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POWDERED ACTIVATED CARBON ADDITION TO ACTIVATED SLUDGE IN THE TREATMENT OF LANDFILL LEACHATE

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POWDERED ACTIVATED CARBON ADDITION

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ABSTRACT

Powdered activated carbon (PAC) addition to activated sludge is a convenient method in the treatment of wastewaters that contain high amounts of nonbiodegradable and inhibitory organics. In the biological treatment of leachate in combination with domestic wastewater, leachate constituents may exert adverse effects on the efficiency of the activated sludge process. The purpose of this study was to investigate the effectiveness and applicability of PAC added activated sludge systems in the treatment of leachate in combination with synthetic domestic wastewater.

The first step in the experimental path of the study was the determination of adsorption characteristics of the activated carbon used in the study. The succeeding steps involved the biological treatment studies in PAC added activated sludge reactors. The second step was treatment of leachate in batch reactors. The third step was treatment in Semi-Continuously Fed Batch reactors which were used to simulate the Continuous-Flow Stirred Tank Reactor (CFSTR). The fourth step was PAC addition to a continuous-flow activated sludge reactor.

The results of the study demonstrated that PAC addition to activated sludge is a promising method for the treatment of leachate in combination with domestic wastewater. PAC addition resulted in considerable reductions in the effluent concentrations of organic matter due to the adsorption of nonbiodegradable organics.

It was found that the removal of organic matter was a simple combination of adsorption and biodegradation in the PAC added activated sludge systems for the conditions encountered in this study. Also, bioregeneration of activated carbon hypothesis was not valid. But, PAC addition increased nitrification rates through the enhancement of nitrifier activities by adsorbing the inhibitory and/or toxic compounds in the leachate.

ÖZET

Aktif Çamura Toz Aktif Karbon eklenmesi, yüksek miktarlarda biyolojik olarak ayrıştırılamayan ve biyolojik arıtımı engelleyici organik maddeler içeren atıksuların arıtımında elverişli bir metottur. Evsel atıksuyla karıştırılmış çöp sızıntı suyunun biyolojik arıtımında, çöp sızıntı suyu muhteviyatının aktif çamur prosesinin verimliliği üzerine olumsuz etkileri olabilir. Bu çalışmanın amacı, toz aktif karbon eklenmiş aktif çamur sistemlerinin sentetik evsel atıksu ile karıştırılmış çöp sızıntı suyunun arıtımındaki verimliliği ve uygulanabilirliğinin araştırılmasıdır.

Çalışmanın deneysel kısmının ilk kademesi, kullanılan aktif karbonun adsorpsiyon özelliklerinin belirlenmesi olmuştur. Takip eden kademeler toz aktif karbon eklenmiş aktif çamur reaktörlerinde arıtımı kapsamıştır. İkinci kademe, çöp sızıntı suyunun kesikli reaktörlerde arıtılması olmuştur. Üçüncü kademe, sürekli-akışlı reaktörleri simule etmek için kullanılan yarı-sürekli beslenen kesikli reaktörlerde arıtım olmuştur. Dördüncü kademe, sürekli-akışlı aktif çamur reaktörlerine toz aktif karbon eklenmesi olmuştur.

Çalışmanın sonuçları, evsel atıksuyla karıştırılmış çöp sızıntı suyunun arıtımında aktif çamura toz aktif karbon eklenmesinin kullanılabilecek bir metot olduğunu göstermiştir. Toz aktif karbon eklenmesi, biyolojik olarak ayrıştırılamayan organik maddelerin adsorpsiyon yolu ile giderilmesine bağlı olarak organik maddelerin çıkış konsantrasyonlarında önemli azalmalara yol açmıştır.

