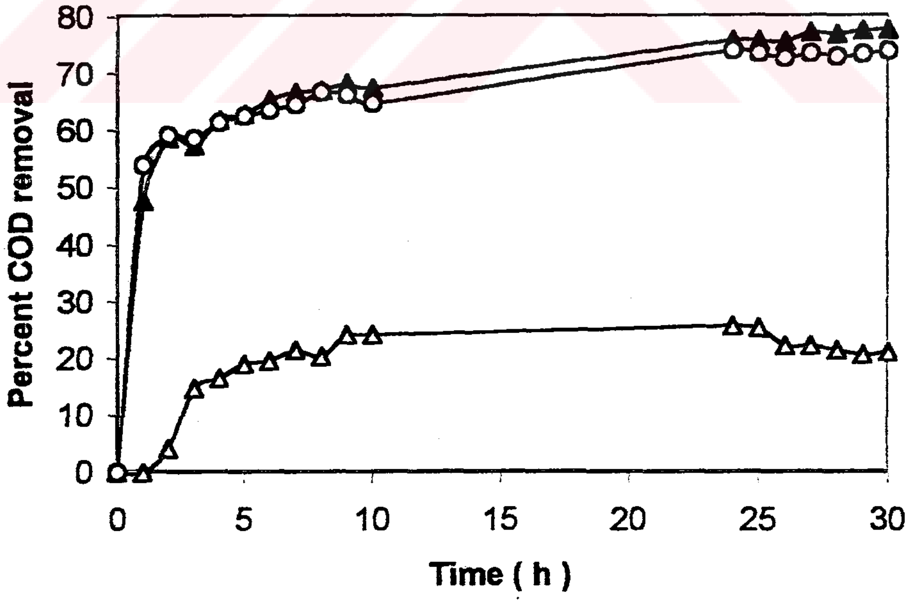

Figure 3.6.7. Variation of percent COD removal with time in fed-batch operation (0.50 g/L PAC) Δ adsorption (A), ○ biological treatment (B) ▲ adsorption and biological treatment (AB).

Figure 3.6.8 depicts variations of COD concentrations with time for the four simultaneous experiments when the PAC concentration was 1 g/L. Similar trends were observed in these experiments; however, contribution of adsorption was more pronounced due to higher PAC concentration (1 g/L). Effluent COD' s at the end of 30 hours of fed-batch operation were 4200 mg/L, 2840 mg/L, 1100 mg/L and 750 mg/L for the control (C), adsorption (A), biodegradation (B) and adsorption-biodegradation (AB) experiments, respectively. Due to more pronounced contribution of adsorption, the effluent COD was reduced from 1100 mg/L (B) to 750 mg/L (AB) at the end of 30 h operation.

Variations of percent COD removals with time are shown in Figure 3.6.9. Percent COD removal also increased significantly by addition of 1 g/L PAC to the biological treatment tank. COD removal for only adsorption (Δ) was nearly 32%. However, COD removals of 74% and 82% were obtained with biodegradation (○) and adsorption-biodegradation (▲) experiments, respectively at the end of 30 h operation

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.54 gX/gS for 1.0 g/L PAC concentration.

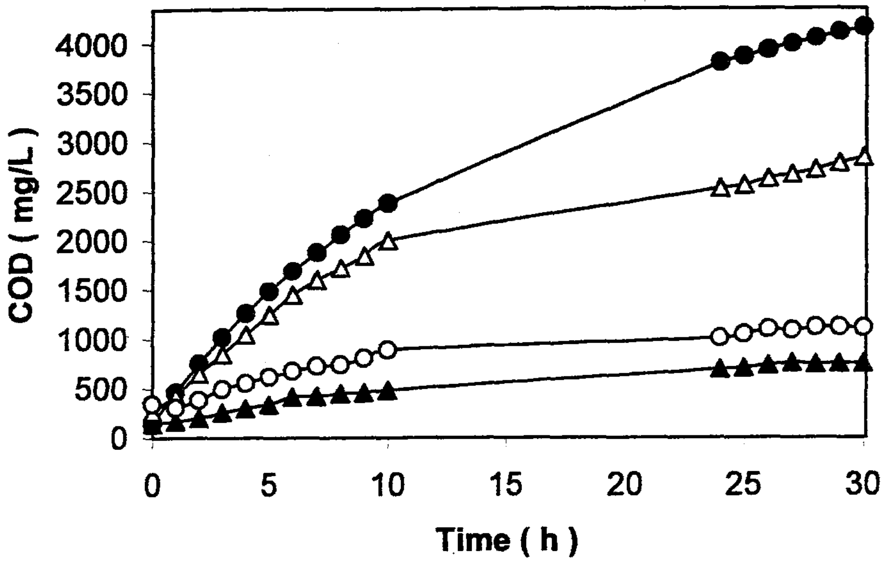

Figure 3.6.8. Variations of COD with time in fed-batch operation (1.0 g/L PAC)
● control (C), Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

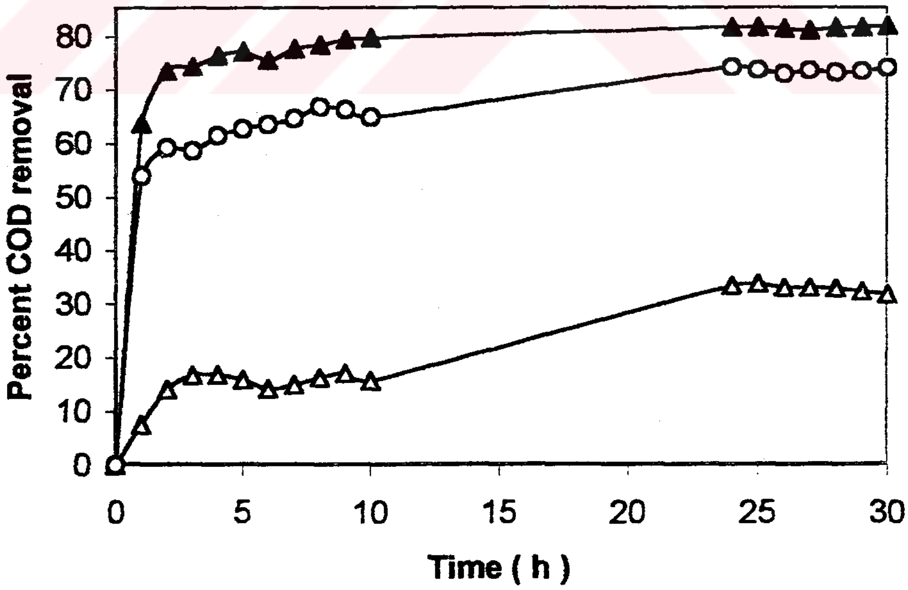

Figure 3.6.9. Variation of percent COD removal with time in fed-batch operation
(1.0 g/L PAC) Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

Figure 3.6.10. depicts variations of COD concentrations with time for the four simultaneous experiments when the PAC concentration was 2 g/L. Similar trends were observed in these experiments; however, contribution of adsorption was more pronounced due to higher PAC concentration (2 g/L). Effluent COD' s at the end of 30 hours of fed-batch operation were 4240 mg/L, 2600 mg/L, 1100 mg/L and 610 mg/L for the control (C), adsorption (A), biodegradation (B) and adsorption-biodegradation (AB) experiments, respectively. Due to more pronounced contribution of adsorption, the effluent COD was reduced from 1100 mg/L (B) to 610 mg/L (AB) at the end of operation.

Percent COD removals with time are shown in Figure 3.6.11. Percent COD removal also increased significantly by addition of 2 g/L PAC to the biological treatment tank. COD removal for only adsorption (Δ) was nearly 38%. However, COD removals of 74% and 86% were obtained with biodegradation (○) and adsorption-biodegradation (▲) experiments, respectively at the end of 30 h operation

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.46 gX/gS for 2.0 g/L PAC concentration.

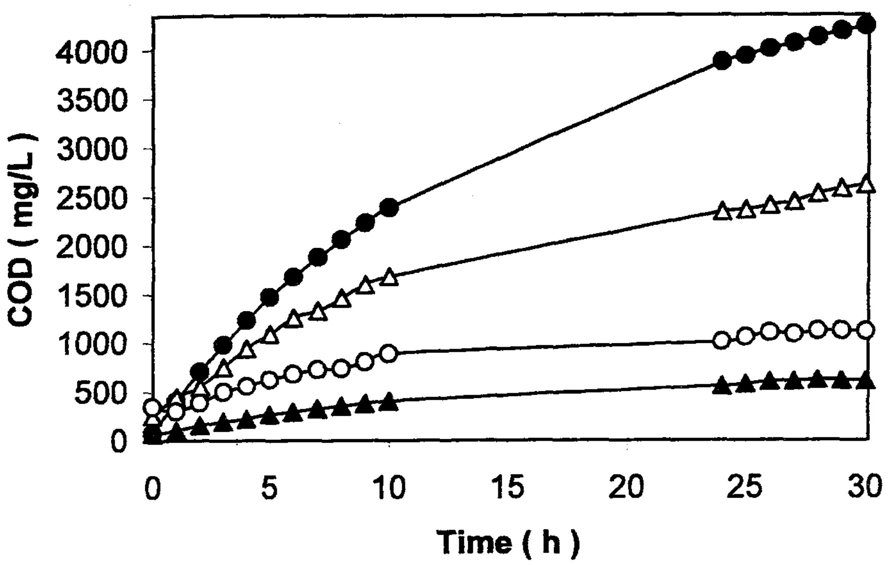

Figure 3.6.10. Variation of COD with time in fed-batch operation (2.0 g/L PAC)

● control (C), Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

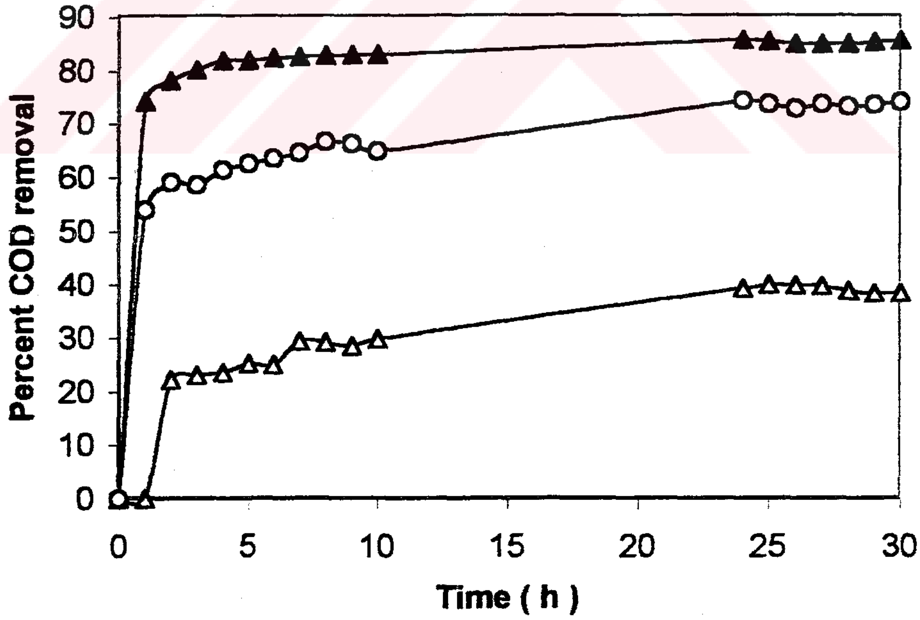

Figure 3.6.11. Variation of percent COD removal with time in fed-batch operation (2.0 g/L PAC)

● control (C), Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

When activated carbon concentrations were increased, COD removals were more effective. Figure 3.6.12. depicts variations of COD contents with time for 3 g/L PAC concentration. Effluent COD contents for the control and the adsorption experiments were 4250 mg/L and 2540 mg/L, respectively. Whereas, effluent COD's were nearly 1100 mg/L and 575 mg/L for the biodegradation (B) and adsorption-biodegradation (AB) experiments.

In Figure 3.6.13 variation of percent COD removal with time is presented. Similar trends were observed in COD removal efficiencies. Nearly 40% COD was removed by only adsorption (Δ); whereas percent COD removals were 74% and 86% for biodegradation (B) and adsorptive-biodegradation (AB), respectively. Again, percent COD removal was zero for the control experiment. Apparently, percent COD removals increased significantly due to contribution of adsorption at a high PAC concentration of 3 g/L.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.46 gX/gS for 3.0 g/L PAC concentration.

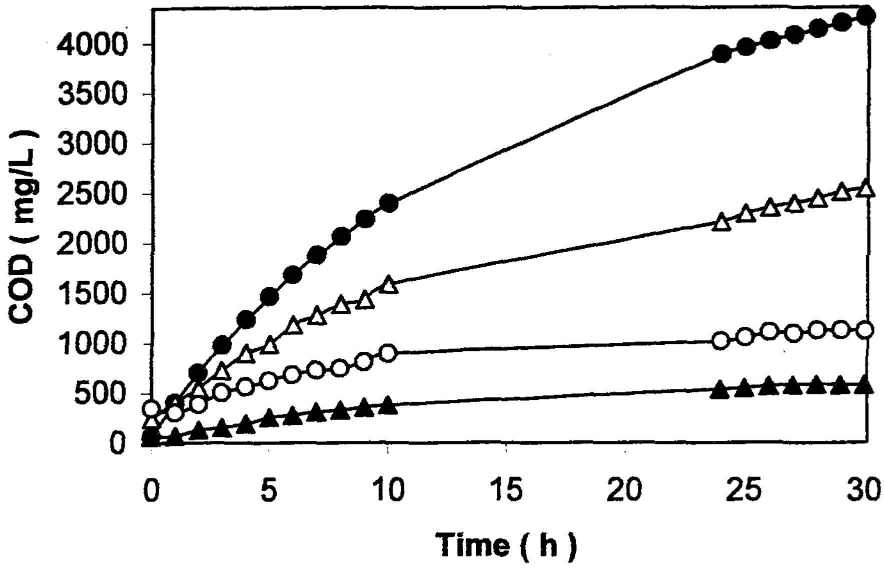

Figure 3.6.12. Variation of COD with time in fed-batch operation (3.0 g/L PAC)
● control (C), Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

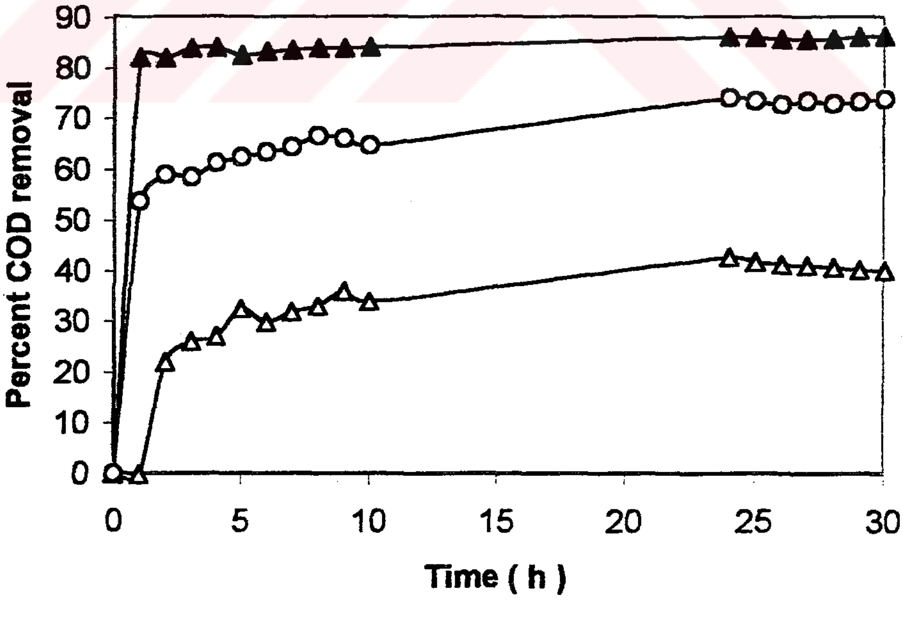

Figure 3.6.13. Variation of percent COD removal with time in fed-batch operation (3.0 g/L PAC) Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

Increased activated carbon concentrations resulted in more effective COD removals. Figure 3.6.14 depicts variations of COD contents with time for 5 g/L PAC concentration. Effluent COD contents for the control and the adsorption experiments were 4300 mg/L and 2200 mg/L, respectively. Whereas, effluent COD's were nearly 1100 mg/L and 540 mg/L for the biodegradation (B) and adsorption-biodegradation (AB) experiments.

Variation of percent COD removal with time is presented in Figure 3.6.15. Similar trends were observed in COD removal efficiencies. Nearly 50% COD was removed by only adsorption (A); whereas percent COD removals were 74% and 87% for biodegradation (B) and adsorptive-biodegradation (AB), respectively. Again, percent COD removal was zero for the control experiment. Apparently, percent COD removals increased significantly due to contribution of adsorption at a high PAC concentration of 5 g/L.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.40 gX/gS for 5.0 g/L PAC concentration.

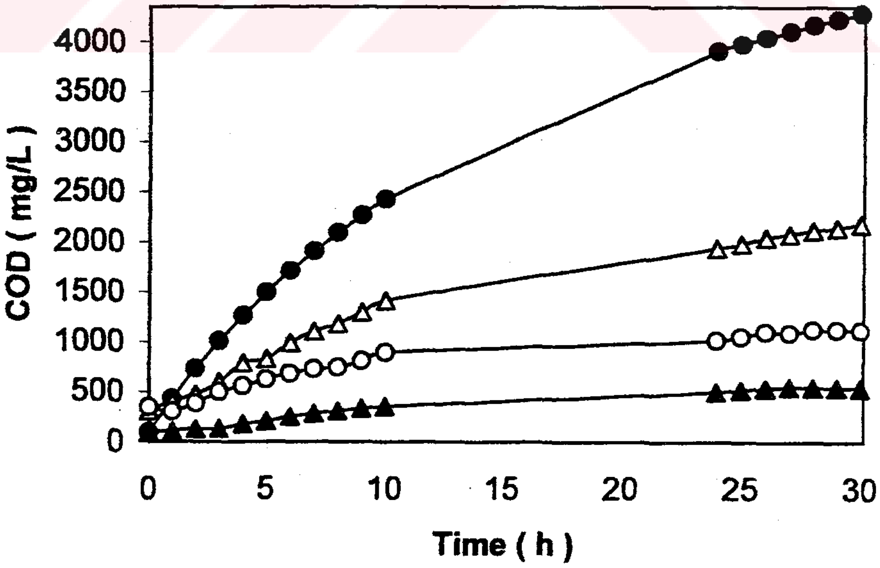

Figure 3.6.14. Variation of COD with time in fed-batch operation (5.0 g/L PAC)
● control (C), Δ adsorption (A), ○ biological treatment (B).
▲ adsorption and biological treatment (AB).

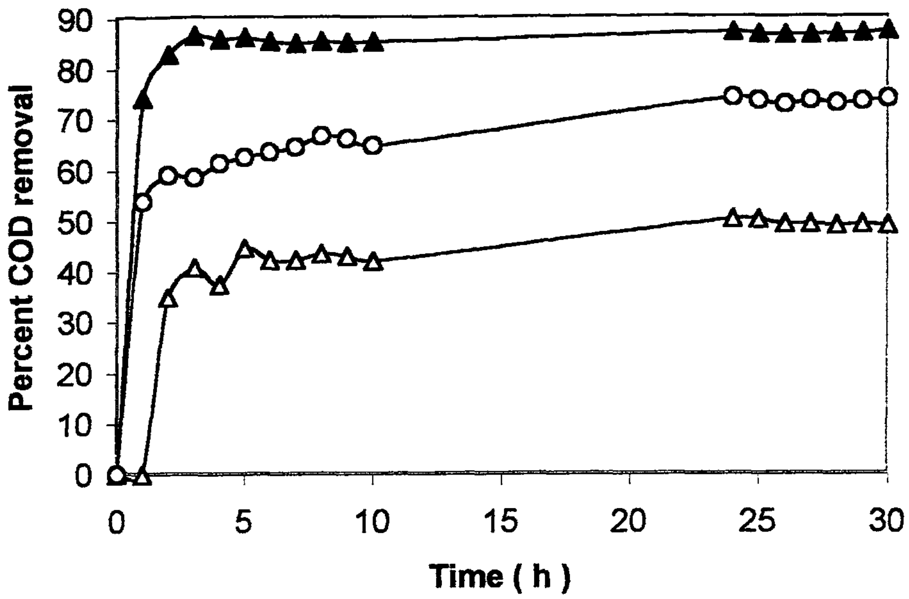

Figure 3.6.15. Variation of percent COD removal with time in fed-batch operation (5.0 g/L PAC) Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

Collected results of effluent COD contents and percent COD removals at the end of 30 h operation with different activated carbon concentrations (0-5 g/L) are depicted in Figure 3.6.16. Effluent COD decreased and percent COD removal increased with the increasing PAC concentration for both adsorption (A) and adsorption-biodegradation (AB) experiments. Effluent COD of nearly 2200 mg/L was obtained with only adsorption corresponding nearly 50% removal with 5 g/L PAC addition. However, the effluent COD for adsorption-biodegradation (AB) experiment was nearly 540 mg/L corresponding to 87% COD removal under the same conditions. COD removal efficiencies increased steeply with the PAC concentration up to 2 g/L and remained almost constant for higher PAC concentrations. PAC concentration of 2 g/L yielded (86%) nearly the same percent COD removal as that of the 5 g/L PAC (87%). Considering the cost of activated carbon, 2 g/L PAC was selected as the most suitable concentration for future use.

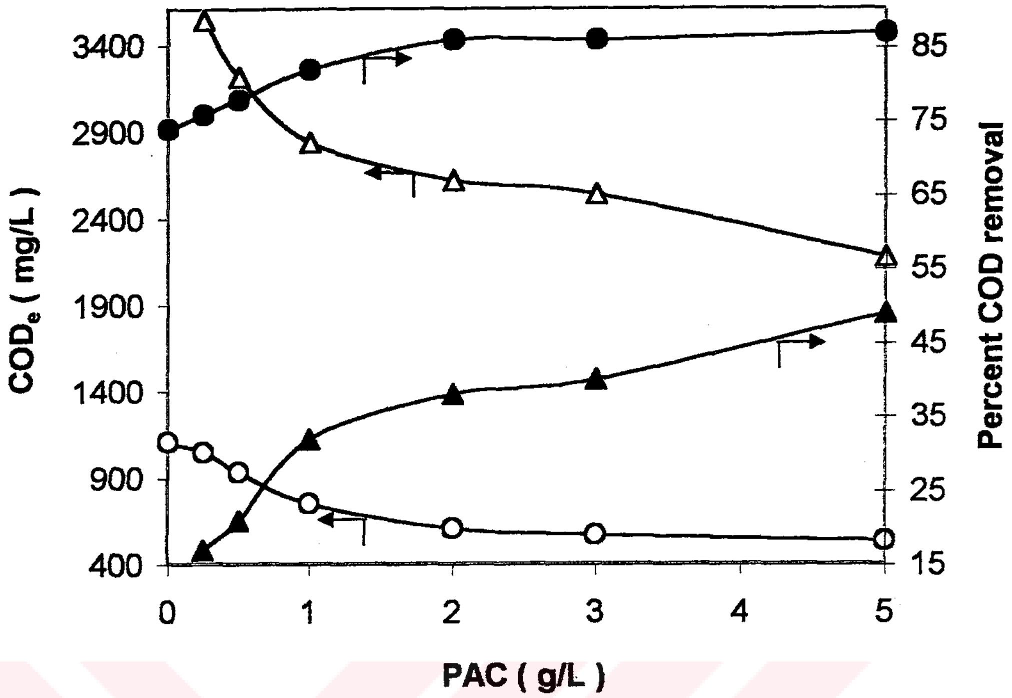

Figure 3.6.16. Variations of the effluent COD and percent COD removals at the end of 30 h fed-batch operation with the adsorbent (PAC) concentration Δ, ▲ adsorption (A); ○, ● adsorption and biological treatment (AB)

Similar plots were made for ammonium-N removal as shown in Figure 3.6.17. Again, percent NH_4-N removal increased with increasing PAC concentration in both adsorptive biological treatment (AB) and only adsorption (A) experiments. In PAC added biodegradation experiments, 26% and 30% NH_4-N removals were obtained with 2 g/L and 5 g/L PAC, respectively. Ammonium-N removal in adsorption experiments (A) were considerably lower than those of the PAC added biological treatment (AB) resulting in only 12 % and 16 % COD removals with 2 g/L and 5 g/L PAC, respectively.