Bu çalışmadaki şartlar altında, toz aktif karbon eklenmiş aktif çamur sistemlerinde organik madde gideriminin, adsorpsiyon ve biyolojik giderimin basit bir bileşimi olduğu bulunmuştur. Aktif karbonun biyorejenerasyonu hipotezi de bu çalışmada elde edilen sonuçlar için geçerli değildir. Ancak toz aktif karbon eklenmesi, çöp sızıntı suyundaki biyolojik arıtımı engelleyici ve/veya zehirli bileşikleri adsorplayarak nitrifikasyon mikroorganizmalarının aktivitesini artırmak suretiyle nitrifikasyon hızlarını artırmıştır.

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LIST OF SYMBOLS

BOD_5	: 5 days Biochemical Oxygen Demand, mg/l
CFSTR	: Continuous-Flow Stirred Tank Reactor
COD	: Chemical Oxygen Demand, mg/l
FA	: Concentration of the free ammonia, mgN/l
F/M	: Food to microorganism ratio, mg COD/mg MLVSS.h
FNA	: Concentration of the free nitrous acid, mgN/l
GAC	: Granular Activated Carbon
k	: Zero-order substrate removal rate, mg COD/l.h
MLCOD	: Total COD of mixed liquor, mg/l
MLSS	: Mixed Liquor Suspended Solids, mg/l
MLVSS	: Mixed Liquor Volatile Suspended Solids, mg/l
NO_x-N	: NO_2-N + NO_3-N, mgN/l
OUR	: Oxygen Uptake Rate, mg O_2/l.h
q	: Zero-order specific substrate removal rate, mg COD/mg MLVSS.h
PAC	: Powdered Activated Carbon
r_{su}	: Substrate removal rate, mg COD/l.h
S	: Substrate concentration, mg/l
S_i	: Inert substrate concentration, mg/l
S_o	: Initial substrate concentration, mg/l
SCFB	: Semi-Continuously Fed Batch
SCOD	: Soluble COD (COD of filtrated sample), mg/l
TCOD	: Total COD (COD of unfiltrated sample), mg/l
TKN	: Total Kjeldahl Nitrogen, mgN/l
VSS	: Volatile Suspended Solids, mg/l
TSS	: Total Suspended Solids, mg/l
X	: Average biomass concentration, mg MLVSS/l
k'	: First-order substrate removal rate, h^{-1}
q'	: First-order specific substrate removal rate, l/mg MLVSS.h
θ	: Hydraulic retention time, h
θ_c	: Solids retention time, days

1. INTRODUCTION

Sanitary landfilling is a method of disposing refuse on land without creating nuisance or hazard to public health and safety. In spite of increased recycling, waste minimization and incineration in recent years, landfilling is still a technologically and economically feasible option for municipal solid waste management.

One of the main concerns associated with the disposal of refuse into landfills is the generation of leachate when water passes through them. Landfill leachate is usually a very high strength wastewater that contains high organic and inorganic constituents. Leachate may cause a considerable water pollution in the receiving media in case of direct discharge. Therefore leachate should be treated before discharge in an on-site treatment plant or should be discharged to a sewage system for a combined treatment.

Selection of the most appropriate method for treatment of leachate is very important and also troublesome because of the highly variable quantity and quality of leachate produced in a landfill. Almost all of the wastewater treatment applications can be used for leachate treatment.

Activated sludge treatment of leachate is a technically and economically feasible option for leachates that contain highly biodegradable organic matter among the other treatment methods. However due to the high strength of leachate, activated sludge process can fail in some cases due to microbial inhibition. Therefore, combined treatment of leachate and domestic wastewater in activated sludge with a suitable influent ratio, may be a convenient method to prevent adverse effects of leachate on biological treatment.

However activated sludge application may not be sufficient alone, because the biological treatment can only remove biodegradable substrates. The refractory organics can often be removed by adsorption on activated carbon. Activated carbon can be added to activated sludge in the form of powdered activated carbon (PAC). PAC added to activated sludge may enhance biological treatment efficiency besides removing the refractory organic compounds and some metals that cannot be removed by biological treatment.

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The aim of this study was to investigate the effectiveness and applicability of PAC added activated sludge systems in the treatment of leachate when combined with synthetic domestic wastewater.

The method employed in this study involved the addition of PAC to lab-scale Batch, Semi-Continuously Fed Batch (SCFB) and Continuous-flow activated sludge reactors. Experiments were conducted in both the conventional activated sludge reactors and PAC added activated sludge reactors for comparison purposes. The effluents from the reactors were analyzed for COD removal, ammonia removal and nitrification. Also the oxygen uptake rate, biomass concentration and pH in the reactors were analyzed throughout the study. The materials and methods used in this study are explained in detail in Section 3. The results obtained in the experimental work were discussed in Section 4.

2. THEORETICAL BACKGROUND

2.1. Landfill Leachate

2.1.1.Definition

Leachate is the name given to water that has passed through solid waste in a landfill. Leachate contains a variety of organic and inorganic pollutants generated by the chemical or biochemical reactions occurring within the landfill and by solubilization of solid waste constituents inside the landfill. Depending on the composition and extent of decomposition of the solid wastes and hydrogeological factors, leachate may become highly contaminated and thus become a highly polluted wastewater, the treatment of which is a major problem in wastewater engineering practices.

2.1.2. Leachate Generation in a Landfill

Solid wastes inside a landfill undergo various biological, physical, and chemical changes simultaneously. The water carries extractable chemicals with it when moving through the landfill. The decomposition, stabilization, and extraction of pollutants from a landfill depend upon composition of the wastes, degree of compaction, moisture content, presence of toxic and inhibitory chemicals, amount of percolating water, amount of nutrients, and temperature inside the landfill (1).

Leachate originates from the mass transfer from wastes to leaching water. The mechanism that regulates the mass transfer can be devided into three categories: (1) hydrolysis of solid waste and biological degradation, (2) solubilization of soluble salts contained in the waste, (3) dragging of particulate matter. The categories of this mechanism play a vital role on the quality of leachate generated (2).

2.1.2.1. Factors Influencing Leachate Generation

Many factors interact in the generation of variable quantity and quality of leachate from landfills. Some of the factors that affect leachate generation are: amount of precipitation, surface run-off, infiltration, evapotranspiration, freezing, and the other factors mentioned above that influence the extent of waste decomposition and stabilization.

The amount of leachate generation is closely related to the hydrological cycle. Depending on surface conditions, the precipitation falling on the land surface infiltrates through the cover soil or leaves the site as surface run-off. A portion of infiltrated water may be lost by evapotranspiration or it may be absorbed by soil. The infiltrated water inside the landfill site is iniitally absorbed by the solid wastes until the field capacity is exceeded. Reaching the field capacity may take from several months to several years. Until the landfill reaches its field capacity, or in other words becomes saturated, little or no leachate is produced (3).

The factors affecting leachate generation in a landfill site are mainly the climate, site topography, final cover material, vegetation cover, nature of solid waste, and site planning and operation.

The climate is very important for the amount of leachate generation, because the amount of annual precipitation is dependent on the climate. Site topography of the landfill site determines the amount of infiltrated water and surface run-off. If the site topography enhances surface runoff, less leachate is generated inside the landfill. The final cover material also enhances or prevents precipitation of rain water due to the permeability of the soil used as final cover material. If there is a vegetation cover on the landfill site, some of the water will be used and be sent to the air by evapotranspiration.

Nature of solid waste affects leachate generation by the moisture content and biodegradability of the solid waste. Organic solid wastes contain high amounts of moisture and moisture is produced as a product of degradation. Recirculation of leachate also increases the quantity of leachate generated, because recirculation increases solid waste decomposition by the increased moisture distribution.