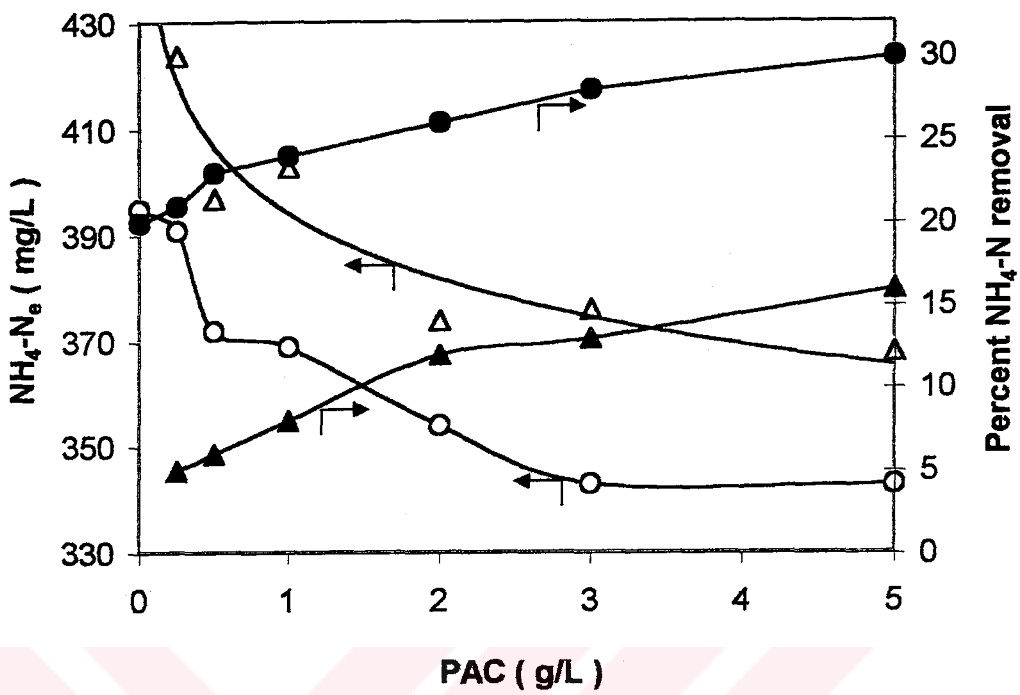

Figure 3.6.17. Variations of the effluent NH_4-N and percent NH_4-N removals at the end of 30 h fed-batch operation with the adsorbent (PAC) concentration. △, ▲ adsorption (A); ○, ● adsorption and biological treatment (AB)

3.6.2. Kinetic Analysis and Determination of Kinetic Constants

An empirical model was developed to quantify the effect of adsorbent addition onto the biological treatment process. The empirical equation has the following form,

$$E_{AB} - E_B = a\,(PAC)^b \qquad (3.6.1.)$$

where E_{AB} and E_B are percent COD removals at the end of 30 hour operation, for PAC-added biological treatment (AB) and PAC-free biological treatment (B), respectively; PAC is the concentration of powdered activated carbon added (g/L) ; a and b are empirical constants.

In logarithmic form, eqn 3.6.1 becomes,

$$\mathrm{Ln}\,(E_{AB} - E_B) = \mathrm{Ln}\,a + b\,\mathrm{Ln}\,(PAC) \qquad (3.6.2.)$$

A plot of Ln (E_{AB} –E_B) versus Ln (PAC) would yield a line with a slope of (b) and an intercept of Ln a.

Experimental data for percent COD removal obtained at the end of 30 hours of fed-batch operation with different PAC concentrations (data in Figure 3.6.18) were plotted in form of Ln(E_{AB}–E_B) versus Ln(PAC) in Figure 3.6.18. From the slope and the intercept of the best-fit line the following values were obtained for (a) and (b).

$a = 0.0584$ and $b = 0.6174$ ($r^2 = 0.93$)

Therefore, eqn 3.6.1. for COD removal efficiency in the presence of PAC takes the following form,

$$E_{AB} - E_B = 0.0584\,(PAC)^{0.6174} \qquad (3.6.3.)$$

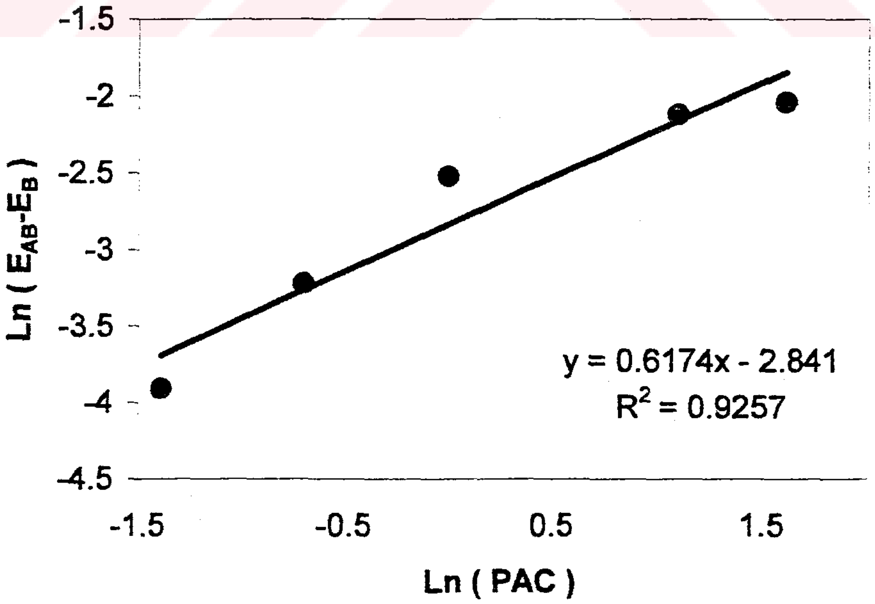

Figure 3.6.18. A plot of Ln (E_{AB}- E_B) versus Ln (PAC) for determination of the constants of the empirical equation for COD removal.

Experimental data for percent NH_4-N removal obtained at the end of 30 hours of fed-batch operation with different PAC concentrations (data in Figure 3.6.19) were plotted in form of Ln ($E_{AB} - E_B$) versus Ln (PAC) in Figure 3.6.18. From the slope and the intercept of the best-fit line the following values were obtained for (a) and (b).

a' = 0.0362 and b' = 0.7143 ($r^2 = 0.94$)

Therefore, eqn 3.6.1 for ammonium-N removal efficiency in the presence of PAC takes the following form,

$$E_{AB} - E_B = 0.0362\ (PAC)^{0.7143} \qquad (3.6.4.)$$

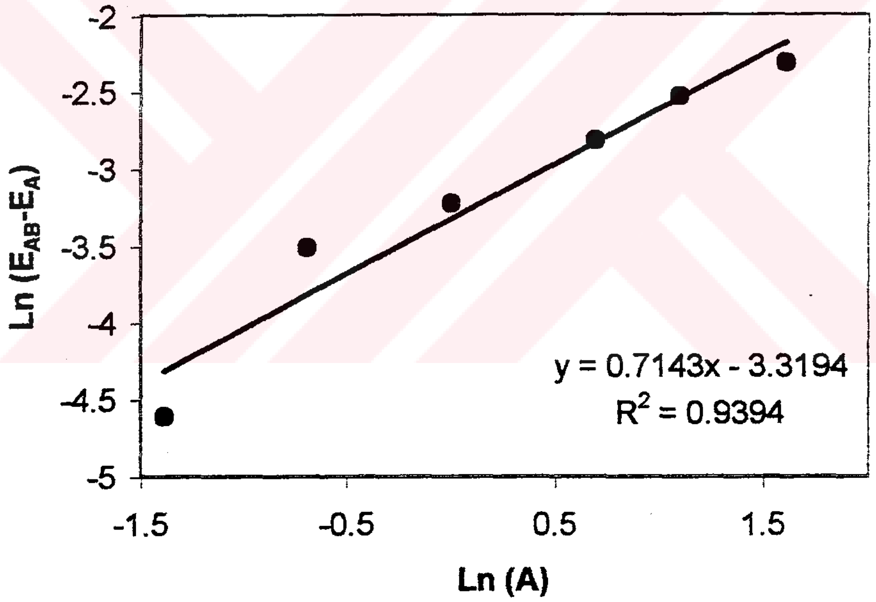

Figure 3.6.19. A plot of Ln (E_{AB}- E_B) versus Ln (PAC) for determination of the constants of the empirical equation for NH_4-N removal.

3.6.3. Powdered Zeolite (PZ) added Biological Treatment

A set of experiments with different zeolite (Z) concentrations (0-5 g/L) were conducted in an aeration tank operated in fed-batch mode by using the pretreated leachate. Each set of experiments consisted of four simultaneous experiments.

Control (C) experiments were performed without any microorganisms and adsorbent. Biological treatment (B) experiments were performed only by using the activated sludge culture without any adsorbent addition. Only adsorbent (Z) was added to the aeration tank devoid of microorganisms in adsorption experiments (A). Simultaneous adsorption and biological treatment (AB) experiments were performed by addition of adsorbent to the aeration tank containing activated sludge organisms. Four simultaneous experiments were performed under the same initial and operating conditions. Percent COD removals were based on control experiment's COD contents since no COD removal was realized in the control tank ($E = 1 - S / S_c$).

Variation of COD concentration with time for the zeolite concentration of 0.25 g/L is depicted in Figure 3.6.20. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4300 mg/L at the end of 30 h operation period. Similar trend was observed in the adsorption experiment (Δ) where COD in the aeration tank increased steadily with time. However, COD levels were lower than those of the control experiments because of COD removal by adsorption resulting in a COD content of nearly 4050 mg/L at the end of 30 h of operation. COD profiles in biological oxidation (B) and adsorbent added biological treatment (AB) were almost the same, slightly increasing within the first 10 hours and levelling off afterwards. The final COD contents in those experiments were nearly 1110 mg/L for only biological treatment (B) and 1100 mg/L for adsorptive biological treatment (AB). Because of low zeolite concentration (0.25 g/L), adsorption was not significant and the major mechanism for COD removal was biological oxidation in this case.

Variations of percent COD removal with time in fed-batch operation when zeolite is 0.25 g/L is presented in Figure 3.6.21. Percent COD removals in adsorption experiment was nearly 6%; whereas, nearly 74% and 74% COD removals were obtained with the biological treatment (B) and adsorptive biological treatment (AB), respectively at the end of operation. COD removals in the control experiment were assumed to be zero by definition. Again, due to low activated carbon concentration the difference in COD removal performances of the biodegradation (B) and adsorption-biodegradation (AB) experiments was negligible.

Variation of wastewater volume with time is shown in Figure 3.6.22. Starting from a 3.0 L of initial volume, wastewater volume in the tank increased with time linearly as expected.

In Figure 3.6.23. variation of total amount of biomass with time is presented. Total amount of biomass increased with time linearly because of increasing reactor volume with time.

Variation of COD removal rate with COD loading rate is depicted in Figure 3.6.24. COD removal rate decreased with increasing COD loading rate.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.60 gX/gS for 0.25 g/L zeolite concentration.

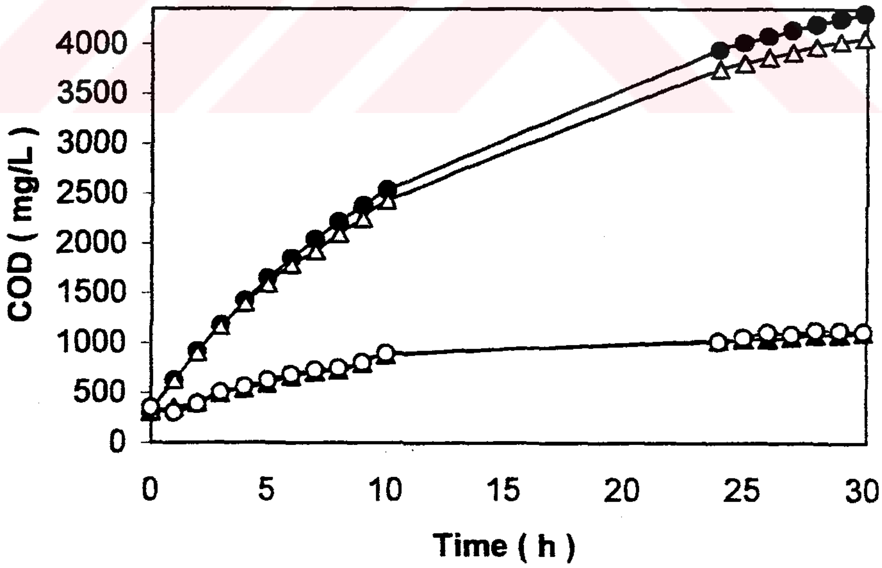

Figure 3.6.20. Variations of COD with time in fed-batch operation (0.25 g/L Zeolite)

● control (C), Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

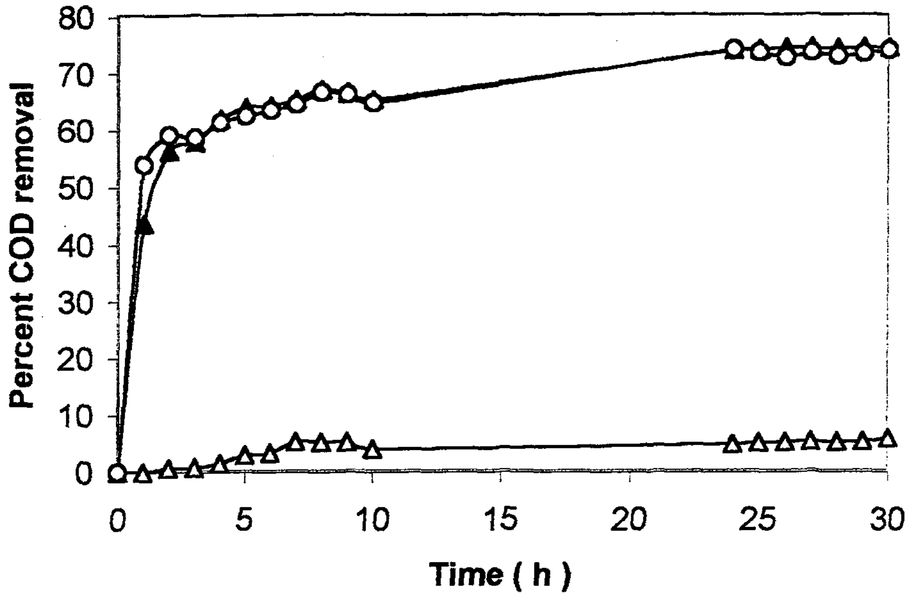

Figure 3.6.21. Variations of percent COD removal with time in fed-batch operation (0.25 g/L Zeolite) Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment(AB).

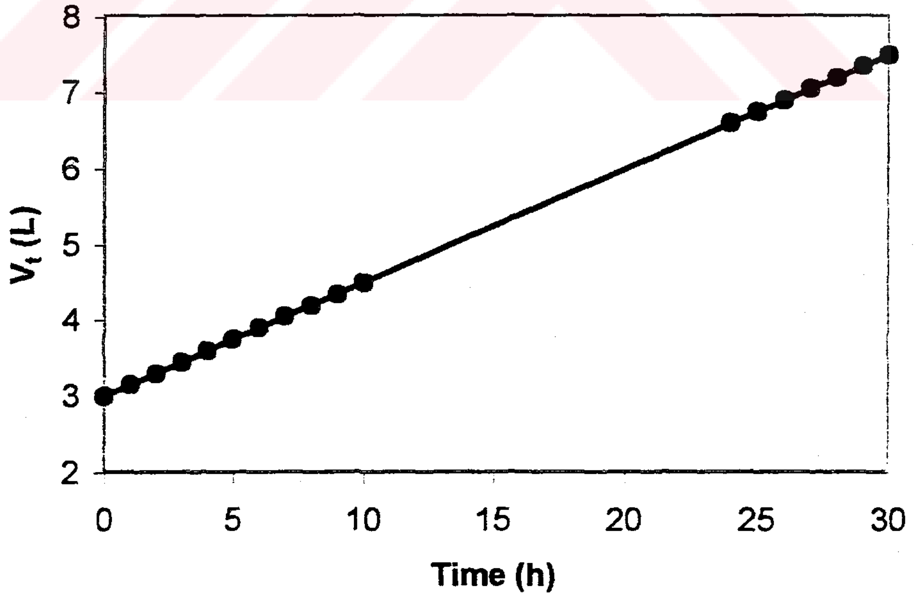

Figure 3.6.22. Variation of reactor volume with time (0.25 g/L Zeolite)

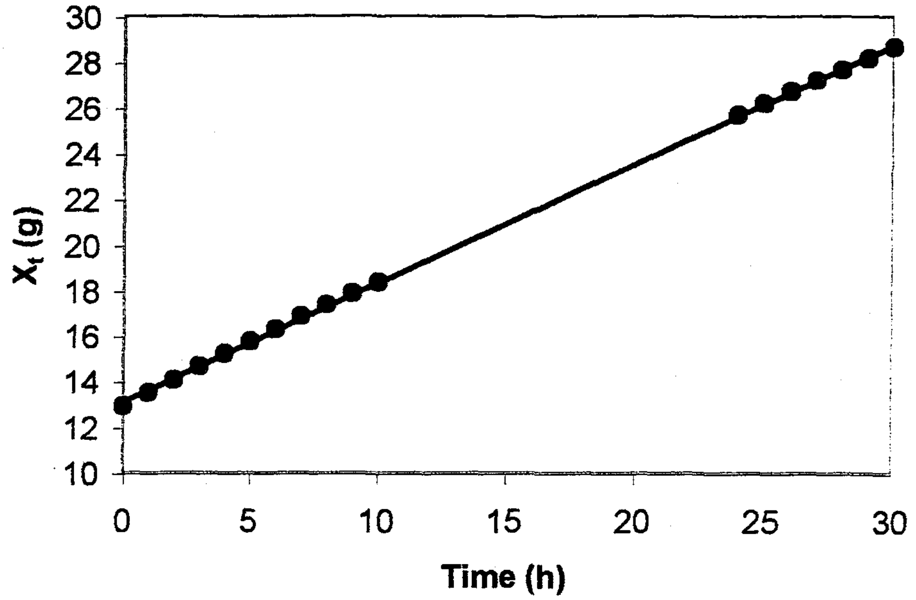

Figure 3.6.23. Variations of total amount of biomass with time (0.25 g/L Zeolite)

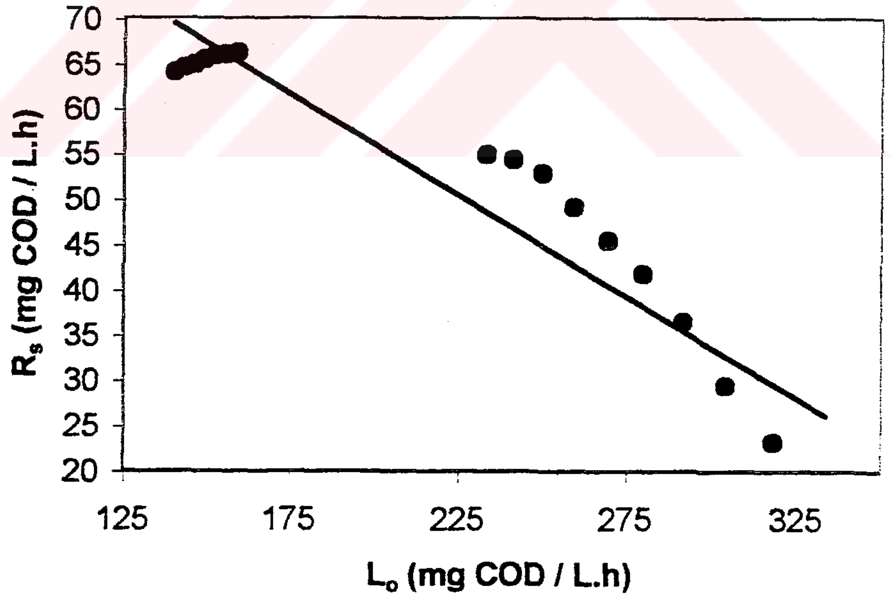

Figure 3.6.24. Variations of COD removal rate with COD loading rate (0.25 g/L Zeolite)

In Figure 3.6.25 variation of COD concentration with time for the zeolite concentration of 0.50 g/L is depicted. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4340 mg/L at the end of 30 h operation period. Similar trend was observed in the adsorption experiment (Δ) where COD in the aeration tank increased steadily with time. However, COD levels were lower than those of the control experiments because of COD removal by adsorption resulting in a COD content of nearly 3905 mg/L at the end of 30 h of operation. COD profiles in biological oxidation (B) and adsorbent added biological treatment (AB) showed a similar trend, slightly increasing within the first 10 hours and levelling off afterwards. The final COD contents in those experiments were nearly 1110 mg/L for only biological treatment (B) and 1065 mg/L for adsorptive biological treatment (AB). Because of low zeolite concentration (0.50 g/L), adsorption was not significant and the major mechanism for COD removal was biological oxidation in this case.

Variation of percent COD removal with time in fed-batch operation when zeolite is 0.50 g/L is presented in Figure 3.6.26. Percent COD removals in adsorption experiment was nearly 10%; whereas, nearly 74% and 75% COD removals were obtained with the biological treatment (B) and adsorptive biological treatment (AB), respectively at the end of operation. COD removals in the control experiment were assumed to be zero by definition. Again, due to low (0.5 g/L) zeolite concentration the difference in COD removal performances of the biodegradation (B) and adsorption-biodegradation (AB) experiments was negligible.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.57 gX/gS for 0.50 g/L zeolite concentration.

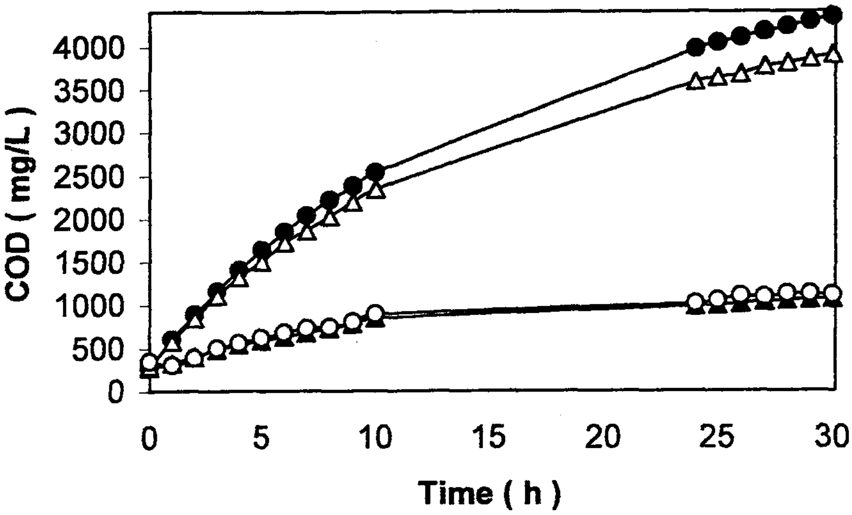

Figure 3.6.25. Variation of COD concentration with time in fed-batch operation (0.50 g/L Zeolite)● control (C), Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

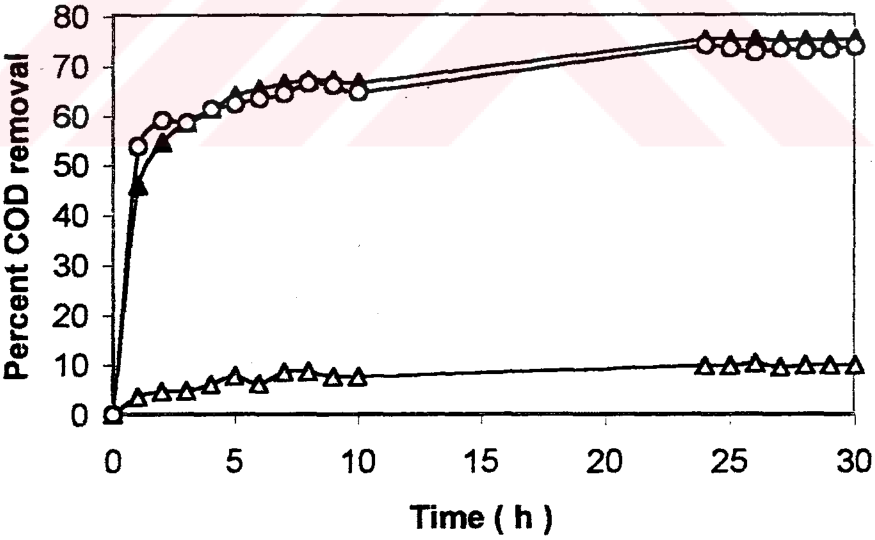

Figure 3.6.26. Variation of percent COD removal with time in fed-batch operation (0.50 g/L Zeolite) Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

Figure 3.6.27 depicts variations of COD concentrations with time for the four simultaneous experiments when the zeolite concentration was 1 g/L. Similar trends were observed in these experiments. Effluent COD' s at the end of 30 hours of fed-batch operation were 4300 mg/L, 3725 mg/L, 1100 mg/L and 1040 mg/L for the control (C), adsorption (A), biodegradation (B) and adsorption-biodegradation (AB) experiments, respectively. Despite a relatively high concentration of zeolite (1 g/L), the effluent COD was reduced from 1100 mg/L (B) to 1040 mg/L (AB) at the end of operation.