2.1.2.2. Leachate Generation in Different Phases of Waste Stabilization

As the landfill ages, it passes through three stages at which the quality and quantity of leachate generation vary. The first stage is the aerobic decomposition phase. This phase is generally very short because of the limited amount of oxygen in the landfill relative to the high biochemical oxygen demand of the solid waste. The only layer of a landfill in aerobic phase is the upper layer where oxygen is trapped in fresh waste and is supplied by rainwater. During this phase, the landfill temperature rises well above ambient temperature due to a large amount of heat produced. Leachate produced during this phase dissolves highly soluble salts in the solid waste. Usually the aerobic phase is short and no substantial leachate generation will take place.

The second stage is an anaerobic stage at which large amounts of volatile fatty acids (VFA) such as acetic acid are produced by facultative anaerobic microorganisms, namely acidogenesis microorganisms. During this phase, the pH drops to between 4 and 6, and this helps to solubilize inorganic materials resulting in high inorganic ions (for example Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+) concentrations in the leachate generated in this stage. The sulphides, generated by the reduction of sulphates, may precipitate the iron, manganese and heavy metals that were dissolved by the acid fermentation. The chemical and biochemical oxygen demand of leachate, and the BOD/COD ratio are also very high at this stage due to the high VFA concentrations. Ammonia concentration is also high at this stage due to hydrolysis and fermentation of protein containing compounds.

The third stage, the methanogenic phase, occurs when the methane producing bacteria build up inside the landfill. Methane bacteria , which are strict anaerobes, convert volatile fatty acids (VFA) and other organic matter to methane and carbon dioxide. As the VFA concentration decreases, the pH increases hence a feed-forward increase in methane production takes place. During this stage, both the organic and inorganic constituents in the leachate and the BOD/COD ratio decrease in the leachate generated (1,2).

2.1.3. Characterization of Landfill Leachate

The characteristics of landfill leachate is site-specific and depends on variables such as the nature of solid waste, climatic and hydrogeological influence, phases of solid waste

decomposition, chemical and physical properties of percolating water, characteristics of soil cover and depth of refuse. The leachate characteristics are often reported as ranges, which are quite broad (4). Leachate characteristics in acidic and methanogenic phases obtained from various landfills are shown in Table 2.1.

The nature of solid waste influences the composition of leachate, because it influences the degradation of waste in the landfill. Particularly, the presence of substances which are toxic or inhibitory to bacterial flora may inhibit biological degradation processes within the landfill, resulting in high organic constituents in the leachate. The inorganic content of leachate depends on pH, the contact between solid waste and leaching water and the chemical balance at the solid-liquid interface. Metals are released from the solid wastes under acidic conditions.

Chemical processes such as precipitation, dissolution, redox and sorption reactions are also influenced by pH. In the acidic phase, low pH increases solubilization of chemical constituents (oxides, hydroxides, and carbonated species) and decrease the sorptive capacity of waste. Reducing conditions, at which the Redox potential is negative, are encountered in the anaerobic phases of landfill stabilization and influence the solubility of nutrients and metals in leachate.

The most important factor that effects leachate composition is the landfill age. Landfill age may be determined either from the deposition of waste or from the first appearance of leachate. Landfill age indicates the phase and degree of waste stabilization in the landfill. The organic and inorganic pollutant load in leachate composition reaches maximum during the first years of operation (2-3 years) and then gradually decreases (2). As the landfill ages, a decrease in volatile fatty acids, and an increase in fulvic-like fractions is observed. Deactivation in bacterial and viral populations with landfill age is another phenomena. The possible reasons for this deactivation are adverse environmental conditions such as temperature rise or persistent low pH (1).

The decrease in organic compounds in leachate with increasing landfill age is more rapid than the decrease in inorganic compounds. The decrease in organics is both due to decomposition and washout, whereas the decrease in inorganics is only due to washout by

percolating water. The ratio of total volatile solids to total fixed solids also decreases as the landfill ages.