Percent COD removals with time are shown in Figure 3.6.28. COD removal for only adsorption (Δ) was nearly 14%. However, COD removals of 74% and 76% were obtained with biodegradation (o) and adsorption -biodegradation (▲) experiments, respectively at the end of 30 h operation

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.59 gX/gS for 1.0 g/L zeolite concentration.

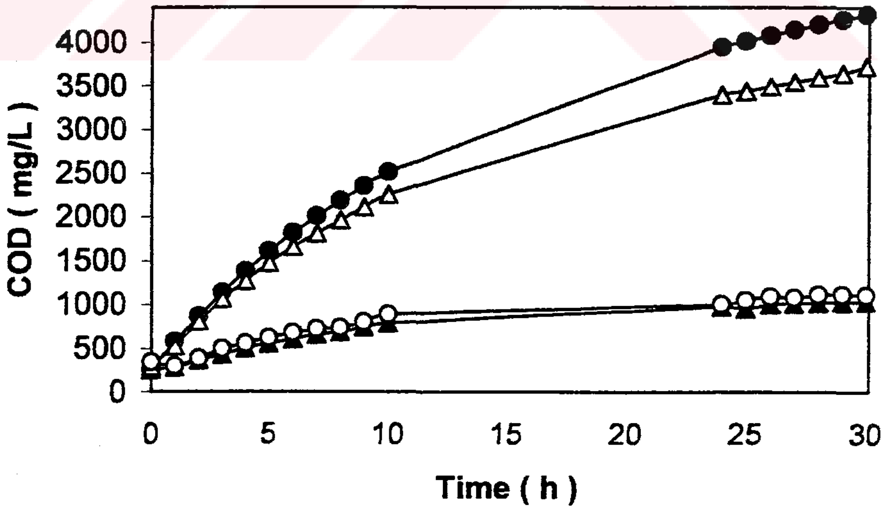

Figure 3.6.27. Variations of COD with time in fed-batch operation (1.0 g/L zeolite)

● control (C). Δ adsorption (A). ○ biological treatment (B).

▲ adsorption and biological treatment (AB).

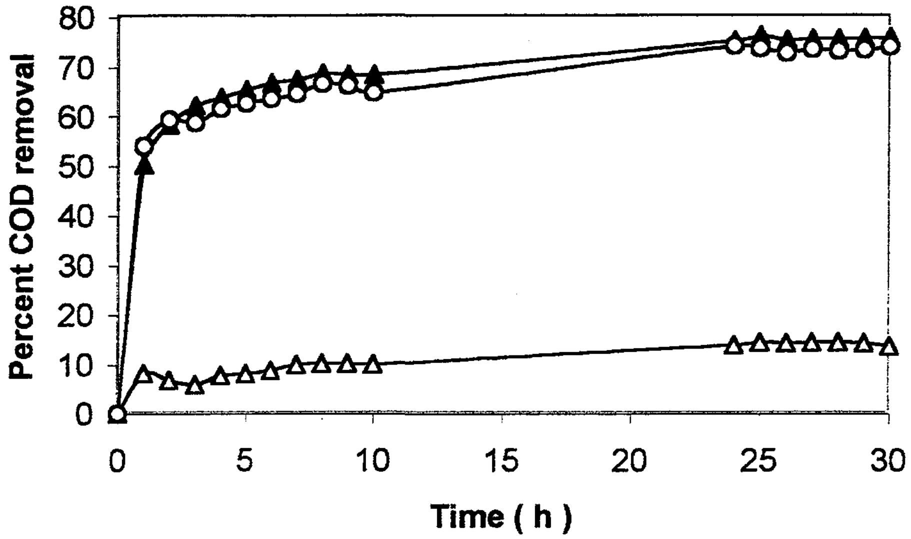

Figure 3.6.28. Variation of percent COD removal with time in fed-batch operation (1.0 g/L zeolite) Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

Figure 3.6.29 depicts variations of COD concentrations with time for the four simultaneous experiments when the zeolite concentration was 2 g/L. Similar trends were observed in these experiments. Effluent COD' s at the end of 30 hours of fed-batch operation were 4300 mg/L, 3575 mg/L, 1100 mg/L and 1010 mg/L for the control (C), adsorption (A), biodegradation (B) and adsorption-biodegradation (AB) experiments, respectively. In spite of high concentration of zeolite (2 g/L), the effluent COD was reduced from 1100 mg/L (B) to 1010 mg/L (AB) at the end of operation.

Percent COD removals with time are shown in Figure 3.6.30. Percent COD removal also increased insignificantly by addition of 2 g/L zeolite to the biological treatment tank. COD removal for only adsorption (Δ) was nearly 17%. COD removals of 74% and 76% were obtained with biodegradation (○) and adsorption-biodegradation (▲) experiments, respectively at the end of 30 h operation

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.60 gX/gS for 2.0 g/L zeolite concentration.

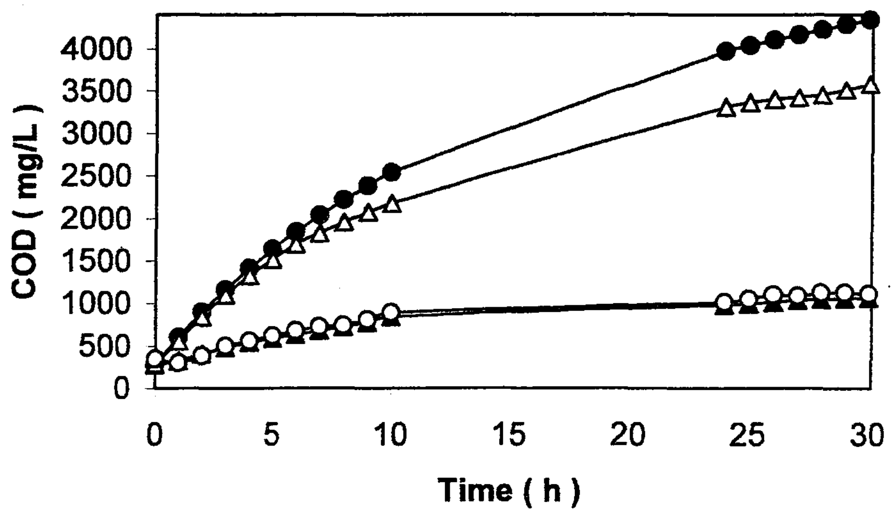

Figure 3.6.29. Variation of COD with time in fed-batch operation (2.0 g/L zeolite)

● control (C), Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

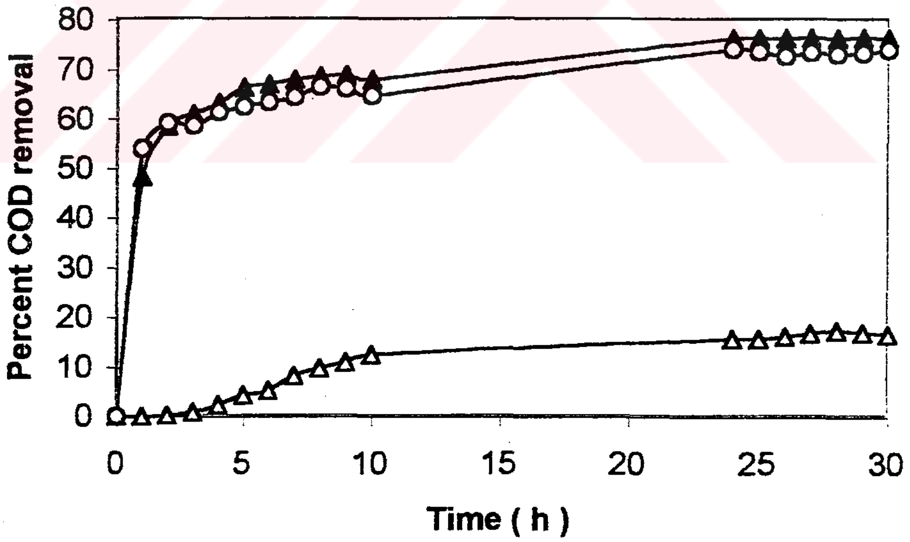

Figure 3.6.30. Variation of percent COD removal with time in fed-batch operation (2.0 g/L zeolite) Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

Percent COD removals were not affected significantly by zeolite addition even at higher zeolite concentrations. Figure 3.6.31 depicts variations of COD contents with time for 3 g/L zeolite concentration. Effluent COD contents for the control and the adsorption experiments were 4300 mg/L and 3500 mg/L, respectively. Effluent COD's were nearly 1100 mg/L and 1005 mg/L for the biodegradation (B) and adsorption-biodegradation (AB) experiments.

In Figure 3.6.32 variation of percent COD removal with time is presented. Similar trends were observed in COD removal efficiencies. Nearly 18% COD was removed by only adsorption (Δ), percent COD removals were 74% and 77% for biodegradation (B) and adsorptive-biodegradation (AB), respectively. Again, percent COD removal was zero for the control experiment.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.57 gX/gS for 3.0 g/L zeolite concentration.

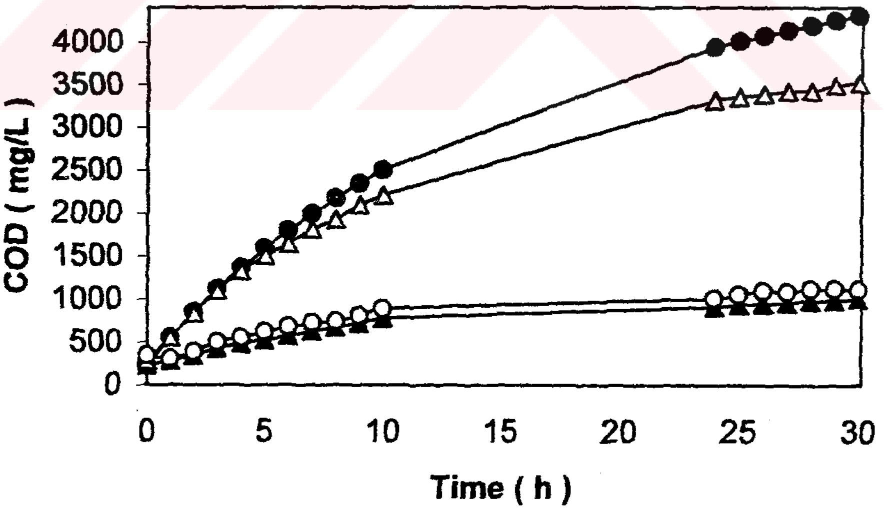

Figure 3.6.31. Variation of COD with time in fed-batch operation (3.0 g/L zeolite)

● control (C), Δ adsorption (A), ○ biological treatment (B),

▲ adsorption and biological treatment (AB).

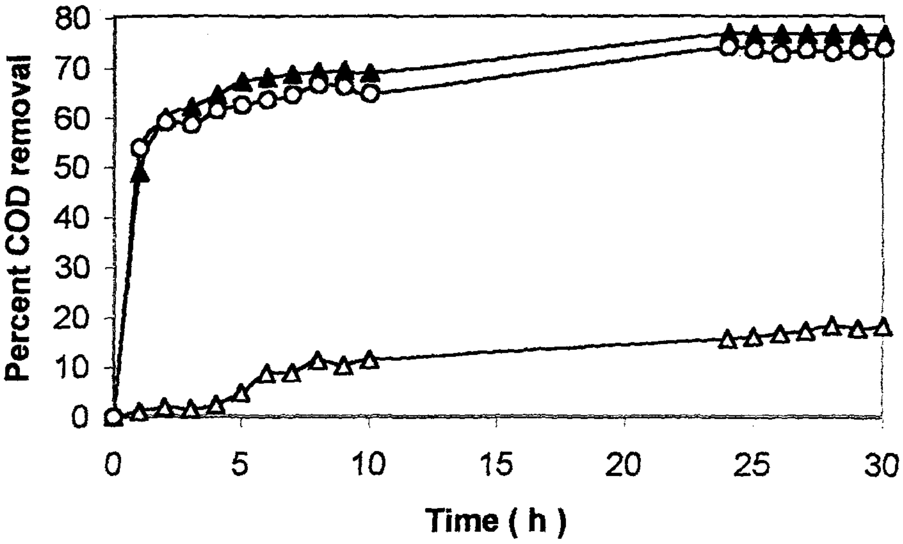

Figure 3.6.32. Variation of percent COD removal with time in fed-batch operation (3.0 g/L zeolite) Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

Figure 3.6.33 depicts variation of COD contents with time for 5 g/L zeolite concentration. Effluent COD contents for the control and the adsorption experiments were 4300 mg/L and 3550 mg/L, respectively. Effluent COD's were nearly 1100 mg/L and 995 mg/L for the biodegradation (B) and adsorption-biodegradation (AB) experiments.

Variation of percent COD removal with time is presented in Figure 3.6.34. Similar trends were observed in COD removal efficiencies. Nearly 18% COD was removed by only adsorption (Δ), percent COD removals were 74% and 77% for biodegradation (B) and adsorptive-biodegradation (AB), respectively. Again, percent COD removal was zero for the control experiment.

The growth yield coefficient for microbial culture was found to be $Y_{X/S}$=0.56 gX/gS for 5.0 g/L zeolite concentration.

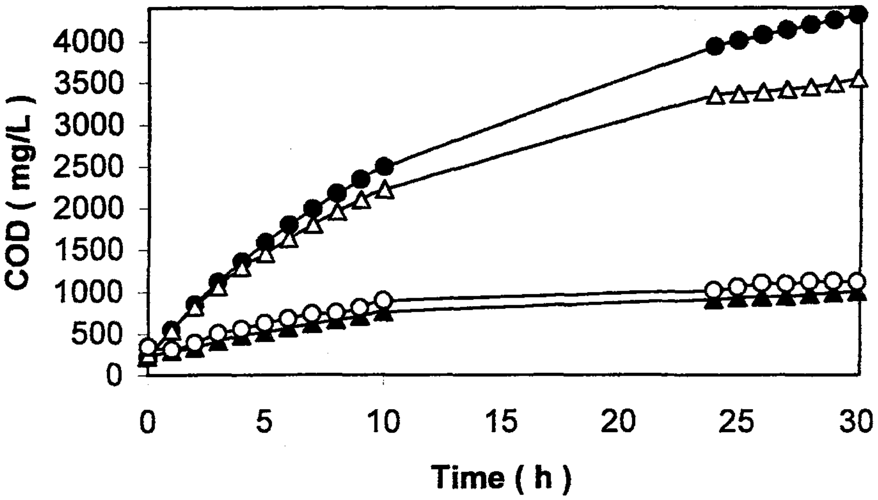

Figure 3.6.33 Variation of COD with time in fed-batch operation (5.0 g/L zeolite)
● control (C), Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

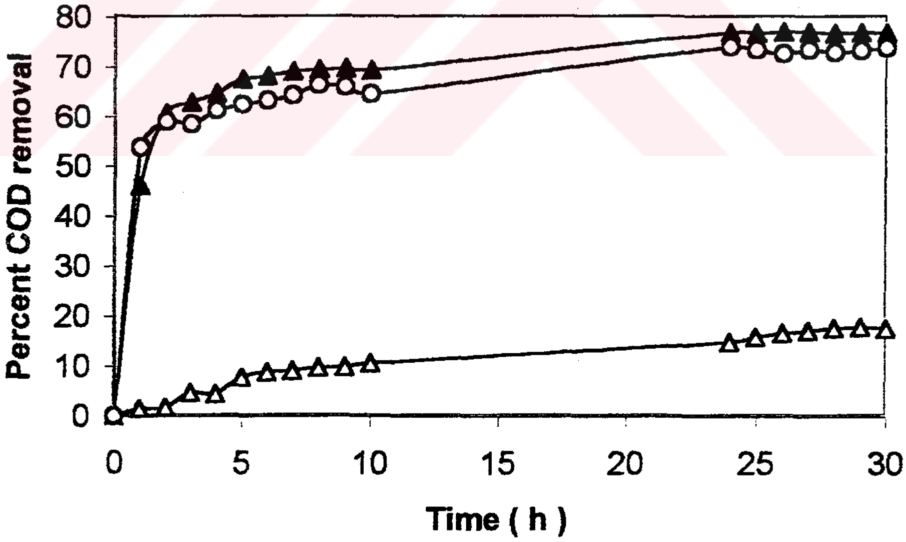

Figure 3.6.34. Variation of percent COD removal with time in fed-batch operation (5.0 g/L zeolite) Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

Collected results of effluent COD contents and percent COD removals at the end of 30 h operation with different zeolite concentrations (0-5 g/L) are depicted in Figure 3.6.35. Effluent COD decreased and percent COD removal increased with the increasing zeolite concentration for both adsorption (A) and adsorption-biodegradation (AB) experiments. Effluent COD of nearly 3550 mg/L was obtained with only adsorption corresponding nearly 18% COD removal with 5 g/L zeolite addition. However, the effluent COD for adsorption-biodegradation (AB) experiment was nearly 995 mg/L corresponding to 77% COD removal under the same conditions. COD removal efficiencies did not increase significantly, when the zeolite concentration increased up to 5 g/L.

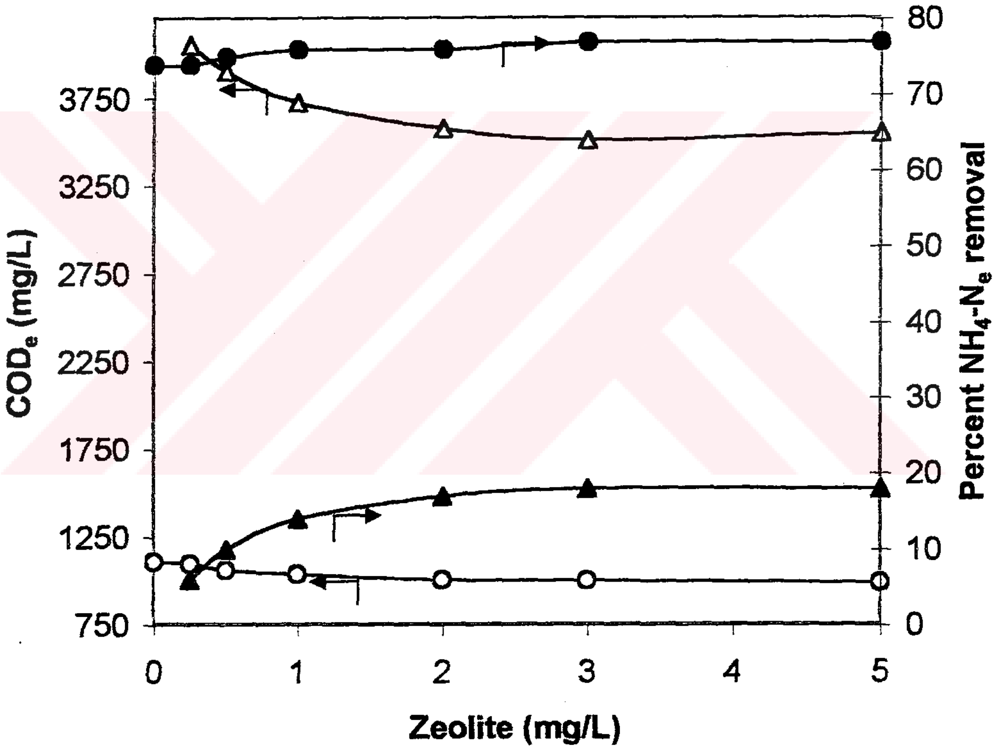

Figure 3.6.35. Variations of the effluent COD and percent COD removals at the end of 30 h fed-batch operation with the adsorbent (Z) concentration

Δ, ▲ adsorption (A); ○, ● adsorption and biological treatment (AB)

Variations of the effluent NH_4-N and percent NH_4-N removals at the end of 30 h fed-batch operation with the adsorbent (zeolite) concentration are shown in Figure 3.6.36. Again, percent NH_4-N removal increased with increasing zeolite concentration in both adsorptive biological treatment (AB) and only adsorption (A) experiments. In zeolite added biotreatment experiments, 34% and 40% NH_4-N removals were obtained with 2 g/L and 5 g/L PAC, respectively. Ammonium-N removal in adsorption experiments (A) were considerably lower than those of the zeolite added biological treatment (AB) resulting in only 21% and 28% NH_4-N removals with 2 g/L and 5g/L zeolite, respectively.

Adsorption capacity of zeolite for COD was lower than that of the PAC. However, zeolite was proven to be a better adsorbent for NH_4-N removal as compared to PAC. Considering the low adsorption capacity of zeolite for COD removal, this adsorbent was not used in future experiments.

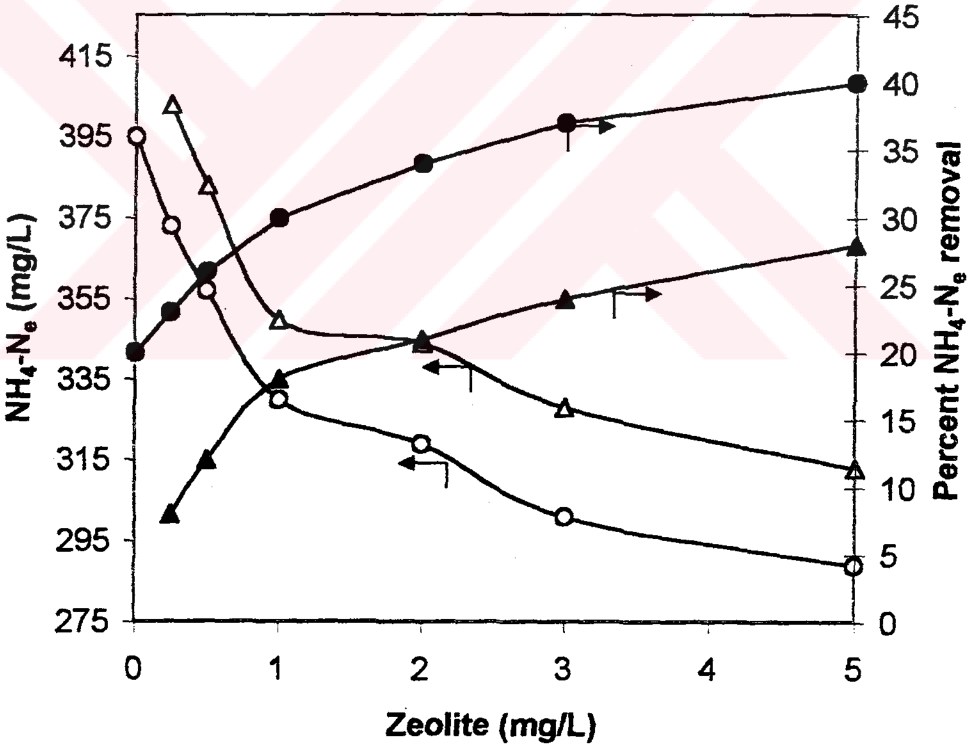

Figure 3.6.36. Variations of the effluent NH_4-N and percent NH_4-N removals at the end of 30 h fed-batch operation with the adsorbent (Z) concentration.

△, ▲ adsorption (A); ○, ● adsorption and biological treatment (AB)

3.6.4. Kinetic Analysis and Determination of Kinetic Constants

An empirical model was developed to quantify the effect of adsorbent addition onto the biological treatment process. The empirical equation has the following form,

$$E_{AB} - E_B = a\,(Z)^b \qquad (3.6.5.)$$

where E_{AB} and E_B are percent COD removals at the end of 30 hour operation, for zeolite-added biological treatment (AB) and zeolite-free biological treatment (B), respectively; Z is the concentration of zeolite added (g/L) ; a and b are empirical constants.

In logarithmic form, eqn 3.6.5 becomes,

$$\mathrm{Ln}\,(E_{AB} - E_B) = \mathrm{Ln}\,a + b\,\mathrm{Ln}\,(Z) \qquad (3.6.6.)$$

A plot of Ln (E_{AB} –E_B) versus Ln (Z) would yield a line with a slope of (b) and an intercept of Ln a.

Experimental data for percent COD removal obtained at the end of 30 hours of fed-batch operation with different zeolite concentrations (data in Figure 3.6.37) were plotted in form of Ln (E_{AB} – E_B) versus Ln (Z) in Figure 3.6.40. From the slope and the intercept of the best-fit line the following values were obtained for (a) and (b).

$$a = 0.0496 \quad \text{and} \quad b = 0.58 \qquad (r^2 = 0.91)$$

Therefore, eqn 3.6.5 for COD removal efficiency in the presence of zeolite takes the following form,

$$E_{AB} - E_B = 0.0496\,(Z)^{0.58} \qquad (3.6.7.)$$

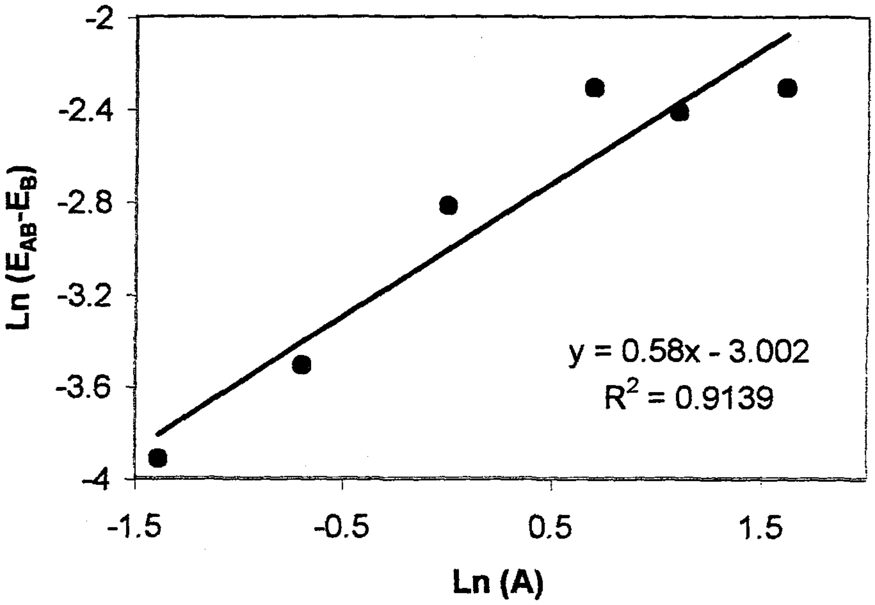

Figure 3.6.37. A plot of Ln (E_{AB}-E_B) versus Ln (Z) for determination of the constants of the empirical equation for COD removal.

Experimental data for percent NH_4-N removal obtained at the end of 30 hours of fed-batch operation with different zeolite concentrations (data in Figure 3.6.38) were plotted in form of Ln ($E_{AB} - E_B$) versus Ln (Z) in Figure 3.6.41. From the slope and the intercept of the best-fit line the following values were obtained for (a) and (b).

$$a' = 0.0849 \quad \text{and} \quad b' = 0.6244 \qquad (r^2 = 0.96)$$

Therefore, eqn 3.6.5 for ammonium-N removal efficiency in the presence of zeolite takes the following form,

$$E_{AB} - E_B = 0.0849\,(Z)^{0.6244} \qquad (3.6.8.)$$

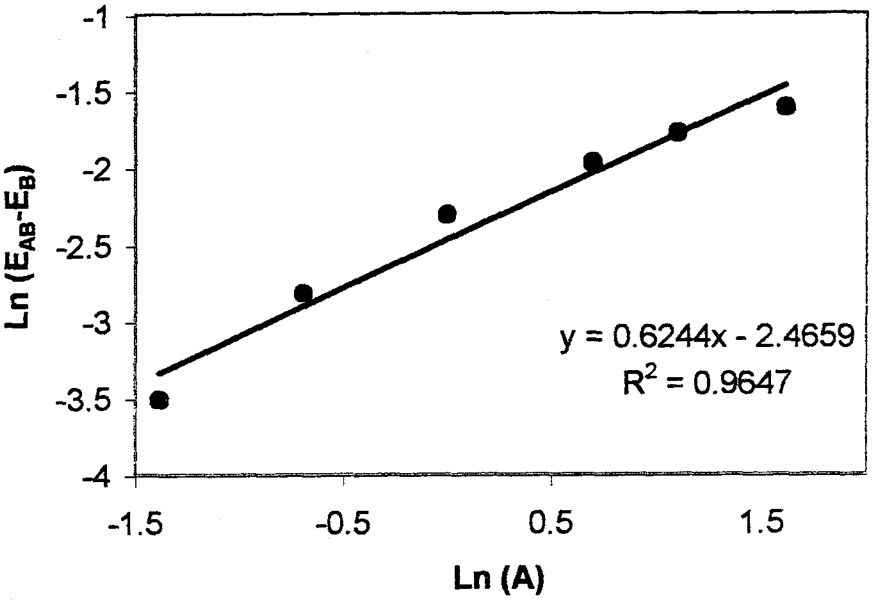

Figure 3.6.38. A plot of Ln (E_{AB}-E_B) versus Ln (Z) for determination of the constants of the empirical equation for NH_4-N removal.

3.6.5. Comparison of Zeolite(Z) and Powdered Activated Carbon (PAC) Added Biological Treatment

Time course of COD concentrations in the aeration tank operated in fed-batch mode are depicted in Figure 3.6.39 for both PAC and zeolite when the adsorbent concentration was 2 g/L in adsorbent added biological treatment (AB). Percent COD removals increased with time for the first 10 hours of operation and remained nearly constant for both adsorbents. COD content in the control experiment increased steadily with time due to accumulation of COD in the absence of any adsorbents and organisms. Percent COD removal in the control experiment was considered to be zero and COD removals in other experiments were based on the COD content of the control experiment. Percent COD removals at the end of 30 hours of operation were 86% and 76% resulting in final COD contents of 610 mg/L and 1010 mg/L for the PAC and zeolite, respectively. Effluent COD contents increased with time for both adsorbents, since COD loading rate was much higher than COD removal rates by adsorption and biological treatment. However, the increases in COD in the experimental tanks were much lower than those obtained in the control tank, indicating effective removal of COD by adsorption and biological oxidation. COD removal with the PAC as adsorbent was much better than zeolite in adsorbent added biological oxidation as clearly shown in Figure 3.6.41.

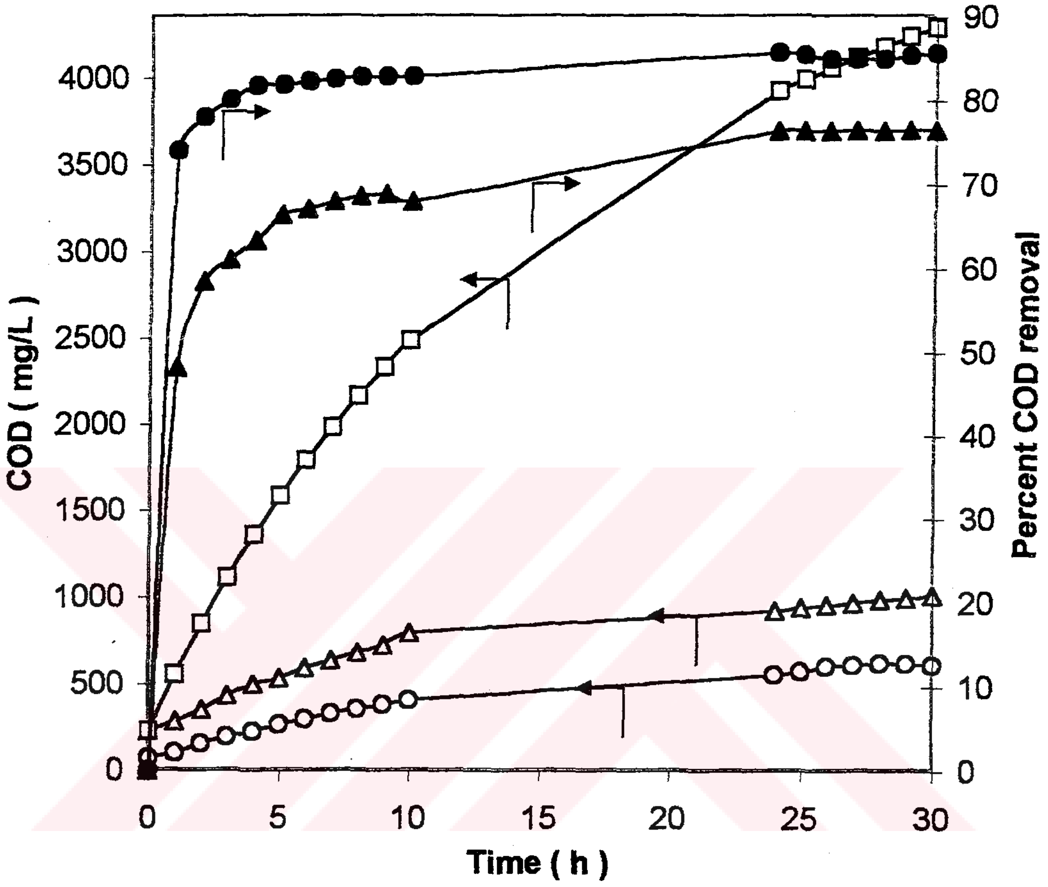

Figure 3.6.39. Variations of percent COD removal and the effluent COD with time in adsorbent added biological treatment of pre-treated landfill leachate by fed-batch operation, (A)= 2 g/L.

□ Control ; ○ ● PAC ; Δ ▲ Zeolite.

Effluent COD contents and percent COD removals are presented in Figure 3.6.40 and 3.6.41 for adsorption (A) and adsorbent added biological treatment (AB) with PAC and zeolite at the end of 30 hours of fed-batch operation. Adsorbent concentrations were varied between 1g/L and 5 g/L. COD removal in the control experiment was considered to be zero and all percent removals were based upon control experiment COD values ($E = 1 - S / S_c$).

Figure 3.6.40 depicts variation of effluent COD and percent COD removal with adsorbent concentrations at the end of 30 h of operation for only adsorption (A) without biological treatment. Percent COD removals increased and the final COD contents decreased with increasing adsorbent concentration for both PAC and zeolite. Nearly, 49% and 18% COD removals resulting in 2180 mg/L and 3550 mg/L final COD concentrations were obtained with 5 g/L PAC and zeolite, respectively at the end of 30 hours operation. Obviously, PAC has performed much better than zeolite as an adsorbent for the removal of COD by adsorption. Variations of effluent COD contents and percent COD removals for adsorbent added biological treatment (AB) are depicted in Figure 3.6.41. Similar to Figure 3.6.40, percent COD removals increased and final COD contents decreased with increasing adsorbent concentration. Nearly, 87% and 77% COD removals with the final COD contents of 540 mg/L and 1000 mg/L were obtained with PAC and zeolite concentrations of above 2 g/L, respectively. Since the adsorbent concentrations above 2 g/L did not improve COD removals significantly for both adsorbents, adsorbent concentration of 2 g/L is recommended for practical use.

It is quite clear from the comparison of Figure 3.6.40 and 3.6.41. that, adsorbent added biological treatment (AB) is superior to adsorption (A) and biological treatment (B) alone, in terms of COD removal from the leachate.

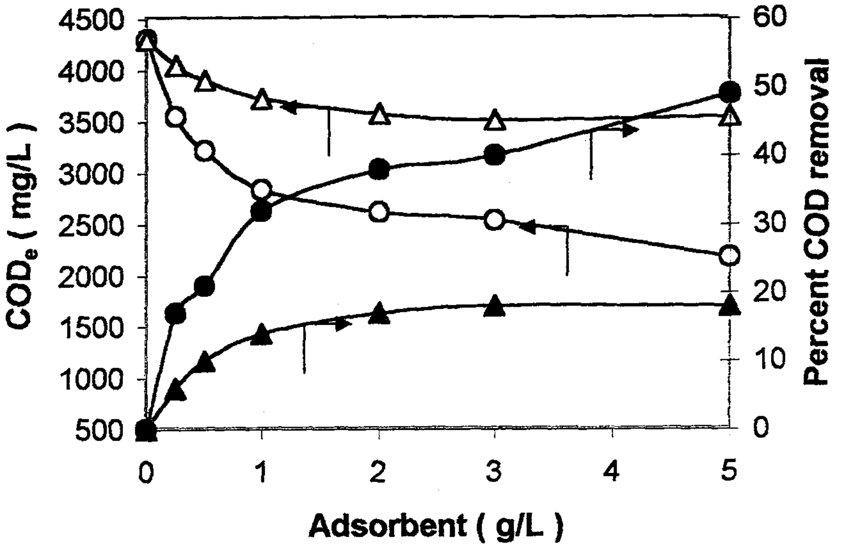

Figure 3.6.40. Variation of the effluent COD at the end of 30 h operation with the adsorbent concentration for only adsorption experiments (A)
○ ● PAC ; Δ ▲ Zeolite.

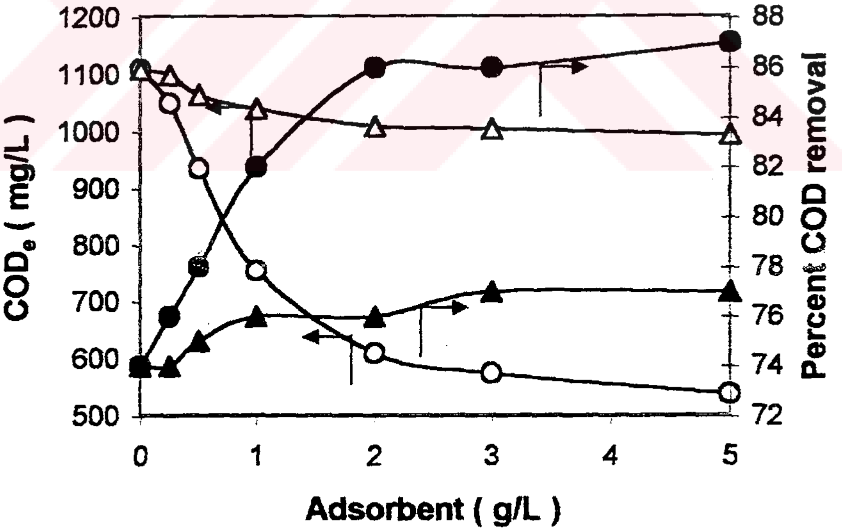

Figure 3.6.41. Variation of percent COD removal at the end of 30 h operation with the adsorbent concentration for adsorbent added biological treatment (AB) ○ ● PAC ; Δ ▲ Zeolite.

Since the ammonium-N content of the leachate was prohibitively high, removal of NH_4-N was also considered as another criterion in comparing PAC with zeolite as adsorbent. Figure 3.6.42 and 3.6.43 depict variations of NH_4-N removal efficiencies and final NH_4-N contents with the adsorbent concentrations at the end of 30 h of fed-batch operation.

Figure 3.6.42 depicts variations of final NH_4-N content and NH_4-N removal efficiency with adsorbent (PAC and zeolite) concentrations for only adsorption (A) without any biological treatment. Percent ammonium-N removals increased and final NH_4-N contents decreased with increasing adsorbent concentrations for both zeolite and PAC. Zeolite has performed significantly better than PAC for ammonium-N removal because of its high capacity for ammonium ion adsorption. Nearly 28% and 16% NH_4-N removals were obtained with the final NH_4-N concentrations of 310 mg/L and 370 mg/L with 5 g/L zeolite and PAC, respectively at the end of 30 hours operation. Variations of percent NH_4-N removal and the effluent NH_4-N contents with the adsorbent concentrations are depicted in Figure 3.6.43. for adsorbent added biological treatment (AB). Similar to Figure 3.6.42., percent NH_4-N removals obtained with zeolite are much better than those obtained with the PAC. Percent NH_4-N removals increased and the final NH_4-N contents decreased with increasing adsorbent concentrations. Nearly, 40% and 30% NH_4-N removals with final NH_4-N concentrations of 290 mg/L and 340 mg/L were obtained with 5 g/L zeolite and PAC concentrations, respectively at the end of 30 h fed-batch operation.

Again adsorbent added biological treatment (AB) resulted in much higher percent NH_4-N removals as compared to adsorption (A) alone, no matter what kind of adsorbent was used. Percent NH_4-N removal increased from 28% for only by adsorption to 40% for adsorbent added biological treatment with zeolite as adsorbent, whereas this increase was from 16% to 30% when PAC was used.

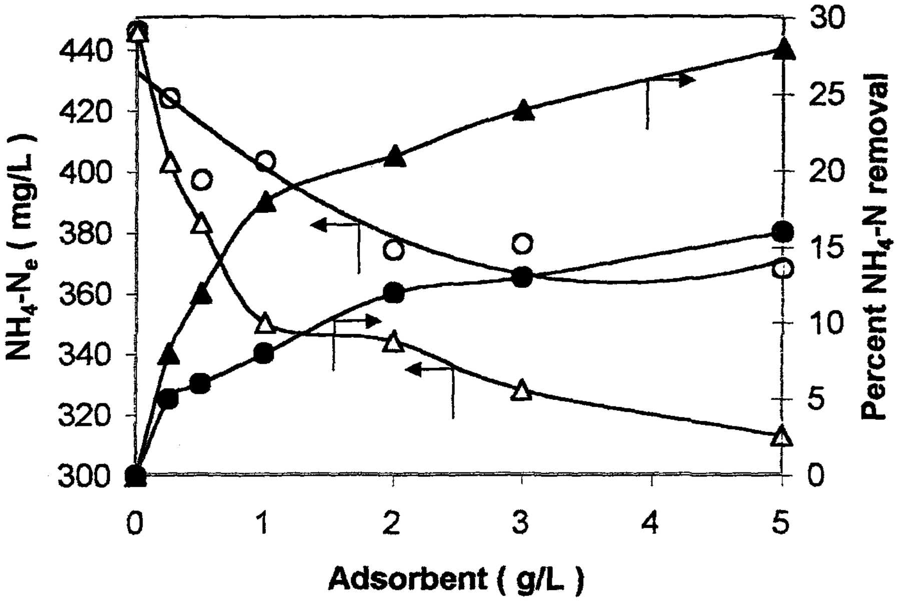

Figure 3.6.42. Variation of the effluent NH_4-N at the end of 30h operation with the adsorbent concentration for only adsorption(A)

○ ● PAC ; Δ ▲ Zeolite.

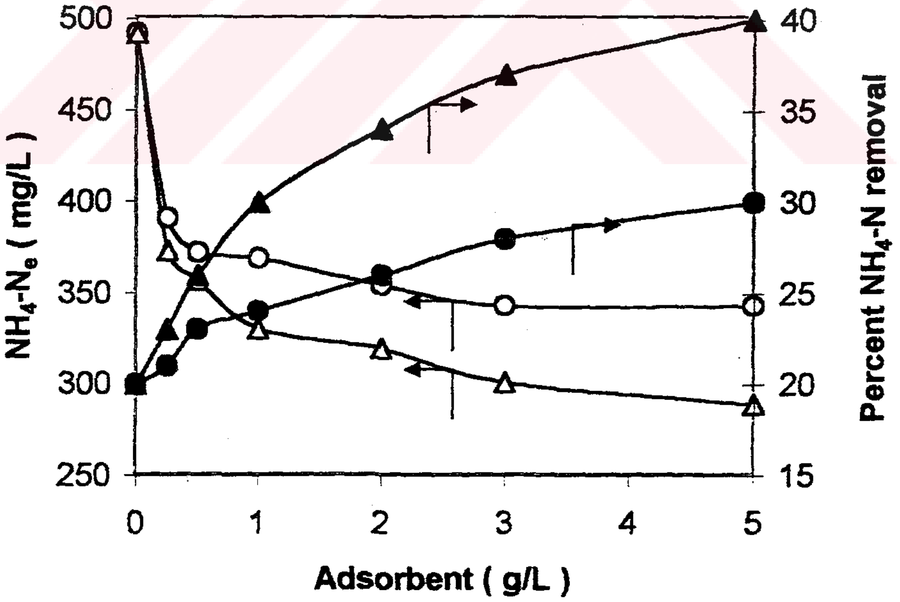

Figure 3.6.43. Variation of percent ammonium-N removal at the end of 30h operation with the adsorbent concentration for adsorbent added biological treatment (AB).

○,● PAC ; Δ ,▲ Zeolite.

In addition to these experiments, to observe effect of COD and NH_4-N removals, PAC and zeolite were used together in Fed-Batch biological treatment operation mode. PAC and zeolite concentration were kept 1 g/L through the operation time. Figure 3.6.44 depict variations of COD contents with time for 1 g/L PAC and 1 g/L zeolite concentrations. Effluent COD contents for the control and the adsorption experiments were 4300 mg/L and 3300 mg/L, respectively. Whereas, effluent COD's were nearly 1100 mg/L and 992 mg/L for the biodegradation (B) and adsorption-biodegradation (AB) experiments.

Variation of percent COD removal with time is presented in Figure 3.6.45. Similar trends were observed in COD removal efficiencies. Nearly 23% COD was removed by only adsorption (Δ); whereas percent COD removals were 74% and 79% for biodegradation (B) and adsorptive-biodegradation (AB), respectively. Again, percent COD removal was zero for the control experiment.

Effluent NH_4-N concentration and ammonium nitrogen removal were nearly 336 mg/L and 27%, respectively

When PAC and zeolite were used together, significant COD and NH_4-N removals were not achieved.

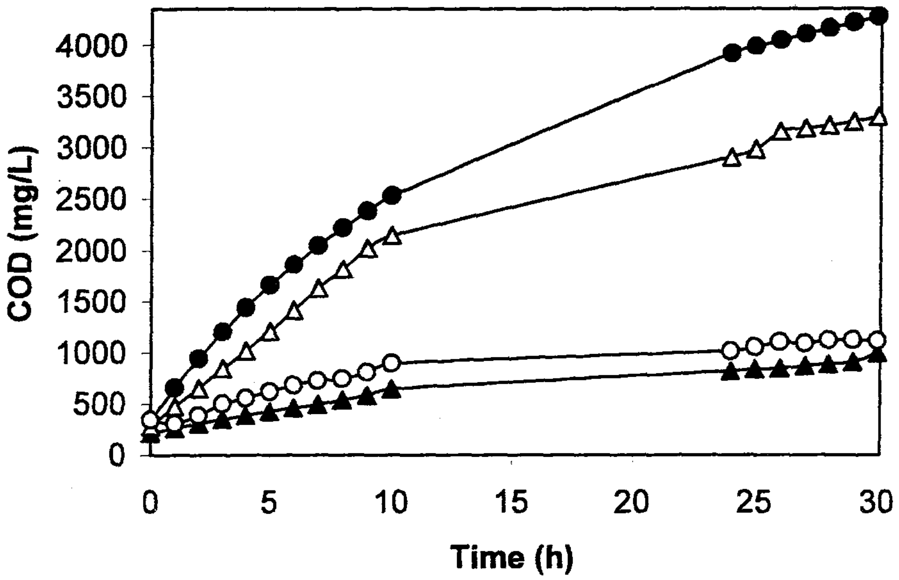

Figure 3.6.44. Variation of COD with time in fed-batch operation (1.0 g/L PAC + 1.0 g/L Zeolite)

● control (C), Δ adsorption (A), ○ biological treatment (B), ▲ adsorption and biological treatment (AB).

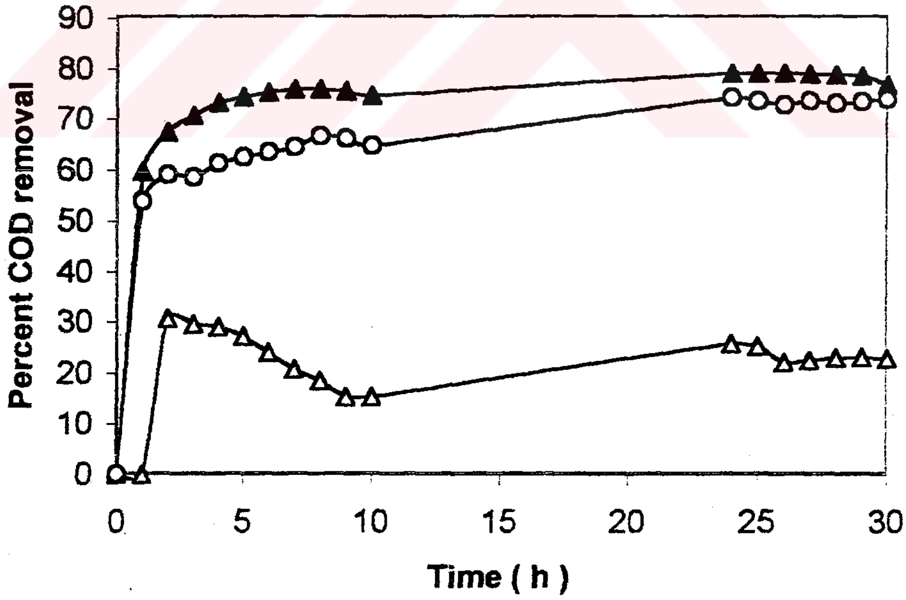

Figure 3.6.45. Variation of percent COD removal with time in fed-batch operation (1.0 g/L PAC + 1 g/L Zeolite)

Δ adsorption (A), ○ biological treatment (B),
▲ adsorption and biological treatment (AB).