It has been shown that the concentrations of organics are high during the active stages of decomposition and decreases as the fill stabilizes (5). For a new landfill (less than 2 years), the COD is in the range of 3000-60000 mg/l with a typical value of 18000 mg/l and BOD is in the range of 2000-30000 mg/l with a typical value of 10000 mg/l. The BOD to COD ratio is also significantly high in a young landfill leachate favoring biological treatment. In mature landfills the organic matter consists mainly of non-biodegradable organics, and this results in very low BOD/COD ratios. In a study, a decrease in BOD/COD ratio from 0.47 to 0.07 in 23 years has been reported. In another study, BOD/COD ratio decreased from 0.8 to 0.05 within a period of 17 years (1).

Mature landfill leachates may or may not contain high amounts of ammonia. But most of the leachates from old landfills contain very high amounts of ammonia that requires additional treatment. The low BOD/COD ratios imply that biological treatment itself can not be a good option to treat leachate from an old landfill. Hence, advanced treatment methods should be performed in order to achieve a good removal of organics in old landfill leachates.

Landfill leachate from a municipal solid waste landfill may contain high amounts of pathogenic microorganisms. The microorganisms found in leachate are basically bacteria, viruses, fungi and parasites. These microorganisms in leachate pose health risk when untreated.

Co-disposal of many sorptive material such as incinerator ash, fly ash, kiln dust and limestone cause a reduction in the mobility of many hazardous chemicals in leachate by adsorption of metallic ions, formation of less soluble calcium and carbonate compounds, and precipitation of metals with pH increase (6).

TABLE 2.1. Leachate Characteristics (Parameters with differences between acetic and methanogenic phase) (6).

	Average	Range
Acetic Phase		
pH	6.1	4.5-7.5
BOD_5 (mg/l)	13000	4000-40000
COD (mg/l)	22000	6000-60000
BOD_5/COD	0.58	
SO_4 (mg/l)	500	70-1750
Ca (mg/l)	1200	10-2500
Mg (mg/l)	470	50-1150
Fe (mg/l)	780	20-21000
Mn (mg/l)	25	0.3-65
Zn (mg/l)	5	0.1-120
Methanogenic Phase		
pH	8	7.5-9.0
BOD_5 (mg/l)	180	20-550
COD (mg/l)	3000	500-4500
BOD_5/COD	0.06	
SO_4 (mg/l)	80	10-420
Ca (mg/l)	60	20-600
Mg (mg/l)	180	40-350
Fe (mg/l)	15	3-280
Mn (mg/l)	0.7	0.03-45
Zn (mg/l)	0.6	0.03-4
(No differences between phases could be observed)		
Cl (mg/l)	2100	100-5000
Na (mg/l)	1350	50-4000
K (mg/l)	1100	10-2500
Alkalinity ($mgCaCO_3$/l)	6700	300-11500
NH_4-N (mg/l)	750	30-3000
Org N (mg/l)	600	10-4250
Total N (mg/l)	1250	50-5000
NO_3-N (mg/l)	3	0.1-50
NO_2-N (mg/l)	0.5	0-25
Total P (mg/l)	6	0.1-30
AOX* (µg/l)	2000	320-3500
As (µg/l)	160	5-1600
Cd (µg/l)	6	0.5-140
Co (µg/l)	55	4-950
Ni (µg/l)	200	20-2050
Pb (µg/l)	90	8-1020
Cr (µg/l)	300	30-1600
Cu (µg/l)	80	4-1400
Hg (µg/l)	10	0.2-50

*adsorbable organic halogen

2.2. Activated Carbon Adsorption

2.2.1. Definition

Adsorption is recognized as a significant phenomenon in most natural physical, biological and chemical processes. Sorption on solids has become a widely used operation for purification of wastewaters. Activated carbon is the most widely used material in wastewater treatment technologies.

Adsorption is the interface accumulation or concentration of substances at a surface or interface. Adsorption can occur between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being concentrated or adsorbed is termed the adsorbate, and the adsorbing phase is termed the adsorbent.