3.7. Repeated Fed – Batch Experiments

The aim of these studies was to decrease effluent COD and ammonium concentrations. Two set of experiments were performed with and without PAC addition with different cycle times, but the same total operation time of 30 h (3x10 h, 5x6 h) for the repeated fed-batch biological treatment of the pre-treated landfill leachate. In these experiments, the feed flow rate and COD content of the feed were kept constant at 0.15 L/h and 7,000 mg/L, respectively. C/N/P ratio in the feed wastewater was adjusted to 100/10/1.5. The feed wastewater ammonium concentration was nearly 700 mg/L. The initial COD content in the aeration tank was nearly 300 mg/L and the initial biomass concentration was 4200±200 mg biomass/L, on dry weight basis. Powdered activated carbon (PAC) concentration was constant at 2 g/L. Temperature and pH were 20 °C and pH = 8-8.5, throughout the experiments. Vigorous aeration was supplied to the aeration tank to keep the dissolved oxygen (DO) above 2 mg/L. Temperature, pH and DO were monitored and manually controlled during the experiments. A control experiment devoid of microorganisms was run in parallel to the biological treatment experiment for every experimental condition. Percent COD removals in control experiments were considered to be zero and COD content of the control experiments were used as the base in calculation of COD removal efficiencies.

3.7.1. Repeated Fed-Batch Biological treatment without PAC Addition

Time course of COD concentrations in the aeration tank operated in repeated fed-batch mode with different cycle times are depicted in Figure 3.7.1. COD content in the control experiment increased steadily with time due to accumulation of COD in the absence of any adsorbents and organisms.

When a single cycle with an operation time of 30 hours was used in fed-batch mode as used in previous experiments, effluent COD concentration of 1120 mg/L was obtained. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal in the single cycle fed-batch experiment of 30 h was 74% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentrations were 21% and 360 mg/L, respectively at the end of the 30 hours.

When the three-cycle operation with ten hours each was applied (3x10h) in repeated fed-batch mode, effluent COD concentration was reduced to 924 mg/L at the end of 30 hours of total operation time. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 78% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 21% and 360 mg/L, respectively at the end of the 30 hours.

Effluent COD concentration was reduced to 875 mg/L, when five cycle operation of 6 hours each (5x6h) was used in repeated fed-batch mode. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 79% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 10% and 410 mg/L, respectively at the end of the 30 hours. Effluent ammonium-N concentration was higher than the other operations because of accumulation of the ammonium-N in the aeration tank during repeated fed-batch operation.

In summary, when repeated fed-batch operation was used with cycle lengths of 3x10 hours and 5x6 hours, better COD removals were obtained as compared to single cycle fed-batch operation of 30 hours.

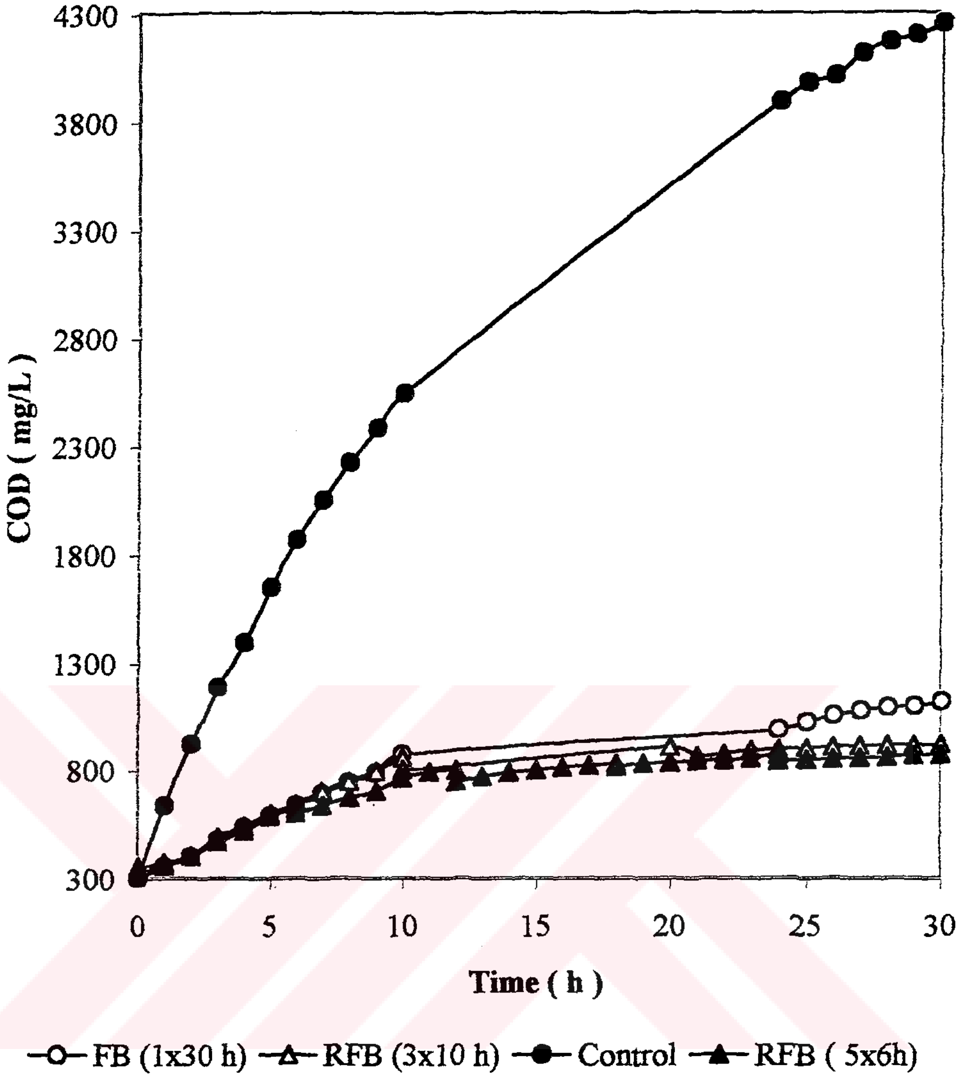

Figure 3.7.1.Variation of COD concentrations with time in the aeration tank operated in repeated fed-batch mode with different cycle lengths.

Variation of initial and final biomass concentrations with different cycle lengths in the aeration tank operated in repeated fed-batch mode are shown in Figure 3.7.2. As clearly seen from the figure, final biomass concentration increased from 5340 mg/L to 5750 mg/L when the cycle length was changed from 3x10 to 5x6 hours. Final biomass concentration in 1x30 h fed-batch operation was 3650 mg/L with initial biomass concentration of nearly 4200 mg/L in all experiments.

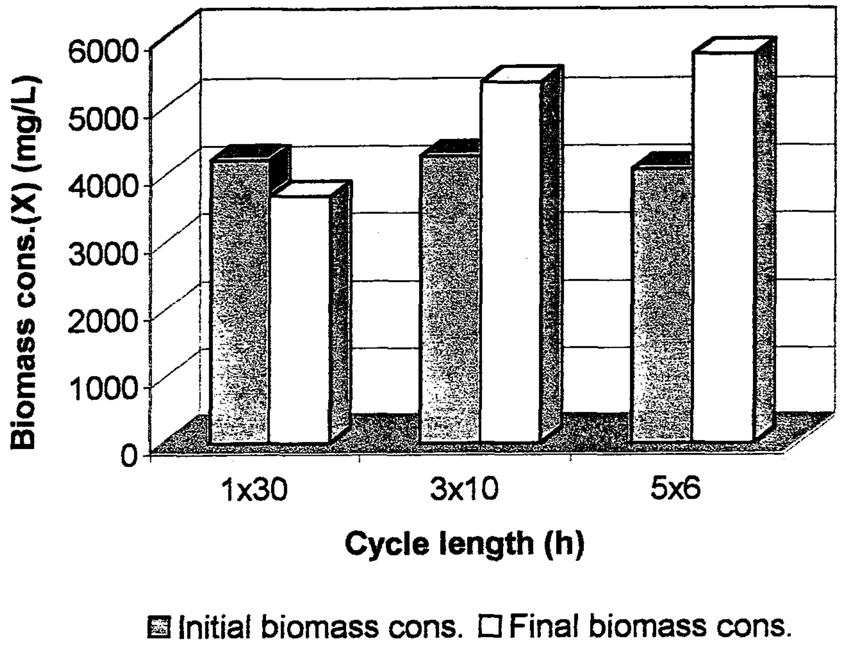

Figure 3.7.2. Variation of initial and final biomass concentration with different cycle lengths in the aeration tank operated in repeated fed-batch mode

3.7.2. Repeated Fed-Batch Biological treatment with PAC Addition

Variations of COD concentration with time in the aeration tank operated in repeated fed-batch mode with different cycle times and PC concentration of 2 g/L are depicted in Figure 3.7.3. COD content in the control experiment increased steadily with time due to accumulation of COD in the absence of any adsorbents and organisms.

When a single cycle operation with 30 hours of total operation period was used in fed-batch mode, the final COD contents in these experiments were nearly 2635 mg/L for only adsorption (A) and 632 mg/L for adsorptive biological treatment (AB). COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 85% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 25% and 352 mg/L, respectively at the end of the 30 hours.

When a three-cycle operation with10 hours each was used (3x10 h) in repeated fed-batch mode, the final COD contents were nearly 1710 mg/L for only adsorption (A) and 398 mg/L for adsorptive-biological treatment (AB). A significant decrease was observed in effluent COD concentration by using repeated fed-batch operation of 3x10 hours as compared to the single cycle operation of 30 hours. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 91% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 22% and 370 mg/L, respectively at the end of the 30 hours. Apparently, ammonium-N removal was not affected by the repeated fed-batch operation.

Effluent COD concentration was reduced to 365 mg/L, when the five-cycle operation of 6 hours each was used in repeated fed-batch operation. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was approximately 91.5% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 22% and 365 mg/L, respectively at the end of the 30 hours.

In summary, when the repeated fed-batch operation with 3x10 hours and 5x6 hours were used, better COD removals were obtained as compared to the single-cycle fed-batch operation of 30 hours duration in the presence of 2 g/L PAC. COD removal results of 3x10 h operation were not that different from that of the 5x6h operation. Therefore, a repeated fed-batch operation of 3x10 h (total 30 h) should be preferred to a single cycle operation of 30 h.

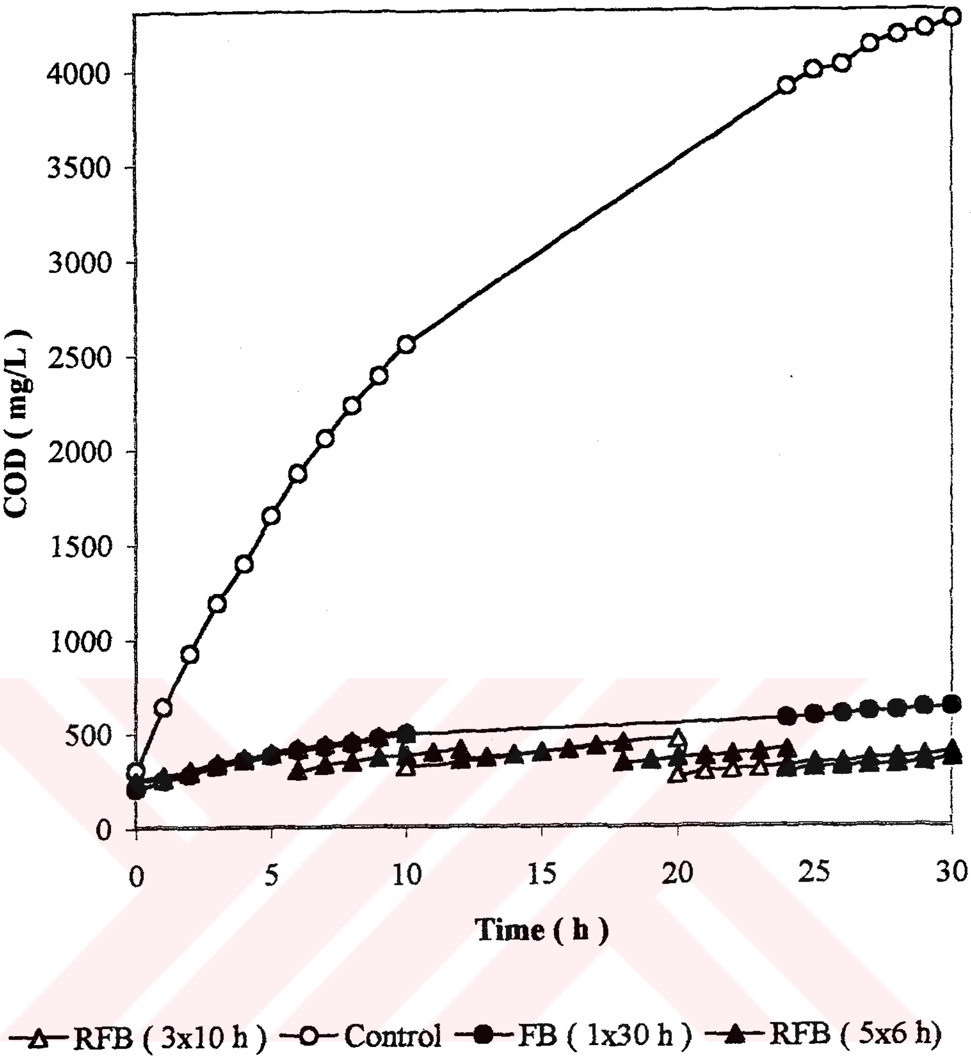

Figure 3.7.3.Variation of COD concentrations with time in the aeration tank operated in repeated fed-batch mode with different cycle times for2 g/L PAC.

Variation of initial and final biomass concentrations with different cycle lengths in repeated fed-batch operation are shown in Figure 3.7.4. As clearly seen from the figure, final biomass concentration increased from 5450 mg/L to 5700 mg/L when the cycle length was changed from 3x10h to 5x6 hours. Final biomass concentration in 1x30 h fed-batch operation was 3450 mg/L and the initial biomass concentrations were nearly 4200 mg/L in all experiments.

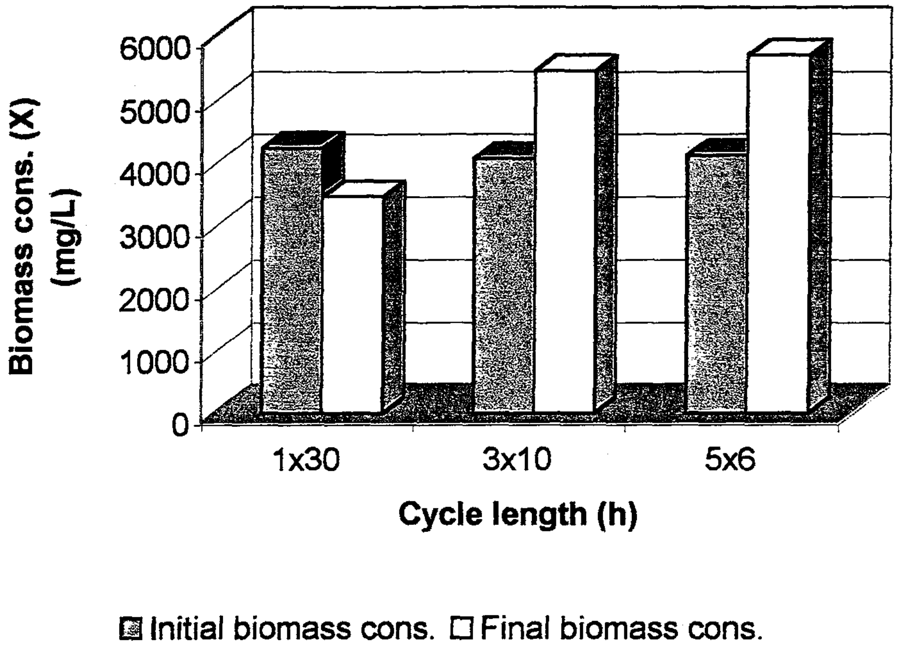

Figure 3.7.4. Variation of initial and final biomass concentration with different cycle lengths in the aeration tank operated in repeated fed-batch mode for 2 g/L PAC.

In addition to these experiments, to observe the system's performance at longer operation times, a three-cycle operation with 30 hours cycle length was used (3x30 h) in repeated fed-batch mode. The final COD contents were nearly 3440 mg/L for only adsorption (A) and 285 mg/L for adsorptive-biological treatment (AB). A significant decrease was observed in effluent COD concentration by using repeated fed-batch operation of 3x30 hours as compared to the five-cycle operation with 6 hours cycle length (5x6 h). Percent COD removals were 91.5% and 93.5% for 5x6 h and 3x30h operations. Percent ammonium-N removal and effluent ammonium concentration were 30% and 224 mg/L, respectively in 3x30 h repeated fed-batch experiment. Whereas, percent ammonium-N removal and effluent ammonium concentration were 22% and 365 mg/L, respectively in 5x6 h repeated fed-batch operation. Apparently, increasing the operation time of the repeated fed-batch treatment reduced final ammonium-N concentration.

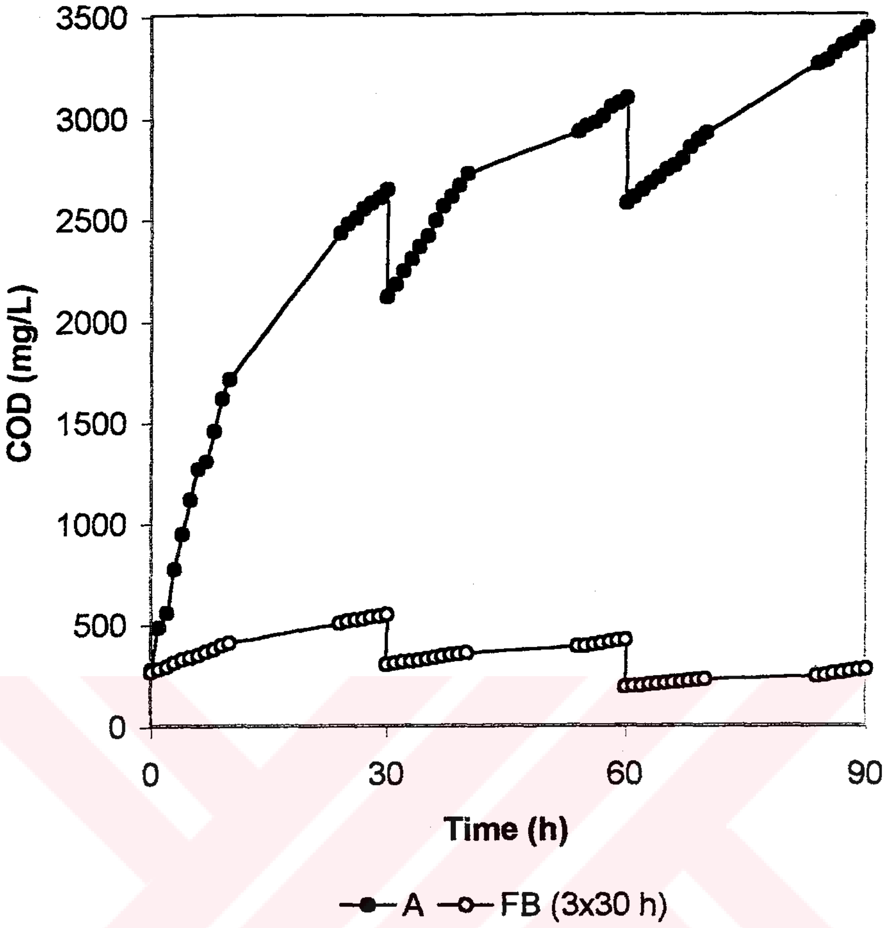

Figure 3.7.5.Variation of COD concentrations with time in the aeration tank operated in repeated fed-batch mode with 3x30 hour cycle length for 2 g/L PAC.

● Adsorption only ○ Repeated fed-batch treatment with PAC

3.8. Effects of Feed N/COD Ratio on Performance of PAC added Fed-Batch Biological Treatment

The objective of these experiments was to investigate effects of N/COD ratio in the feed wastewater on COD and ammonium removal in PAC added fed-batch treatment. Feed flow rate and COD content of the feed were kept constant at Q = 0.15 L/h and 7,000 mg/L. Feed wastewater N/COD ratio was adjusted to different levels by adjusting the NH_4-N level by air stripping of ammonia. The initial COD content in the aeration tank was nearly 300 mg/L and the initial biomass concentration was nearly 4200±200 mg biomass/L, on dry weight basis. Powdered activated carbon (PAC) concentration was kept 2 g/L. Temperature and pH were 20 °C and pH = 8-8.5, throughout the experiments. Vigorous aeration was supplied to the aeration tank to keep the dissolved oxygen (DO) above 2 mg/L. pH and DO were monitored and manually controlled during the experiments. A control experiment devoid of microorganisms was run parallel to the biological treatment experiment for every experimental condition. Percent COD removals in control experiments were considered to be zero and COD content of the control experiments were used as the base in calculation of COD removal efficiencies.

Variations of COD concentration with time as a function of feed N/COD ratio are depicted in Figure 3.8.1. COD content in the control experiment increased steadily with time due to accumulation of COD in the absence of any adsorbents and organisms.

When the N/COD ratio was 0.11 (11%) in fed-batch mode, the final COD contents in this experiment was nearly 2635 mg/L and 632 mg/L for only adsorption (A) and adsorptive biological treatment (AB), respectively. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 85% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 25% and 352 mg/L, respectively at the end of the 30 hours.

When the feed N/COD ratio was 0.093 (9.3%) in fed-batch operation, final COD contents were approximately 2655 mg/L for only adsorption (A) and 640 mg/L for adsorptive biological treatment (AB). Almost no improvement was obtained in the final COD levels when the feed N/COD was reduced to 9.3% from 11%. COD concentration in the control experiment ●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 85% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 28% and 284 mg/L, respectively at the end of the 30 hours indicating an improvement in NH_4-N removal by reducing the feed N/COD ratio.

When the N/COD ratio was 0.068 (6.8%) in the feed wastewater, the final COD contents were nearly 2675 mg/L and 649 mg/L for only adsorption (A) and adsorptive biological treatment (AB), respectively. Again, no significant improvement was observed in COD removal by reducing the feed N/COD ratio. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 85% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 33% and 195 mg/L, respectively at the end of the 30 hours. Apparently, percent NH_4-N removal increased and final NH_4-N level decreased by reducing the feed N/COD ratio.

Further reductions in the feed N/COD ratio did not reduce the final COD level, which were nearly 2685 mg/L for only adsorption (A) and 705 mg/L for adsorptive biological treatment (AB), when the N/COD ratio was 0.038(3.8%) in the feed wastewater. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 83% based on the control experiment. Percent ammonium-N removal and effluent ammonium concentration were 39% and 124 mg/L, respectively at the end of the 30 hours. Reductions in the feed N/COD ratio resulted in significant reductions in NH_4-N content of the effluent.

When the feed N/COD ratio was 0.031 (3.1%), the final COD contents were nearly 2905 mg/L for only adsorption (A) and 945 mg/L for adsorptive-biological treatment (AB). Effluent COD level has increased because of reductions in NH_4-N content of the feed wastewater. This is probably because of nitrogen limitations at low feed N/COD ratios, especially when N/COD< 4%. COD concentration in the control experiment (●) increased steadily because of accumulation of COD compounds in the absence of adsorbents and the organisms, resulting in a COD of nearly 4260 mg/L at the end of 30 h operation period. Percent COD removal was 78% based on the control experiment, which is much lower that those obtained at higher N/COD ratios. Percent ammonium-N removal and effluent ammonium concentration were 44% and 74 mg/L, respectively at the end of the 30 hours. Apparently, effluent NH_4-N level decreased to considerable low levels when the feed N/COD ratio dropped to 3%.