2.2.2. The Relationship Between Surface Tension and Adsorption

Adsorption is a surface phenomenon in which matter is extracted from one phase and concentrated at the surface of a second phase. Such surface reactions must occur as a result of the active forces within the phase or surface boundaries. These forces result in characteristic boundary energies.

A pure liquid drop placed on a flat plate will resist spreading and retain a spherical shape, because it tries to minimize its surface area and thus to minimize its surface energy. This surface tension developed at the surface of the liquid results from the attractive forces between molecules of liquid. A pure liquid always tends to reduce its free energy through the action of surface tension, which is quantitatively equal to the amount of work that would be necessary to compensate the natural reduction in free surface energy. In order to enlarge a liquid surface, the bonds between liquid molecules need to be broken.

A large number of soluble materials, such as detergents, can change the surface tension of a liquid. Such materials decrease the tension at the surface during movement of the solute to the surface. A solute that decreases surface tension must be concentrated at the surface because the solvent molecules have a smaller attractive force for the molecules of the

solute than for each other. The phenomenon of increased concentration of the soluble material in a boundary or surface is adsorption (7).

2.2.3. Types of Adsorption

There are two primary driving forces for adsorption of a solute from a solution onto a solid phase. The first primary driving force is a consequence of lyophobic (solvent disliking) character of the solute relative to the solvent. The second driving force is a consequence of the high affinity of the solute for the particular solid. Adsorption results from the action of these two forces in most of the wastewater treatment practices.

The degree of solubility of a dissolved substance is the most important factor for the intensity of the two driving forces. A hydrophilic substance is less adsorbable on a solid phase because it likes the solvent system. On the other hand, a hydrophobic substance is water disliking and is more likely to be adsorbed on the adsorbent. Many organic contaminants have solubility amphoteric character with both hydrophobic and hydrophilic groups present in the molecule structure. In this case, the hydrophobic part of the molecule is adsorbed, and the hydrophilic part tends to stay in the solution.

The second primary driving force for adsorption; the affinity of solute for the solid may be due to electrical attraction of the solute to the solid, van der Waals attraction or the chemical interaction with the adsorbent.

Adsorption due to electrical adsorption is a process in which ions in the solution concentrate at the adsorbent surface as a result of electrostatic attraction to charged sites at the surface. This type of adsorption is termed the exchange adsorption. Ion exchange is an exchange adsorption phenomenon. The charge of the ion is the determining factor for exchange adsorption. Ion with the higher charge is preferably adsorbed.

Adsorption occurring as a result of van der Waals forces is generally termed physical adsorption. In physical adsorption, adsorbed molecule is not affixed to a specific site but is free to undergo translational movement within the interface. Physical adsorption is predominant at low temperatures, and is characterized by a relatively low adsorption

energy. The adsorbate is less strongly held by the adsorbent compared to chemical adsorption.

Chemical adsorption, or chemisorption, is the phenomenon in which the adsorbate undergoes chemical interaction with the adsorbent. Chemically adsorbed adsorbates are not free to move on the surface or within the interface. Chemical adsorption is characterized by a high adsorption energy, since the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical adsorption is more predominant at high temperatures, because chemical reactions proceed more rapidly at higher temperatures.

The three forms of adsorption interact in most of the adsorption phenomena. Adsorption processes involving organic molecules are designated as specific adsorptions that exhibit a large range of binding energies from values associated with physical adsorption to higher energies involved in chemical adsorption. Therefore it is generally difficult to distinguish between physical and chemical adsorption in wastewater treatment processes aiming the removal of organic contaminants (7).

2.2.4. Factors Influencing Adsorption

Surface Area of Adsorbent:

The extent of adsorption is proportional to specific surface area due to the fact that adsorption is a surface phenomenon. Specific surface area is the available portion of the total surface area for adsorption. Therefore, the more finely divided and the more porous the solid, the greater is the amount of adsorption accomplished per unit weight of a solid adsorbent.