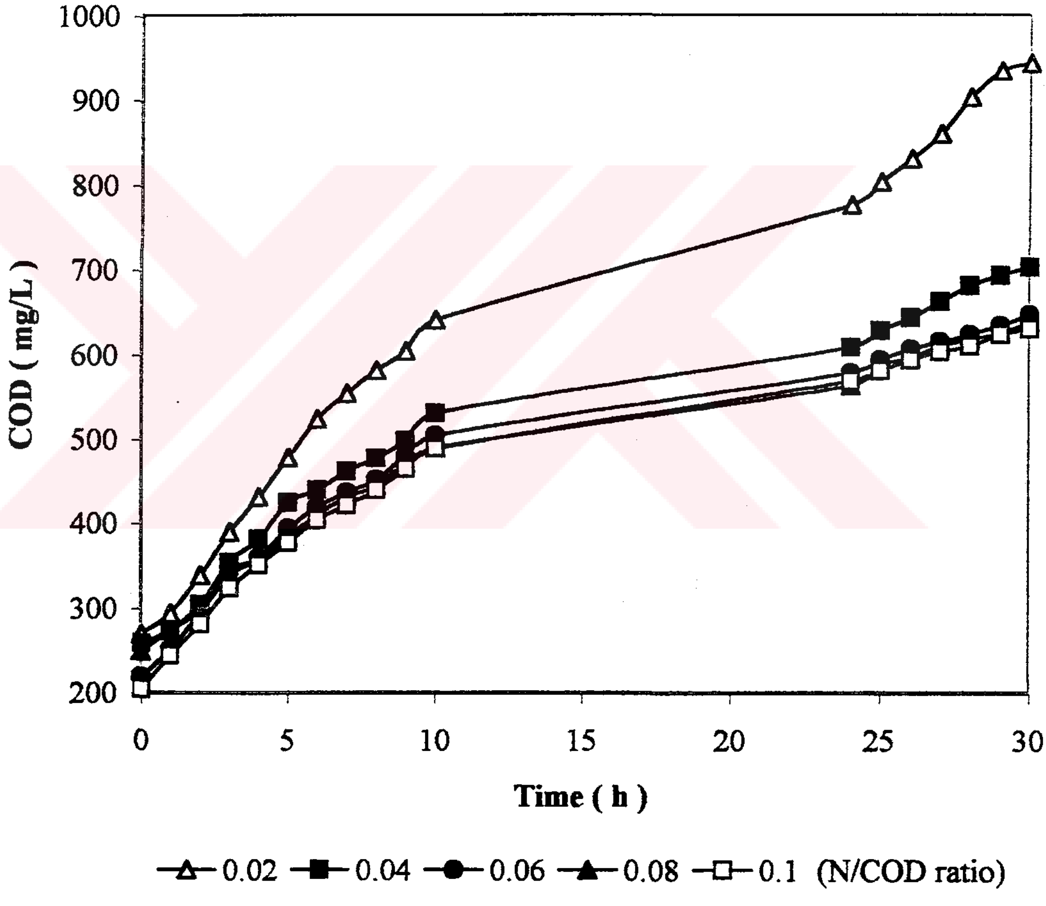

Figure 3.8.1.Variation of COD concentration with time as a function of N/COD ratios

Variation of percent COD removals and the effluent COD's at the end of 30 h operation time with the ratio of nitrogen and COD loading rates ($L_{NH_4\text{-}N}/L_{COD}$) are presented in Figure 3.8.2. COD removal in the control experiment was considered to be zero and all percent removals were based upon control experiment COD values ($E = 1-S/S_c$). Percent COD removals increased and the final COD contents decreased with increasing L_{NH4-N}/L_{COD} ratio. As seen from the figure, L_{NH4-N}/L_{COD} =0.05-0.08 ratio was optimum level to provide high percent COD removals. Percent COD removal decreased to 78%, when L_{NH4-N}/L_{COD} ratio is 0.03.

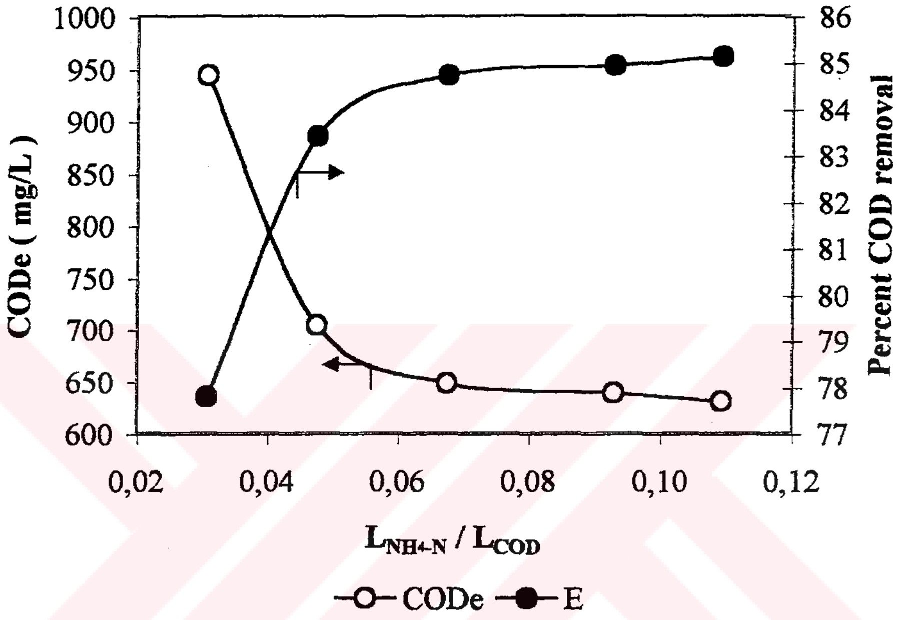

Figure 3.8.2. Variation of percent COD removals and the effluent COD's at the end of 30 h with the L_{NH4-N}/L_{COD} ratio.

Variation of percent NH_4-N removals and the effluent NH_4-N's at the end of 30 h operation time with the L_{NH4-N}/L_{COD} are presented in Figure 3.8.3. Percent ammonium-N removals increased and final NH_4-N contents decreased with decreasing L_{NH4-N}/L_{COD} ratio. Final NH_4-N concentrations decreased, when L_{NH4-N}/L_{COD} ratio decreased, because feed NH_4-N contents decreased.

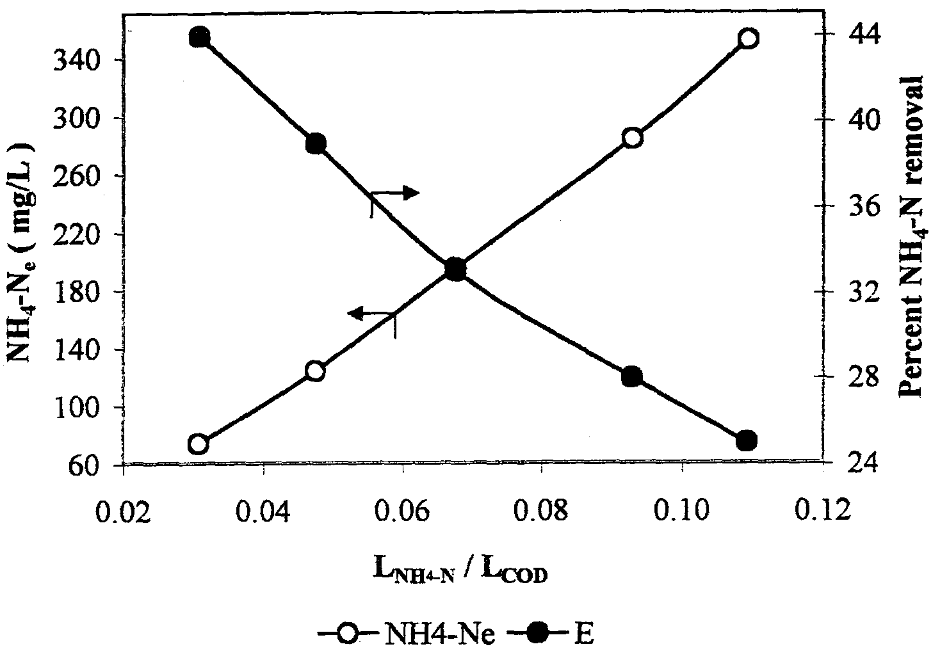

Figure 3.8.3. Variation of percent NH_4-N removals and the effluent NH_4-N's at the end of 30 h operation time with the $L_{NH_4\text{-}N}/L_{COD}$.

3.9. Chemical Oxidation Experiments

Adsorbent supplemented (2 g/L PAC) aerobic biological treatment by repeated fed-batch operation with 3x 10 h cycle length was performed with 100/6/1.5 COD/N/P ratio in the feed. At the end of 30 hour operation time, clear supernatant was removed after settling and centrifuged at 6000 rpm, 30 min to remove PAC and organisms. Collected leachate was subjected to air-stripping for 3 hours at pH=12 to decrease ammonium concentration. Ammonium nitrogen concentration was reduced from 224 mg/L to 2 mg/L. COD concentration was 300 mg/L and did not change after air-stripping. Chemical oxidation experiments were carried out with this landfill leachate and by using H_2O_2, Fenton's reagent and NaOCl as oxidizing agents.

3.9.1. Chemical Oxidation Experiments using H_2O_2

H_2O_2 dosages were varied between 50-250 mg/L, stepwise. Variation of percent COD removal with time for different H_2O_2 dosages is depicted in Figure 3.9.1. As seen from the figure significant COD reductions were achieved at the end of the 2 hours. The COD concentration of leachate decreased from 300 mg/L to 190 mg/L with a %40 removal efficiency with 150 mg/L H_2O_2. However, when H_2O_2 dosages were increased to 200 and 250 mg/L, percent removals were %41 and 42%, respectively. Since no important improvements were obtained in COD removal by increasing H_2O_2 concentration, 150 mg/L H_2O_2 was considered as the optimum dosage in chemical oxidation by H_2O_2.

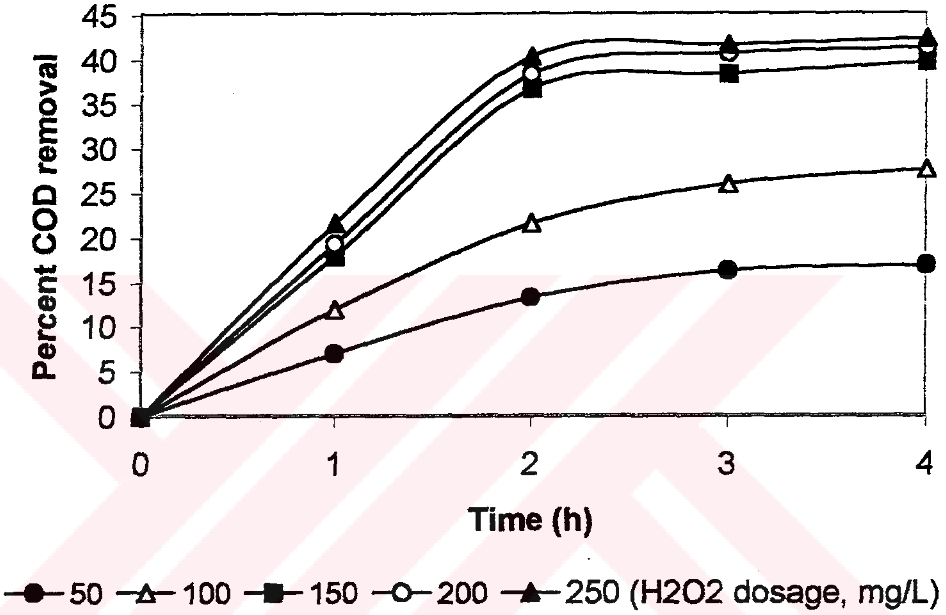

Figure 3.9.1. Variation of percent COD removal with time for different H_2O_2 dosages

3.9.2. Chemical Oxidation Experiments using Fenton's Reagent

In chemical oxidation experiments using H_2O_2 optimum dosage was 150 mg/L. In this set of experiments, H_2O_2 dosage was kept constant at 150 mg/L and $FeSO_4$ dosages were varied between 50-350 mg/L, stepwise. Variation of COD concentration and percent COD removal for different $H_2O_2/FeSO_4$ dosages is depicted in Figure 3.9.2. As can be seen from the figure COD concentration of leachate decreased from 300 mg/L to 95 mg/L with %68 COD removal efficiency for150/250 mg/L $H_2O_2/FeSO_4$ ratio. However, when $H_2O_2/FeSO_4$ ratio was decreased to 150/300 and 150/350 mg/L, percent COD removals were 69% and 70%, respectively. When $H_2O_2/FeSO_4$ ratio was 150/50, 150/100,150/150 and 150/200, COD removal efficiency decreased to 26%, 37%, 43%, and 63%, respectively. Since the highest percent COD removal (68%) was obtained with $H_2O_2/FeSO_4$=150/250 ratio this combination is recommended for future use.

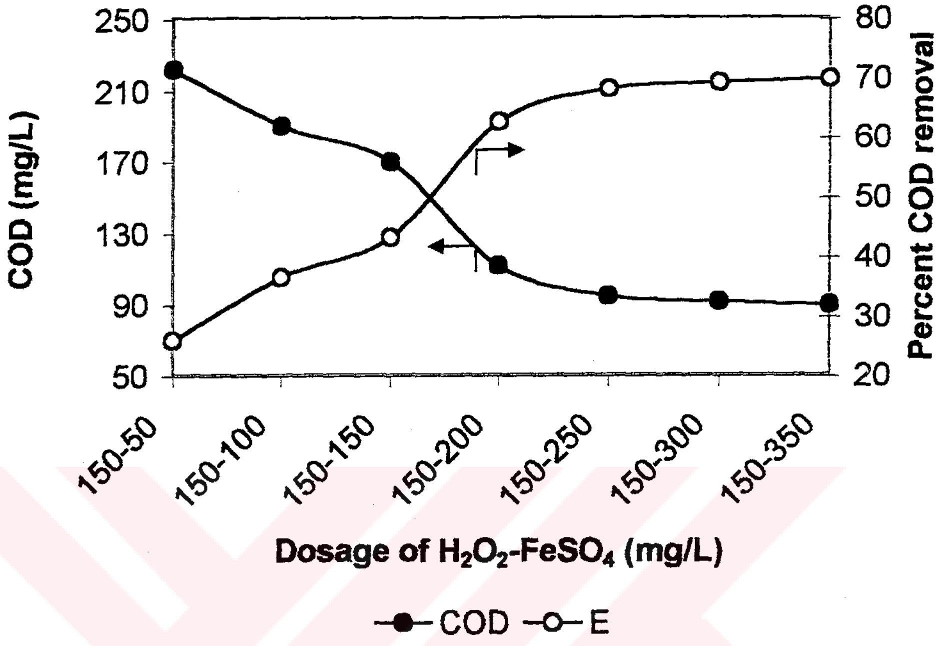

Figure 3.9.2.Variation of COD concentration and percent COD removal with different $H_2O_2/FeSO_4$ ratios.

3.9.3. Chemical Oxidation Experiments using NaOCl

NaOCl concentrations were varied between 50 and 300 mg/L. Variations of COD concentration and percent COD removal with different NaOCl dosages are depicted in Figure 3.9.3. As seen from the figure COD concentration of leachate decreased from 300 mg/L to 170 mg/L with a 43% removal efficiency for 200 mg/L NaOCl dosage. When NaOCl dosage was increased to 250 and 300 mg/L, percent COD removals were 44% and 45%, respectively. For lower NaOCl dosages such as 50, 100, 150 mg/L, removal efficiencies decreased to 16%, 23% and 35%, respectively. Since the highest percent COD removal was obtained with 200 mg/L NaOCl dosage, this dosage is recommended for future use.

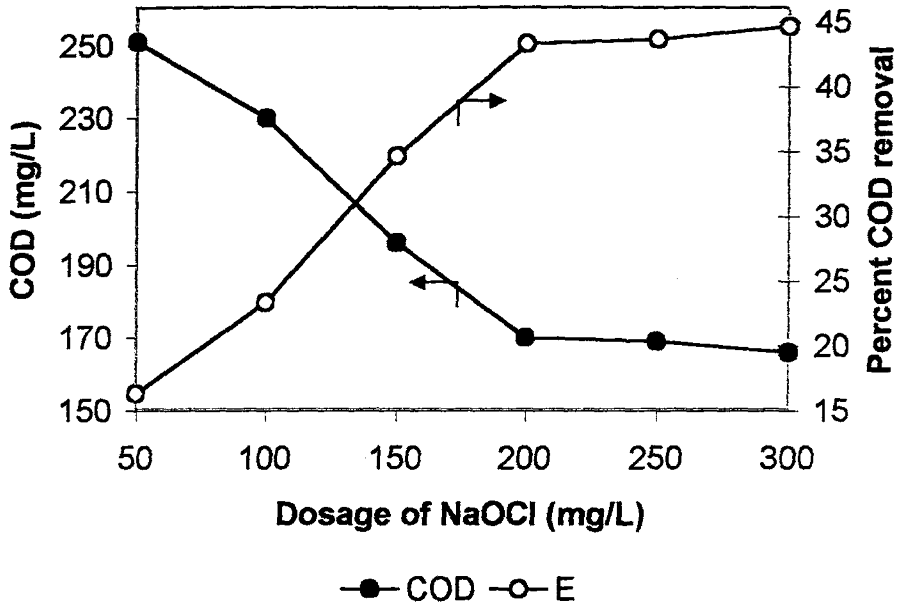

Figure 3.9.3. Variation of COD concentration and percent COD removal with different NaOCl dosages

In summary, Fenton's reagent was the most efficient oxidizing agent among the tested oxidizing agents in chemical oxidation of biologically treated landfill leachate resulting in %68 removal efficiency with 150/250 mg/L $H_2O_2/FeSO_4$ ratio.

CHAPTER FOUR

CONCLUSIONS

Due to high COD and ammonium-N content, direct biological treatment of landfill leachate is difficult and can be realized only with low COD removals. In order to reduce the COD and NH_4-N contents to the treatable levels, the landfill leachate was subjected to preliminary treatment by coagulation-flocculation and air stripping of ammonia. COD and NH_4-N contents of the leachate were reduced to desired levels (COD = 7.000 mg/L and NH_4-N = 700 mg/L) by coagulation-flocculation with lime followed by air stripping of ammonia at pH=12 as pretreatment.

Pretreated leachate was biologically treated in an aeration tank by fed-batch operation. The effects of the feed COD content (S_o) and feed flow rate (Q) on COD removals were investigated. COD removal efficiency (E) decreased and the final COD levels in the tank increased with the increasing feed COD content. Increasing COD loading rates ($L_{COD} = Q\ S_o$) resulted in decreases in final COD removals. The system should be operated at COD loading rates of below 1 g COD/h in order to obtain high percent COD removals after 30 hours of operation. Percent COD removals of 76% and ammonium-N removals of nearly 23% were obtained by fed-batch biological treatment of pre-treated leachate.

Kinetic constants of the system were determined by using the quasi steady-state experimental data obtained at the end of 30 hours of operation and the following values were determined for the k and K_s.

$k = 0.037\ h^{-1} = 0.89\ d^{-1}$, $K_s = 377$ mg/L

In order to improve COD and ammonium nitrogen removals, pretreated landfill leachate was subjected to biological treatment in an aeration tank operated in fed-batch mode in the presence and absence of powdered activated carbon (PAC) and zeolite as adsorbent.

Percent COD removals in adsorbent added biodegradation experiments (AB) were higher than those of biological treatment (B) and adsorption (A) experiments alone. Percent COD removals at the end of 30 hours of fed-batch operation increased with increasing PAC and zeolite concentrations from 0.25 g/L to 2 g/L and levelled off for adsorbent concentrations above 2 g/L. Nearly, 87% and 77% COD removals were achieved with PAC and zeolite concentrations above 2 g/L, respectively at the end of 30 hours of operation time in adsorbent added biological treatment (AB). COD removals in adsorbent-free biological treatment (B) and adsorption alone (A) with 2 g/L adsorbent concentration were 76% and 40% for PAC; 76% and 17% for zeolite, respectively. Ammonium-N removals were 40% and 30% for 5 g/L zeolite and PAC, respectively at the end of 30 hours operation.

PAC has performed better than zeolite for COD removal, whereas ammonium-N removal performance of zeolite was superior to the PAC used. Since, ammonium-N removal can easily be achieved by air stripping at pH > 10, use of zeolite for NH_4-N removal has very little advantage. However, PAC is much more effective than zeolite in COD removal and therefore, should be preferred to zeolite as adsorbent at a concentration of 2 g/L. A mixture of PAC and zeolite may also be used for effective removal of COD and ammonium-N in adsorbent added biological treatment of landfill leachate.

An empirical equation was developed to describe the contribution of adsorption over biological treatment in COD and NH_4-N removals as a function of both PAC and zeolite concentrations. Constants of the empirical equation were determined by using the experimental data.

In order to obtain lower effluent COD and ammonium concentrations, two sets of repeated fed-batch experiments were performed with and without PAC addition with different cycle times and 30 hours of total operation time (3x10 h and 5x6 h). When the operation time was divided to 3x10 hours and 5x6 hours in repeated fed-batch operations, improved COD removals were obtained as compared to 30 hours single-cycle operation with and without PAC addition.

Effects of feed N/COD ratio on COD and ammonium removal in PAC added biological treatment was investigated. Percent COD removals increased and the final COD contents decreased with increasing L_{NH4-N}/L_{COD} ratio.L_{NH_4-N}/L_{COD}=0.05-0.08 ratio was optimum providing highest percent COD removals. Further decreases in L_{NH_4-N}/L_{COD} ratio resulted in reductions in COD removal and improvements in NH_4-N removal. Percent COD removal decreased to 78% when L_{NH_4-N}/L_{COD} was 0.03.

In order to obtain acceptable effluent COD concentrations (< 100 mg/L), chemical oxidation was applied to landfill leachate after PAC added repeated fed-batch treatment (3x30 h), by three oxidizing agents (H_2O_2, Fenton's reagent and NaOCl). COD removal obtained by Fenton's oxidation was much higher than those of H_2O_2 and NaOCl experiments resulting in 68% COD removal and 95 mg/L effluent COD concentration for 150/250 mg/L $H_2O_2/FeSO_4$ ratio.

At the end of pre-treatment, adsorptive biological treatment and chemical oxidation operations, COD and ammonium nitrogen concentrations of the landfill leachate were reduced from 9,500 mg/L and 1,270 mg/L to 95 mg/L and 2 mg/L, respectively.

RECOMMENDATIONS

Following recommendations can be made for future studies on adsorptive biological treatment of landfill leachate by fed-batch operation

1. Adsorption capacities of other low-cost adsorbents may be evaluated. New adsorbents with better adsorption capacity need to be developed and used.

2. Different types of reactors can be used. Performances of sequencing batch reactors or biofilm systems may be investigated.

3. The system can be operated anaerobically to compare with aerobic biological treatment by fed-batch operation, in the presence of adsorbents.

4. Other types of microbial flora or special organisms adapted leachate can be used in order to improve system performance.

5. Continuous experiments such as activated sludge can be carried by considering important operating variables and using statistical experiment design techniques.

NOMENCLATURE

COD	Chemical oxygen demand (mg/L)
E	Percent COD removal ($E = 1 - S/S_c$)
K_s	Saturation constant (mg/L)
k	Maximum COD removal constant (d^{-1})
L_{COD}	COD loading rate (mg COD/L.h, $Q\ S_i/V_t$)
$L_{NH_4\text{-}N}$	NH_4-N loading rate (mg NH_4-N/L.h)
NH_4-N	Ammonium nitrogen concentration (mg/L)
Q	Flow rate of wastewater (L /h)
PAC	Powdered activated carbon concentration (g/L)
R_s	COD removal rate (mg COD/ L.h, $Q\ (S_i\text{-}S_c)/\ V_t$)
S_c	COD in the control tank (mg/L)
S_e	COD in effluent wastewater (mg/L)
S_i	COD in feed wastewater (mg/L)
S_o	Initial COD in the aeration tank (mg/L)
V	Volume of reactor (L)
X	Biomass concentration (g/L)
X_t	Total amount of biomass (g)
Y	Growth yield coefficient (kgX/kgS)
Z	Zeolite concentration (g/L)
μ_m	Maximum specific rate (h^{-1})
θ_H	Hydraulic residence time (h)

REFERENCES

Ahn,D.H., Yun-Chul, C and Won-Seok, C. (2002) Use of coagulant and zeolite to enhance the biological treatment efficiency of high ammonia leachate. J.Environ. Sci. Heal. A Toxic/Hazardous Substances & Environmental Engineering. 37, 163-173.

Amakrane, A., Comel, C and Veron, J. (1997) Landfill leachate pretreatment by coagulation-flocculation. Water Res. 31, 2775-2782.

Badkoubi A., Sarafrazi M.R. and Stevens D.K. (2002) Pre and post treatment of landfill leachate in vertical flow constructed wetland. Internatinal Solid Waste Association. 2, pp. 961-968.

Bohdziewicz, J., Bodzek, M and Górska, J. (2001) Application of pressure-driven membrane techniques to biological treatment of landfill leachate. Process Biochem. 36, 641-646

Cecen, F., Erdincler, A. and Kilic,E. (2002) Effect of powdered activated carbon addition on sludge dewatarability and substrate removal in landfill leachate treatment. Advan. Environ. Res. In press.

Chen, P.H. (1996) Assessment of leachates from sanitary landfills: Impact of age, rainfall and treatment. Environ. Inter. 22, 225-237.

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

Diamadopoulos, E., Samaras, P., Dabou, X and Sakellaropoulos, G.P. (1997) Combined treatment of landfill leachate and domestic sewage in a sequencing batch reactor. Water Sci. Technol.36, 61-68.

Ding, A., Zhang, Z., Fu, J and Cheng, L. (2001) Biological control of leachate from municipal landfills. Chemosphere 44, 1-8.

Geenens, D., Bixio, B and Thoeye, C. (2001) Combined ozone-activated sludge treatment of landfill leachate. Water Sci. Technol. 44, 359-365.

Greennberg A.E., Trusell R.R, & Clesceri L.S., Standard Methods for the Examinations of water and wastewater 17th edn, APHA (American Public Health Association, American Water Works Association and Water Pollution Control Federation.

Gülşen H., Altınbaş M., Alp K., Turan M., Öztürk I., Altın Z. (2002) Combined anaerobic fluidized bed reactor and Fenton's oxidation treatment of landfill leachate. Internatinal Solid Waste Association. 2. pp. 923-930.

Imai, A., Iwami, N., Matsushige, K., Inamori, Y., Sudo, R. (1993) Removal of refractory organics and nitrogen from landfill leachate by the microorganism-attached activated carbon fluidized bed process. Water Res. 27, 143-145.

Im, J., Woo, H., Choi, M., Han, K. and Kim, C. (2001) Simultaneous organic and nitrogen removal from municipal landfill leachate using an anaerobic-aerobic system. Water Res. 35, 2403-2410.

Irene, M and Lo, C. (1996) Characteristics and treatment of leachates from domestic landfills. Environ.International 22, 433-442.

Kadbaşlı I., Tünay O., Şafak A. (2002) Organic matter removal from young landfill leachate by volatilization. Internatinal Solid Waste Association. 2, pp. 917-922.

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 Res.34, 3640-3656.

Kettunen, R.H., Hoilijoki,T.H and Rintala, J.A. (1996) Anaerobic and sequential anaerobic- aerobic treatments of municipal landfill leachate at low temperatures. Bioresource Technol.58, pp.31-40

Kim, S.K. Matsui, S, Pareek, S., Shimizu,Y and Matsuda, T. (1997) Biodegradation of recalcitrant organic matter under sulfate reducing and methanogenic conditions in landfill column reactors. Water Sci. Technol. 36. pp. 91-98.

Koenig, A. and Liu, H.L. (1996) Autotrophic denitrification of landfill leachate using elemental sulfur. Water Sci. Technol. 34, pp. 469-476.

Kurt U., Gönüllü M.T., Avşar Y., Arslankaya E. (2002) Research on treatability of young landfill leachates by Fenton's reaction. Internatinal Solid Waste Association. 2, pp. 901-908.

Li, X.Z., Zhao, Q.L and Hao, X.D. (1999) Ammonium removal from landfill leachate by chemical precipitation. Waste Manage. 19, pp. 409-415.

Li, X. Z. and Zhao, Q. L. (2001) Efficiency of biological treatment affected by high strength of ammonium-nitrogen in leachate and chemical precipitation of ammonium-nitrogen as pretreatment, Chemosphere 44, pp. 37-43.

Lin, S.H. and Chang, C.H. (2000) Treatment of landfill leachate by combined electro-fenton oxidation and sequencing batch reactor method. Water. Res. 34, pp. 4243-4249.

Loukidou, M. X. and Zouboulis, A.I. (2001) Comparison of two biological treatment processes using attached-growth biomass for sanitary landfill leachate treatment. Environ.Pollut. 111, pp. 273-281

Maehlum. T. (1995) Treatment of landfill leachate in on-site lagoons and constructed wetlands. Water Sci. Technol. 32, pp. 129-135.

Marttinen, S.K., Kettunen, R.H., Sormunen, K. M., Soimasuo, R. M. and Rintala, J.A. (2002) Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates. Chemosphere, 46, pp. 851-858.

Morawe, B., Ramteke, D.S. and Vogelpohl, A. (1995) Activated carbon column performance studies of biologically treated landfill leachate. Chem. Eng. Process. 34, pp. 299-303.

Öztürk I., Altınbaş M., Koyuncu I., Arıkan C., Yangın C., (2002) Advanced phisico-chemical treatment experiencies on young municipal landfill leachates. Internatinal Solid Waste Association. 2, pp. 939-946.

Park, S., Choi, K.S., Joe, K. S., Kim, W. H and Kim, H.S. (2001) Variations of landfill leachate's properties in conjunction with the treatment process. Environ. Technol. 22, pp. 639-645.

Pirt, S.J. (1975) Principles of Microbe and Cell Cultivation. Blackwell Scientific, London.

Shiskowski, D.M. and Mavinic, D.S. (1998) Biological treatment of a high ammonia leachate: influence of external carbon during initial startup. Water Res.32, pp. 2533-2541.

Shuler, M.L. and Kargi, F. (2002) Bioprocess Engineering: Basic Concepts. 2nd edn. Prentice Hall, NJ.

Sletten, R.S., Benjamin, M.M., Horng, J.J and Ferguson, J.F. (1995) Physical-chemical treatment of landfill leachate for metals removal. Water Res. 29, pp. 2376-2386.

Steensen, M. (1997) Chemical oxidation for the treatment of leachate-process comparison and results from full-scale plants. Water Sci. Technol. 35, pp. 249-256.

Timur, H and Ozturk, I. (1999) Anaerobic sequencing batch reactor treatment of landfill leachate. Water Res. 33, 3225-32230

Trebouet, D., Schlumpf, J.P., Jaounen, P. and Quemeneur, F. (2001) Stabilized landfill leachate treatment by combined physicochemical-nanofiltration processes. Water Res.35, pp. 2935-2942

Zouboulis A.I., Loukidou M.X., Christodoulou K. (2001) Enyzmatic treatment of sanitary landfill leachate. Chemosphere V.44(5), pp. 1103-1108.

5.2. APPENDICIES

5.2.1. Raw Data for Selection of Adsorbents

Table 5.1. Raw data for selection of adsorbent experiments

	COD's (mg/L)								Percent COD removals						
Time. (h)	**Control**	**PAC**	**Zeolite**	**Bentonite**	**Wood Ash**	**Clay**	**Kaoline**	**Wood chips**	**PAC**	**Zeolite**	**Bentonite**	**Wood Ash**	**Clay**	**Kaoline**	**Wood chips**
0	7500	4802	7063	7194	7424	7293	7358	7457							
1	7500	4048	6539	6637	6801	6998	6965	7391	36	6	4	1	3	2	1
2	7500	4015	6500	6637	6736	6965	6867	7293	46	13	12	9	7	7	1
3	7500	3982	6440	6506	6700	6899	6768	7293	46	13	12	10	7	8	3
4	7500	3982	6277	6441	6637	6703	6834	7260	47	14	13	11	8	10	3
6	7500	3982	6277	6441	6604	6703	6899	7260	47	16	14	12	11	9	3
24	7500	3982	6277	6441	6604	6703	6899	7260	47	16	14	12	11	8	3

5.2.2. Raw Data for Selection of Activated Sludge Culture

Table 5.2. Raw data for selection of activated sludge culture experiments

	COD's (mg/L)					Percent COD removals			
Time(h)	Control	Çigli Activated Sludge	Pakmaya Activated Sludge	Pınar Meat Activated Sludge	Mixed Activated Sludge	Çigli Activated Sludge	Pakmaya Activated Sludge	Pınar Meat Activated Sludge	Mixed Activated Sludge
0	2200	2212	2212	2212	2212				
6	2200	2016	1491	1459	2049	8	32	34	7
12	2200	1459	1196	1393	1786	34	46	37	19
24	2200	1393	1164	1131	1688	37	47	49	23
30	2200	1204	1172	1188	1352	45	47	46	39
36	2200	1090	860	926	1188	50	61	58	46
54	2200	991	778	827	762	55	65	62	65

5.2.3. Raw Data for Pretreatment of Landfill Leachate

Table 5.3. Raw data for coagulation and flocculation experiments

	$FeCl_3$	**ALUM**	**KİREÇ**	**$FeCl_3$**	**ALUM**	**KİREÇ**
Coagulant dose (g/L)	**COD(mg/L)**	**COD(mg/L)**	**COD(mg/L)**	**E(%)**	**E(%)**	**E(%)**
0	5500	5500	5500			
0.5	3392	3227	3294	38	41	40
1	2977	2970	3030	46	46	45
1.5	2602	2899	3590	53	47	35
2	2570	2886	3687	53	48	33
2.5	2175	2688	3544	60	51	36
3	2141	2623	3676	61	52	33
3.5	2340	2537		57	54	

Table 5.4. Raw data for air stripping experiments

NH_4-N (mg/L)					**Percent NH_4-N removals**			
Time (hours)	pH=9	pH=10	pH=11	pH=12	pH=9	pH=10	pH=11	pH=12
0	1200	1200	1200	1200	0	0	0	0
2	820	410	400	280	32	66	67	77
3	625	215	265	110	48	82	78	91
5	385	100	27	21	68	92	98	98
6	248	52	10	5	79	96	99	99
8	150	12	5	3	88	99	99	99

5.2.4. Raw Data for Biological Treatment of Landfill Leachate by Fed-Batch Experiments

Table 5.5. Raw data for different feed COD experiments (S_i=978 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-Experimental	D = Q / V	PH	T	D.O.	X	Xt	Vt	Lo	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	L	mg/L. h	h	gx/gs	%
0	297	297		8.33	15.4	5.4	4.44	13.32	3		0		0
1	335	386	0.057	8.69	19.8	6	4.22	13.42	3.18	55	3.18		0
2	370	356	0.054	8.8	19.9	4.8	4.03	13.53	3.36	52	3.36		4
3	401	336	0.051	8.79	20.8	5.3	3.86	13.65	3.54	50	3.54		16
4	429	356	0.048	8.74	21	5.4	3.69	13.74	3.72	47	3.72		17
5	454	307	0.046	8.72	20.6	5.5	3.56	13.89	3.9	45	3.9		32
6	477	346	0.044	8.51	21.7	5.2	3.42	13.96	4.08	43	4.08		27
7	498	346	0.042	8.52	21.3	5.1	3.30	14.07	4.26	41	4.26		31
8	518	307	0.041	8.5	21.6	5.3	3.21	14.23	4.44	40	4.44		41
9	536	327	0.039	8.49	21.3	5.2	3.10	14.32	4.62	38	4.62		39
10	552	287	0.038	8.47	21.2	5.4	3.02	14.50	4.8	37	4.8		48
24	699	297	0.025	8.41	20.6	5.1	2.20	16.10	7.32	24	7.32	0.60	58

Table 5.6. Raw data for different feed COD experiments (S_i=1840 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Vt	Lo	Qh	Y	E
h	mg/L	mg/L	1/h		^oC	mg/L	g/L	g.	L	mg/L.h	h	gx/gs	%
0	111	111		8.33	15.4	5.4	4.32	12.96	3		0		
1	209	169	0.057	8.69	19.8	6	4.12	13.11	3.18	104	3.18		19
2	296	143	0.054	8.8	19.9	4.8	3.95	13.26	3.36	99	3.36		52
3	375	175	0.051	8.79	20.8	5.3	3.79	13.40	3.54	94	3.54		53
4	446	162	0.048	8.74	21	5.4	3.64	13.55	3.72	89	3.72		64
5	510	162	0.046	8.72	20.6	5.5	3.51	13.70	3.9	85	3.9		68
6	569	175	0.044	8.51	21.7	5.2	3.39	13.84	4.08	81	4.08		69
7	622	188	0.042	8.52	21.3	5.1	3.28	13.98	4.26	78	4.26		70
8	672	225	0.041	8.5	21.6	5.3	3.18	14.10	4.44	75	4,44		67
9	717	239	0.039	8.49	21.3	5.2	3.08	14.23	4.62	72	4.62		67
10	760	242	0.038	8.47	21.2	5.4	2.99	14.37	4.8	69	4.8		68
24	1131	291	0.025	8.41	20.6	5.1	2.22	16.24	7.32	45	7.32		74
25	1148	336	0.024	8.34	21.7	4.6	2.17	16.28	7.5	44	7.5		71
26	1165	296	0.023	8.35	22.1	5.4	2.15	16.50	7.68	43	7.68		75
27	1180	306	0.023	8.39	22.3	5.2	2.11	16.61	7.86	42	7.86		74
28	1195	315	0.022	8.39	22.4	5	2.08	16.73	8.04	41	8.04		74
29	1209	348	0.022	8.48	22.4	5	2.04	16.78	8.22	40	8.22		71
30	1223	325	0.021	8.49	22.5	4.3	2.02	16.97	8.4	39	8.4	0.49	73

Table 5.7. Raw data for different feed COD experiments (S_i=2815 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Vt	Lo	Qh	Y	E
h	mg/L	mg/L	1/h		^{0}C	mg/L	g/L	g.	L	mg/L.h	h	gx/gs	%
0	300	300		8.67	21.2	2	4.88	14.64	3		0		
1	442	418	0.057	8.45	21.3	4.2	4.68	14.89	3.18	159	3.18		5
2	569	364	0.054	8.29	20.8	3.4	4.51	15.15	3.36	151	3.36		36
3	684	389	0.051	8.28	21.4	4.2	4.35	15.40	3.54	143	3.54		43
4	787	412	0.048	8.26	21.8	4	4.21	15.64	3.72	136	3.72		48
5	880	428	0.046	8.72	21.8	3.8	4.07	15.89	3.9	130	3.9		51
6	966	428	0.044	8.51	21.9	3.6	3.95	16.14	4.08	124	4.08		56
7	1043	389	0.042	8.52	22.1	3.3	3.85	16.41	4.26	119	4.26		63
8	1116	485	0.041	8.5	22.3	3.4	3.74	16.59	4.44	114	4.44		57
9	1182	454	0.039	8.49	22.2	3.2	3.65	16.86	4.62	110	4.62		62
10	1243	434	0.038	8.47	22.3	3.2	3.57	17.13	4.8	106	4.8		65
24	1784	501	0.025	8.41	22	2.8	2.79	20.44	7.32	69	7.32		72
25	1809	501	0.024	8.34	22	3.2	2.76	20.68	7.5	68	7.5		72
26	1833	501	0.023	8.35	21.8	4.5	2.72	20.92	7.68	66	7.68		73
27	1855	501	0.023	8.39	21.8	4.1	2.69	21.16	7.86	64	7.86		73
28	1877	495	0.022	8.39	22.5	4.3	2.66	21.42	8.04	63	8.04		74
29	1897	479	0.022	8.48	22.5	3.9	2.64	21.71	8.22	62	8.22		75
30	1917	489	0.021	8.47	22.5	3.8	2.61	21.92	8.4	60	8.4	0.58	74

Table 5.8. Raw data for different feed COD experiments (S_i=4171 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Vt	Lo	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	L	mg/L.h	h	gx/gs	%
0	322	322		8.48	21.2	3.9	4.87	14.61	3		0		
1	540	360	0.057	8.44	21.6	3.7	4.71	14.99	3.18	236	3.18		33
2	734	415	0.054	8.4	21.7	4.8	4.57	15.35	3.36	223	3.36		43
3	909	473	0.051	8.33	21.8	4.8	4.44	15.70	3.54	212	3.54		48
4	1067	460	0.048	8.41	22.4	3.8	4.32	16.07	3.72	202	3.72		57
5	1210	508	0.046	8.37	22.2	3.2	4.21	16.42	3.9	193	3.9		58
6	1341	492	0.044	8.41	22.3	4.4	4.11	16.79	4.08	184	4.08		63
7	1460	492	0.042	8.24	22.3	3.6	4.03	17.15	4.26	176	4.26		66
8	1570	514	0.041	8.23	22.3	2.7	3.94	17.49	4.44	169	4.44		67
9	1672	489	0.039	8.3	22.4	2.3	3.87	17.88	4.62	163	4.62		71
10	1765	501	0.038	8.28	21.8	2.5	3.80	18.23	4.8	156	4.8		72
24	2594	656	0.025	8.29	21.9	1.1	3.13	22.93	7.32	103	7.32		75
25	2631	688	0.024	8.3	21.9	1.1	3.09	23.19	7.5	100	7.5		74
26	2667	697	0.023	8.3	21.9	1.5	3.06	23.51	7.68	98	7.68		74
27	2702	652	0.023	8.29	21.8	2.4	3.05	23.98	7.86	96	7.86		76
28	2735	681	0.022	8.34	21.9	3.5	3.02	24.24	8.04	93	8.04		75
29	2766	684	0.022	8.35	22	3.4	2.99	24.58	8.22	91	8.22		75
30	2796	675	0.021	8.37	22.3	2.9	2.97	24.95	8.4	89	8.4	0.55	76

Table 5.9. Raw data for different feed COD experiments (S_i=5115 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	688	688		8.74	20.7	2.5	4.38	13.14		3	0		
1	939	733	0.057	8.51	20.7	2.3	4.19	13.32	290	3.18	3.18		22
2	1162	740	0.054	8.45	21.7	2	4.02	13.50	274	3.36	3.36		36
3	1363	788	0.051	8.42	21.6	1.8	3.86	13.68	260	3.54	3.54		42
4	1545	756	0.048	8.4	21.5	2.4	3.73	13.86	248	3.72	3.72		51
5	1710	813	0.046	8.44	21.9	2.7	3.60	14.03	236	3.9	3.9		52
6	1860	775	0.044	8.46	21.6	2.5	3.48	14.22	226	4.08	4.08		58
7	1997	855	0.042	8.48	21.4	2.2	3.37	14.37	216	4.26	4.26		57
8	2124	862	0.041	8.49	21.7	2.1	3.28	14.55	207	4.44	4.44		59
9	2240	860	0.039	8.51	21.7	2.7	3.19	14.73	199	4.62	4.62		62
10	2348	869	0.038	8.55	21.6	2.8	3.10	14.90	192	4.8	4.8		63
24	3301	984	0.025	8.43	21.7	1.9	2.36	17.24	126	7.32	7.32		70
25	3344	972	0.024	8.44	21.5	1.6	2.32	17.43	123	7.5	7.5		71
26	3386	984	0.023	8.41	21.4	1	2.29	17.59	120	7.68	7.68		71
27	3425	997	0.023	8.54	22	3.5	2.26	17.74	117	7.86	7.86		71
28	3463	997	0.022	8.59	21.9	3.6	2.23	17.91	115	8.04	8.04		71
29	3499	970	0.022	8.58	21.8	3.2	2.20	18.12	112	8.22	8.22		72
30	3534	970	0.021	8.59	21.9	3	2.18	18.31	110	8.4	8.4	0.37	73

Table 5.10. Raw data for different feed COD experiments (S_i=5980 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	322	322		8.37	22.6	3	4.41	13.23		3	0		
1	642	459	0.057	8.4	22.9	2.9	4.23	13.46	338	3.18	3.18		29
2	928	465	0.054	8.55	23.8	3.2	4.07	13.69	320	3.36	3.36		50
3	1185	530	0.051	8.54	23.8	2.5	3.93	13.91	304	3.54	3.54		55
4	1417	552	0.048	8.55	23	3	3.80	14.13	289	3.72	3.72		61
5	1628	563	0.046	8.57	23	3.2	3.68	14.35	276	3.9	3.9		65
6	1820	595	0.044	8.65	23.3	3.3	3.57	14.57	264	4.08	4.08		67
7	1995	645	0.042	8.65	23.4	3.2	3.47	14.78	253	4.26	4.26		68
8	2157	659	0.041	8.67	23.4	2.9	3.38	14.99	242	4.44	4.44		69
9	2306	699	0.039	8.66	23.5	3.4	3.29	15.20	233	4.62	4.62		70
10	2444	745	0.038	8.68	23.5	3.2	3.21	15.40	224	4.8	4.8		70
24	3661	975	0.025	8.83	23.8	3.3	2.49	18.20	147	7.32	7.32		73
25	3717	1005	0.024	8.83	23.7	3.4	2.45	18.38	144	7.5	7.5		73
26	3770	985	0.023	8.87	23.8	3.9	2.42	18.61	140	7.68	7.68		74
27	3820	995	0.023	8.86	23.6	3.3	2.39	18.80	137	7.86	7.86		74
28	3869	1015	0.022	8.76	23.8	3	2.36	18.99	134	8.04	8.04		74
29	3915	1050	0.022	8.78	23.8	4.4	2.33	19.15	131	8.22	8.22		73
30	3959	1023	0.021	8.78	23.7	4.3	2.31	19.39	128	8.4	8.4	0.39	74

Table 5.11. Raw data for different feed COD experiments (S_i=7050 mg/L. Q=0.18 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	347	347		8.73	22.1	3	4.64	13.92		3	0		
1	726	620	0.057	8.57	22.2	2.5	4.56	14.50	399	3.18	3.18		15
2	1065	666	0.054	8.47	22.6	2.2	4.49	15.08	378	3.36	3.36		37
3	1369	702	0.051	8.48	22.7	2.6	4.42	15.65	358	3.54	3.54		49
4	1644	764	0.048	8.58	23	2.5	4.36	16.21	341	3.72	3.72		54
5	1894	811	0.046	8.59	23.1	2.4	4.30	16.76	325	3.9	3.9		57
6	2121	828	0.044	8.89	23.5	2.3	4.24	17.31	311	4.08	4.08		61
7	2330	847	0.042	8.63	23.8	2.2	4.19	17.87	298	4.26	4.26		64
8	2521	872	0.041	8.66	23.7	2.3	4.15	18.41	286	4.44	4.44		65
9	2697	899	0.039	8.65	23.6	2.1	4.10	18.95	275	4.62	4.62		67
10	2861	983	0.038	8.66	23.5	2	4.05	19.44	264	4.8	4.8		66
24	4303	1183	0.025	8.71	23.7	2.1	3.65	26.72	173	7.32	7.32		73
25	4369	1149	0.024	8.7	23.8	2.1	3.64	27.33	169	7.5	7.5		74
26	4432	1219	0.023	8.67	23.4	2	3.61	27.70	165	7.68	7.68		72
27	4492	1210	0.023	8.78	23.4	1.8	3.59	28.26	161	7.86	7.86		73
28	4549	1243	0.022	8.82	23	1.8	3.57	28.70	158	8.04	8.04		73
29	4604	1235	0.022	8.82	22.9	2.6	3.56	29.25	154	8.22	8.22		73
30	4656	1250	0.021	8.85	22.9	2.5	3.54	29.74	151	8.4	8.4	0.51	73

Table 5.12. Raw data for different feed flow rate experiment (S_i=7000 mg/L. Q=0.05 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	449	449		8.8	22.7	3	4.96	14.88		3	0		
1	555	474	0.016	8.71	23.2	3.4	4.91	14.98	113	3.05	3.05		15
2	657	487	0.016	8.65	22.9	3.3	4.87	15.08	111	3.1	3.1		26
3	756	514	0.016	8.67	23.2	3.6	4.82	15.18	109	3.15	3.15		32
4	852	513	0.016	8.74	23.3	3	4.78	15.28	108	3.2	3.2		40
5	944	523	0.015	8.64	23.5	2.7	4.73	15.38	106	3.25	3.25		45
6	1035	531	0.015	8.7	23.4	2.6	4.69	15.48	104	3.3	3.3		49
7	1122	540	0.015	8.73	24	2.9	4.65	15.58	103	3.35	3.35		52
8	1207	546	0.015	8.77	23.6	2.2	4.61	15.68	101	3.4	3.4		55
9	1289	540	0.014	8.83	24	2.3	4.58	15.79	100	3.45	3.45		58
10	1369	552	0.014	8.84	24.1	2.2	4.54	15.88	98	3.5	3.5		60
24	2289	705	0.012	8.83	24.2	2	4.10	17.23	82	4.2	4.2		69
25	2343	710	0.012	8.83	24.2	2.1	4.08	17.33	81	4.25	4.25		70
26	2396	728	0.012	8.79	24.2	2.2	4.05	17.42	80	4.3	4.3		70
27	2448	715	0.011	8.84	24.2	2.9	4.03	17.52	79	4.35	4.35		71
28	2498	734	0.011	8.84	24	3	4.00	17.61	78	4.4	4.4		71
29	2548	725	0.011	8.84	23.8	3.1	3.98	17.71	77	4.45	4.45		72
30	2596	706	0.011	8.86	23.7	3	3.96	17.82	77	4.5	4.5	0.32	73