Nature of the Adsorbate:

The degree of solubility of the solute is of primary concern for adsorption equilibria. There is an inverse relationship between the extent of adsorption of a particulate solute and its solubility in the solvent from which the adsorption occurs. High solubility means stronger solute-solvent bonds than the attraction forces between the solute and the adsorbent.

Polarity of the adsorbate is another important factor. A polar solute is preferably adsorbed by a polar adsorbent, and a nonpolar solute is more easily adsorbed by a nonpolar adsorbent. Dissociation constants of weak acids and bases, e.g. organic acids, also influence the extent of adsorption. Dissociation constants determine the extent of ionization, and hence the adsorption of a particular acid or base is influenced since the adsorption of ionic and molecular forms differ.

pH :

Many organics form negative ions at high pH values, positive ions at low pH values, and neutral molecules at intermediate pH ranges. Adsorption of many organic materials is higher with neutral orientations. In general, adsorption of organic pollutants by activated carbon from water is increased with decreasing pH. This results from the neutralization of negative charges at the surface of the carbon at low pH values due to high hydrogen concentration. Thereby hindrance of diffusion due to negative charges is reduced and more active sites become available for adsorption. The degree of this effect varies due to the type and activation technique of the active carbon, and the characteristics of the wastewater.

Temperature:

Since the adsorption reactions are exothermic, the extent of adsorption generally increases with decreasing temperature.

2.2.5. Adsorption Equilibrium and the Adsorption Isotherms

When an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long time, the adsorbent and the surrounding fluid reach a dynamic equilibrium. At this position of equilibrium, there is a defined distribution of solute between the solid and liquid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process; it may be a function of the concentration of the solute, the concentration and nature of competing solutes, the nature of the solution, and so on.

The relation between amount adsorbed, q, and concentration in the liquid phase, C, at temperature, T, is called the adsorption isotherm at T.

$$q = q(C) \text{ at } T \tag{2.1}$$

The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk liquid at constant temperature (Eq. 2.1). The amount of adsorbed material per unit weight of adsorbent increases with increasing concentration , but not in direct proportion (8).

Adsorption isotherms are described in many mathematical forms, some of which are based on simplified physical picture of adsorption, while others are purely emprical and intended to correlate the experimental data in simple equations.

2.2.5.1. The Langmuir Isotherm

The Langmuir adsorption model is valid for monolayer adsorption, in which localized adsorption takes place on an energetically uniform surface without any interaction between adsorbed molecules. It is assumed that energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is given in Equation 2.2.

$$q_e = \frac{Q^\circ bC}{(1+bC)} \tag{2.2}$$

in which C is the measured concentration in solution at equilibrium, Q° is the number of moles of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface, q_e is the number of moles of solute adsorbed per unit weight at concentration C, and b is a constant related to the energy of adsorption. The linear form of the Langmuir equation is given in Equation 2.3, The linear form is illustrated in Figure 2.1a, from the slope and intercept of which b and Q° can be obtained.

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \left(\frac{1}{bQ^\circ}\right)\left(\frac{1}{C}\right) \tag{2.3}$$

2.2.5.2. The BET Isotherm

Te Brunauer, Emmeth, Teller (BET) model represents isotherms reflecting apparent multilayer adsorption. BET isotherm is more generally applicable than the Langmuir isotherm and reduces to Langmuir model when the limit of adsorption is a monolayer. The BET model assumes that a number of layers of adsorbate molecules form at the surface and that the Langmuir equation applies to each layer. A further assumption of the BET model is that a given layer does not need complete formation prior to initiation of subsequent layers. With the additional assumption that layers beyond the first have equal energies of adsorption for adsorption from solution, the BET equation takes the following simplified form;

$$q_e = \frac{BCQ^\circ}{(C_s - C)[1 + (B-1)(C/C_s)]} \tag{2.4}$$

where C_s is the saturation coefficient of the solute and B is a constant expressive of the energy of interaction with the surface. The linerarized form of the BET equation is given in Equation 2.5. The linear form is illustrated in Figure 2.1b, from the slope and intercept of which B and Q° can be obtained.