Table 5.13. Raw data for different feed flow rate experiment (S_i=7000 mg/L. Q=0.10 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		^oC	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	159	159		8.56	22.1	2.7	4.02	12.06		3	0		
1	379	224	0.032	8.48	23.4	2.3	3.92	12.16	225	3.1	3.1		41
2	585	264	0.031	8.77	23.5	2.1	3.83	12.26	218	3.2	3.2		55
3	779	289	0.030	8.7	24	2	3.75	12.36	211	3.3	3.3		63
4	961	336	0.029	8.76	23.9	2.3	3.67	12.46	205	3.4	3.4		65
5	1133	370	0.029	8.83	24.4	2.1	3.59	12.56	199	3.5	3.5		67
6	1295	392	0.028	8.85	24.9	4	3.52	12.66	194	3.6	3.6		70
7	1449	426	0.027	8.66	24.8	2	3.45	12.76	189	3.7	3.7		71
8	1594	454	0.026	8.89	25.1	2.3	3.38	12.85	184	3.8	3.8		72
9	1732	506	0.026	8.85	24.7	2.6	3.32	12.94	179	3.9	3.9		71
10	1863	521	0.025	8.91	24.5	2.5	3.26	13.04	174	4	4	0.39	72

Table 5.14. Raw data for different feed flow rate experiment (S_i=7000 mg/L. Q=0.21 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		^oC	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	166	166		8.94	23.1	3	4.06	12.18		3	0		
1	608	278	0.065	8.6	23.6	4.2	3.91	12.54	453	3.21	0.21		54
2	995	337	0.061	8.6	23.4	3	3.77	12.89	425	3.42	0.42		66
3	1338	431	0.058	8.54	23.5	5	3.65	13.24	400	3.63	0.63		68
4	1643	475	0.055	8.56	24.1	3	3.54	13.58	378	3.84	0.84		71
5	1917	540	0.052	8.58	23.8	3.1	3.43	13.91	359	4.05	1.05		72
6	2164	595	0.049	8.54	24.5	2.1	3.34	14.24	341	4.26	1.26		73
7	2387	637	0.047	8.49	24.5	1.9	3.26	14.57	325	4.47	1.47		73
8	2591	672	0.045	8.49	24.4	1.8	3.18	14.89	311	4.68	1.68		74
9	2776	684	0.043	8.49	24.3	1.4	3.11	15.23	297	4.89	1.89		75
10	2947	711	0.041	8.71	24.3	1.6	3.05	15.55	285	5.1	2.1	0.26	76

Table 5.15. Raw data for different feed flow rate experiment (S_i=7000 mg/L. Q=0.36 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	356	356		8.78	19.8	3	4.10	12.3		3	0		
1	1066	713	0.107	8.48	21.4	2.2	3.95	13.26	731	3.36	3.36		33
2	1638	895	0.097	8.51	21.7	2	3.81	14.17	660	3.72	3.72		45
3	2109	1049	0.088	8.58	22.5	1.9	3.68	15.03	602	4.08	4.08		50
4	2504	1024	0.081	8.6	22.7	1.8	3.59	15.96	553	4.44	4.44		59
5	2840	1050	0.075	8.61	22.9	1.7	3.51	16.85	512	4.8	4.8		63
6	3129	1100	0.070	8.65	22.9	3.5	3.43	17.72	476	5.16	5.16		65
7	3380	1100	0.065	8.66	22.8	2.7	3.37	18.62	445	5.52	5.52		67
8	3600	1155	0.061	8.67	22.8	2.4	3.31	19.45	418	5.88	5.88		68
9	3795	1225	0.058	8.64	23.1	2	3.24	20.25	393	6.24	6.24		68
10	3969	1230	0.055	8.63	23	1.9	3.20	21.12	372	6.6	6.6	0.44	69

Table 5.16. Raw data for different feed flow rate experiment (S_i=7000 mg/L. Q=0.45 L/h. V_o=3 L)

T	S-Control	S-experimental	D = Q / V	PH	T	D.O.	X	Xt	Lo	Vt	Qh	Y	E
h	mg/L	mg/L	1/h		°C	mg/L	g/L	g.	mg/L.h	L	h	gx/gs	%
0	275	275		8.3	23.3	2.4	4.14	12.42		3	0		
1	1155	733	0.130	8.34	23.8	2	4.08	14.07	916	3.45	3.45		37
2	1832	869	0.115	8.69	23.8	2.1	4.01	15.65	810	3.9	3.9		53
3	2368	975	0.103	8.79	23.7	1.9	3.95	17.18	726	4.35	4.35		59
4	2804	1065	0.094	8.6	23.7	1.8	3.89	18.68	658	4.8	4.8		62
5	3166	1100	0.086	8.58	23.8	1.6	3.85	20.19	602	5.25	5.25		65
6	3470	1195	0.079	8.72	24	1.9	3.79	21.60	554	5.7	5.7		66
7	3730	1259	0.073	8.77	24.2	1.8	3.74	23.01	514	6.15	6.15		66
8	3954	1260	0.068	8.76	24.3	1.9	3.72	24.52	479	6.6	6.6		68
9	4150	1299	0.064	8.69	24.3	1.8	3.68	25.94	448	7.05	7.05		69
10	4322	1297	0.060	8.71	24.4	1.8	3.66	27.45	421	7.5	7.5	0.58	70

5.2.5. Raw Data for Adsorbent Added Biological Treatment of Landfill Leachate by Fed-Batch Operation

Table 5.19. Raw data for powdered activated carbon (PAC) added biological treatment (0.25 g/L PAC. Q=0.15 L/h. Si=7000 mg/L)

Time	**S-Control**	**S-Experimental (AB)**	**S-Experimental (A)**	**E-AB**	**E-A**	**Vt**
h	mg/L	mg/L	mg/L	%	%	L
0	305	305	322	0	0	0
1	623	351	630	44	0	3.15
2	911	398	905	56	1	3.3
3	1175	495	1166	58	1	3.45
4	1417	540	1395	62	2	3.6
5	1639	591	1590	64	3	3.75
6	1844	659	1782	64	3	3.9
7	2034	705	1925	65	5	4.05
8	2211	727	2095	67	5	4.2
9	2375	795	2251	67	5	4.35
10	2528	878	2425	65	4	4.5
24	3943	1025	3750	74	5	6.6
25	4011	1035	3805	74	5	6.75
26	4075	1040	3861	74	5	6.9
27	4137	1055	3912	74	5	7.05
28	4196	1075	3975	74	5	7.2
29	4253	1085	4023	74	5	7.35
30	4307	1100	4053	74	6	7.5

Table 5.20. Raw data for powdered activated carbon (PAC) added biological treatment (0.50 g/L PAC. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	202	202	305	0	0	0
1	520	272	560	48	0	3.15
2	809	334	775	59	4	3.3
3	1072	457	915	57	15	3.45
4	1314	501	1098	62	16	3.6
5	1537	571	1246	63	19	3.75
6	1742	605	1401	65	20	3.9
7	1932	645	1518	67	21	4.05
8	2109	697	1680	67	20	4.2
9	2273	722	1725	68	24	4.35
10	2426	791	1840	67	24	4.5
24	3842	922	2855	76	26	6.6
25	3909	945	2920	76	25	6.75
26	3974	964	3090	76	22	6.9
27	4035	915	3140	77	22	7.05
28	4095	944	3215	77	21	7.2
29	4151	926	3295	78	21	7.35
30	4206	935	3320	78	21	7.5

Table 5.21. Raw data for powdered activated carbon (PAC) added biological treatment (1.0 g/L PAC. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	146	146	269	0	0	0
1	465	169	430	64	7	3.15
2	755	200	648	73	14	3.3
3	1019	262	849	74	17	3.45
4	1262	297	1050	76	17	3.6
5	1485	339	1250	77	16	3.75
6	1691	414	1450	76	14	3.9
7	1881	422	1602	78	15	4.05
8	2059	447	1725	78	16	4.2
9	2223	457	1845	79	17	4.35
10	2377	484	2005	80	16	4.5
24	3797	695	2530	82	33	6.6
25	3865	710	2560	82	34	6.75
26	3930	732	2630	81	33	6.9
27	3991	758	2675	81	33	7.05
28	4051	750	2720	81	33	7.2
29	4108	755	2780	82	32	7.35
30	4162	755	2840	82	32	7.5

Table 5.22. Raw data for powdered activated carbon (PAC) added biological treatment (2.0 g/L PAC. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	75	75	**254**	0	0	0
1	406	105	**447**	74	0	3.15
2	706	155	**549**	78	22	3.3
3	981	195	**755**	80	23	3.45
4	1233	224	**942**	82	24	3.6
5	1464	265	**1095**	82	25	3.75
6	1678	297	**1258**	82	25	3.9
7	1876	327	**1325**	83	29	4.05
8	2059	354	**1458**	83	29	4.2
9	2230	381	**1595**	83	28	4.35
10	2390	408	**1680**	83	30	4.5
24	3863	553	**2345**	86	39	6.6
25	3933	574	**2359**	85	40	6.75
26	4000	601	**2405**	85	40	6.9
27	4065	611	**2448**	85	40	7.05
28	4126	620	**2525**	85	39	7.2
29	4185	615	**2579**	85	38	7.35
30	4242	610	**2617**	86	38	7.5

Table 5.23. Raw data for powdered activated carbon (PAC) added biological treatment (3.0 g/L PAC. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	64	64	245	0	0	0
1	397	70	405	82	0	3.15
2	699	125	545	82	22	3.3
3	975	155	720	84	26	3.45
4	1228	194	895	84	27	3.6
5	1461	254	985	83	33	3.75
6	1676	278	1175	83	30	3.9
7	1875	305	1276	84	32	4.05
8	2060	329	1380	84	33	4.2
9	2232	355	1425	84	36	4.35
10	2393	378	1580	84	34	4.5
24	3875	529	2210	86	43	6.6
25	3945	543	2290	86	42	6.75
26	4013	566	2350	86	41	6.9
27	4077	575	2395	86	41	7.05
28	4139	580	2446	86	41	7.2
29	4199	575	2505	86	40	7.35
30	4256	575	2540	86	40	7.5

Table 5.24. Raw data for powdered activated carbon (PAC) added biological treatment (5.0 g/L PAC. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	95	95	305	0	0	0
1	428	110	400	74	0	3.15
2	730	125	475	83	35	3.3
3	1006	135	595	87	41	3.45
4	1259	179	787	86	37	3.6
5	1492	205	825	86	45	3.75
6	1707	249	985	85	42	3.9
7	1906	284	1100	85	42	4.05
8	2091	305	1180	85	44	4.2
9	2263	335	1290	85	43	4.35
10	2423	354	1405	85	42	4.5
24	3905	499	1940	87	50	6.6
25	3976	521	1980	87	50	6.75
26	4043	535	2048	87	49	6.9
27	4108	548	2080	87	49	7.05
28	4170	545	2120	87	49	7.2
29	4229	545	2140	87	49	7.35
30	4286	539	2179	87	49	7.5

Table 5.25. Raw data for zeolite (Z) added biological treatment (0.25 g/L Zeolite. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	305	305	322	0	0	0
1	623	351	630	44	0	3.15
2	911	398	905	56	1	3.3
3	1175	495	1166	58	1	3.45
4	1417	540	1395	62	2	3.6
5	1639	591	1590	64	3	3.75
6	1844	659	1782	64	3	3.9
7	2034	705	1925	65	5	4.05
8	2211	727	2095	67	5	4.2
9	2375	795	2251	67	5	4.35
10	2528	878	2425	65	4	4.5
24	3943	1025	3750	74	5	6.6
25	4011	1035	3805	74	5	6.75
26	4075	1040	3861	74	5	6.9
27	4137	1055	3912	74	5	7.05
28	4196	1075	3975	74	5	7.2
29	4253	1085	4023	74	5	7.35
30	4307	1100	4053	74	6	7.5

Table 5.26. Raw data for zeolite (Z) added biological treatment (0.50 g/L Zeolite. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	278	278	301	0	0	0
1	600	324	578	46	4	3.15
2	894	405	851	55	5	3.3
3	1161	480	1105	59	5	3.45
4	1407	542	1320	61	6	3.6
5	1632	585	1505	64	8	3.75
6	1841	635	1725	66	6	3.9
7	2034	680	1859	67	9	4.05
8	2213	725	2020	67	9	4.2
9	2380	778	2195	67	8	4.35
10	2535	844	2340	67	8	4.5
24	3972	980	3580	75	10	6.6
25	4040	995	3640	75	10	6.75
26	4106	1010	3680	75	10	6.9
27	4168	1030	3765	75	10	7.05
28	4228	1045	3804	75	10	7.2
29	4286	1058	3856	75	10	7.35
30	4341	1065	3905	75	10	7.5

Table 5.27. Raw data for zeolite (Z) added biological treatment (1.0 g/L Zeolite. Q=0.15 L/h. Si=7000 mg/L)

Time	**S-Control**	**S-Experimental (AB)**	**S-Experimental (A)**	**E-AB**	**E-A**	**Vt**
h	mg/L	mg/L	mg/L	%	%	L
0	254	254	296	0	0	0
1	576	287	529	50	8	3.15
2	870	363	810	58	7	3.3
3	1137	431	1070	62	6	3.45
4	1383	502	1275	64	8	3.6
5	1608	559	1478	65	8	3.75
6	1817	605	1657	67	9	3.9
7	2009	655	1810	67	10	4.05
8	2189	685	1966	69	10	4.2
9	2355	745	2114	68	10	4.35
10	2511	793	2259	68	10	4.5
24	3947	978	3396	75	14	6.6
25	4016	955	3435	76	14	6.75
26	4081	1005	3495	75	14	6.9
27	4144	1013	3546	76	14	7.05
28	4204	1024	3595	76	14	7.2
29	4261	1032	3650	76	14	7.35
30	4317	1040	3725	76	14	7.5

Table 5.28. Raw data for zeolite (Z) added biological treatment (2.0 g/L Zeolite. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	230	230	296	0	0	0
1	552	286	560	48	0	3.15
2	845	351	843	58	0	3.3
3	1112	433	1102	61	1	3.45
4	1358	498	1324	63	2	3.6
5	1583	532	1513	66	4	3.75
6	1791	590	1697	67	5	3.9
7	1984	635	1821	68	8	4.05
8	2163	679	1952	69	10	4.2
9	2329	725	2075	69	11	4.35
10	2485	795	2175	68	12	4.5
24	3920	925	3305	76	16	6.6
25	3988	940	3361	76	16	6.75
26	4054	956	3395	76	16	6.9
27	4116	968	3423	76	17	7.05
28	4176	985	3450	76	17	7.2
29	4234	995	3510	76	17	7.35
30	4289	1010	3576	76	17	7.5

Table 5.29. Raw data for zeolite (Z) added biological treatment (3.0 g/L Zeolite. Q=0.15 L/h. Si=7000 mg/L)

Time	S-Control	S-Experimental (AB)	S-Experimental (A)	E-AB	E-A	Vt
h	mg/L	mg/L	mg/L	%	%	L
0	232	232	284	0	0	0
1	555	283	549	49	1	3.15
2	849	340	832	60	2	3.3
3	1117	423	1098	62	2	3.45
4	1363	483	1329	65	3	3.6
5	1590	520	1509	67	5	3.75
6	1798	575	1638	68	9	3.9
7	1992	624	1813	69	9	4.05
8	2171	669	1924	69	11	4.2
9	2339	715	2096	69	10	4.35
10	2495	775	2205	69	12	4.5
24	3935	910	3312	77	16	6.6
25	4003	932	3352	77	16	6.75
26	4069	945	3384	77	17	6.9
27	4131	957	3416	77	17	7.05
28	4192	975	3420	77	18	7.2
29	4249	986	3492	77	18	7.35
30	4305	1005	3512	77	18	7.5

Table 5.30. Raw data for zeolite (Z) added biological treatment (5.0 g/L Zeolite. Q=0.15 L/h. Si=7000 mg/L)

Time	**S-Control**	**S-Experimental (AB)**	**S-Experimental (A)**	**E-AB**	**E-A**	**Vt**
h	mg/L	mg/L	mg/L	%	%	L
0	220	220	260	0	0	0
1	545	293	536	46	2	3.15
2	840	329	824	61	2	3.3
3	1110	410	1056	63	5	3.45
4	1357	476	1295	65	5	3.6
5	1584	512	1459	68	8	3.75
6	1794	568	1634	68	9	3.9
7	1989	612	1805	69	9	4.05
8	2169	659	1956	70	10	4.2
9	2337	705	2102	70	10	4.35
10	2494	760	2226	70	11	4.5
24	3941	905	3352	77	15	6.6
25	4010	924	3368	77	16	6.75
26	4076	932	3390	77	17	6.9
27	4139	945	3420	77	17	7.05
28	4200	967	3452	77	18	7.2
29	4258	978	3486	77	18	7.35
30	4313	995	3552	77	18	7.5

5.2.5. Raw Data for Repeated Fed-Batch Experiments

Table 5.31. Raw data for repeated fed-batch treatment without PAC addition (Q=0.15 L/h. Si=7000 mg/L)

		1x30 hours	3x10 hours						5x6 hours									
T	Control	FB	T	COD	t	COD	t	COD	t	COD	t	COD	t	COD	t	COD	t	COD
h	mg/L	mg/L	H	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	
0	305	305	0	355	10	805	21	870	0	340	6	605	12	749	18	820	24	845
1	640	359	1	378	20	910	22	878	1	362	7	642	13	775	19	832	25	851
2	925	405	2	410			23	895	2	410	8	675	14	792	20	835	26	854
3	1190	482	3	495			21	870	3	475	9	705	15	804	21	844	27	860
4	1395	541	4	547			22	878	4	525	10	765	16	815	22	849	28	864
5	1650	592	5	602			23	895	5	590	11	795	17	825	23	857	29	871
6	1870	640	6	647			24	898	6	625	12	805	18	832	24	875	30	875
7	2055	695	7	705			25	905										
8	2225	745	8	750			26	911										
9	2385	790	9	799			27	915										
10	2550	875	10	860			28	920										
24	3900	990					29	920										
25	3985	1025					30	922										
26	4020	1055																
27	4121	1080																
28	4175	1095																
29	4205	1100																
30	4260	1120																

Table 5.32. Raw data for repeated fed-batch treatment with PAC addition (PAC cons=2.0 g/L. Q=0.15 L/h. Si=7000 mg/L)

		1x30 hours	**3x10 hours**						**5x6 hours**									
Time	Control	FB	t	COD	t	COD	t	COD	t	COD	t	COD	t	COD	t	COD	t	COD
h	mg/L	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L	h	mg/L
0	305	305	0	260	10	320	20	278	0	245	6	305	12	355	18	340	24	305
1	640	359	1	275	20	465	21	295	1	260	7	330	13	369	19	352	25	312
2	925	405	2	305			22	305	2	295	8	345	14	382	20	365	26	320
3	1190	482	3	340			23	312	3	330	9	367	15	395	21	372	27	325
4	1395	541	4	365			24	325	4	359	10	380	16	410	22	385	28	332
5	1650	592	5	392			25	337	5	387	11	395	17	425	23	394	29	340
6	1870	640	6	420			26	345	6	415	12	410	18	447	24	405	30	365
7	2055	695	7	435			27	357										
8	2225	745	8	452			28	369										
9	2385	790	9	475			29	375										
10	2550	875	10	497			30	398										
24	3900	990																
25	3985	1025																
26	4020	1055																
27	4121	1080																
28	4175	1095																
29	4205	1100																
30	4260	1120																

Table 5.33. Raw data for repeated fed-batch (3x30 h) treatment with PAC addition (PAC cons=2.0 g/L. Q=0.15 L/h. Si=7000 mg/L)

t	COD-A	COD-FB	t	COD-A	COD-FB	t	COD-A	COD-FB
h	mg/L	mg/L	h	mg/L	mg/L	h	mg/L	mg/L
0	280	270	30	2120	305	60	2575	195
1	490	283	31	2180	311	61	2605	198
2	560	295	32	2245	318	62	2642	203
3	775	314	33	2305	322	63	2675	207
4	950	330	34	2364	329	64	2702	212
5	1120	341	35	2420	334	65	2739	215
6	1270	354	36	2495	341	66	2760	219
7	1310	369	37	2562	347	67	2795	222
8	1460	382	38	2610	352	68	2847	225
9	1620	402	39	2665	357	69	2885	229
10	1715	414	40	2720	363	70	2920	232
24	2430	509	54	2925	394	84	3265	248
25	2475	516	55	2959	397	85	3280	253
26	2505	523	56	2975	405	86	3317	261
27	2550	531	57	3005	411	87	3355	264
28	2580	539	58	3052	417	88	3372	271
29	2605	542	59	3070	421	89	3405	279
30	2645	551	60	3095	426	90	3440	285

5.2.6. Raw Data for different feed COD/N Ratio for COD and ammonium Removal in PAC added Biological Treatment

Table 5.34. Raw data for different feed COD/N ratio in PAC added fed-batch treatment (Q=0.15 L/h. Si=7000 mg/L. PAC=2 g/L)

		COD/NH_4-N (PAC=2 g/L)				
T	Control	AB(100/10)	AB(100/8)	AB(100/6)	AB(100/4)	AB(100/2)
h	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
0	305	205	250	220	260	270
1	640	245	275	252	275	295
2	925	282	298	295	305	340
3	1190	325	340	345	355	390
4	1395	352	359	360	382	432
5	1650	378	385	395	425	479
6	1870	405	410	420	440	525
7	2055	422	432	437	462	555
8	2225	440	445	452	478	582
9	2385	465	472	480	499	605
10	2550	489	491	505	532	642
24	3900	570	565	580	610	778
25	3985	582	589	595	630	805
26	4020	595	597	608	645	832
27	4121	605	612	617	664	862
28	4175	612	620	625	683	905
29	4205	625	627	636	695	936
30	4260	632	640	649	705	945

Table 5.35. Raw data with different $L_{NH4\text{-}N}/L_{COD}$ ratio for COD and ammonium removal in PAC added fed-batch treatment (Q=0.15 L/h. Si=7000 mg/L. PAC=2 g/L)

$L_{NH4\text{-}N}/L_{COD}$	CODe	E	NH_4-Ne	E
g NH_4-N/g COD	mg/L	%	mg/L	%
0.031	945	77.81	74	44
0.048	705	83.45	124	39
0.068	649	84.76	195	33
0.093	640	84.97	284	28
0.109	632	85.16	352	25

5.2.7. Raw Data for Chemical Oxidation Experiments.

Table 5.36. Raw data for chemical oxidation experiments using H_2O_2. (pH=3)

Time	**COD (mg/L)**					**Percent COD removal**				
	Dosage of H_2O_2					Dosage of H_2O_2				
	50	100	150	200	250	50	100	150	200	250
h	mg/L	mg/L	mg/L	mg/L	mg/L	%	%	%	%	%
0	300	300	300	300	300	0	0	0	0	0
1	279	264	246	242	235	7	12	18	19	22
2	260	235	190	185	179	13	22	37	38	40
3	251	222	185	178	175	16	26	38	41	42
4	249	217	181	176	173	17	28	40	41	42

Table 5.37. Raw data for chemical oxidation experiment using Fenton's Reagent (pH=3)

Dosage of H_2O_2-Fe^{+2}(mg/L)	**150-50**	**150-100**	**150-150**	**150-200**	**150-250**	**150-300**	**150-350**
Initial COD conc. (mg/L)	300	300	300	300	300	300	
Effluent COD Cons.(mg/L)	222	190	170	112	95	92	90
Percent COD removal (%)	26	37	43	63	68	69	70

Table 5.38. Raw data for chemical oxidation experiment using NaOCl. (pH=9)

Dosage of NaOCl (mg/L)	**50**	**100**	**150**	**200**	**250**	**300**
Initial COD conc. (mg/L)	300	300	300	300	300	300
Effluent COD Cons.(mg/L)	251	230	196	170	169	166
Percent COD removal (%)	16	23	35	43	44	45