$$\frac{C}{(C_s - C)q_e} = \frac{1}{BQ^\circ} + \left(\frac{B-1}{BQ^\circ}\right)\left(\frac{C}{C_s}\right) \tag{2.5}$$

2.2.5.3. The Freundlich Isotherm

Freundlich equation is a special case for heterogeneous surface energies in which the energy term, b, in the Langmuir equation (Eq. 2.2) varies as a function of surface coverage, q_e, strictly due to variations in heat of adsorption. Freundlich equation has the general form

$$q_e = K_F\, C^{1/n} \tag{2.6}$$

in which K_F and n are constants.

Freundlich equation is usually converted to the logarithmic form for better data interpretation (Equation 2.7).

$$\text{Log } q_e = \text{Log } K_F + 1/n \text{ Log } C \qquad (2.7)$$

The linear form for Freundlich equation is illustrated in Figure 2.1c. From the slope and intercept of the plot, the Freundlich constants K_F and n can be determined.

The Freundlich equation agrees quite well with the Langmuir equation at moderate concentration ranges. However, unlike the Langmuir equation, it does not reduce to a linear adsorption expression at very low concentrations, and does not agree well with the Langmuir equation at very high concentrations, since n must reach a limit when the surface is fully covered. Freundlich equation is commonly used for comparison of powdered carbons for water treatment (7).

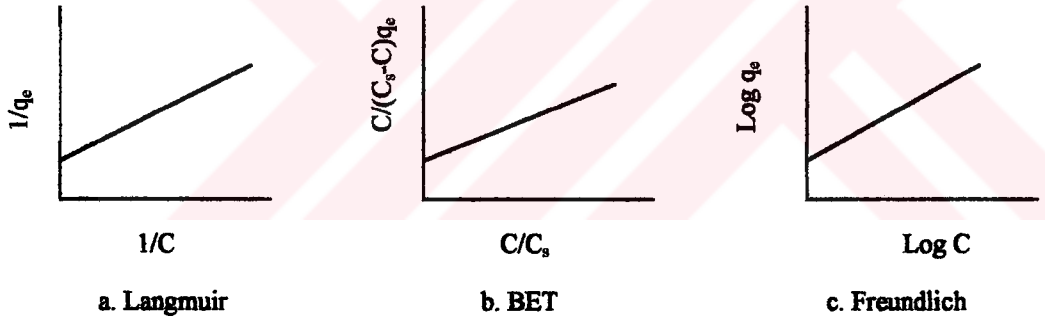


FIGURE 2.1. Linear forms for graphical representation of adsorption equations (7).

2.2.6. Activated Carbon

Activated carbons are the microporous carbonaceous adsorbents. A large variety of organic solutes and a more limited number of inorganic solutes can be removed from aqueous waste streams by adsorption onto activated carbon. A list of organic matter that can be adsorbed by activated carbon is listed in Table C1 in Appendix C (4). Activated carbon has a high adsorptive surface area (500-1500 m^2/g) and is used as powdered activated carbon (PAC) or granular activated carbon (GAC) bed. Carbon adsorption process works best with chemicals that have a low water solubility, high molecular weight, low polarity, and low degree of ionization.

2.2.6.1. Preparation of Activated Carbons

Commercially available activated carbons are prepared from carbon-containing source materials such as coal (anthracite or brown coal), lignite, wood, nut shell, petroleum and sometimes synthetic high polymers. These materials are first pyrolized and carbonized at several hundred degrees centigrade. The volatile fraction and low molecular products of hydrolysis are removed during this process, and the residual carbonaceous material undergo the following activation process by using oxidation gases, such as steam at above 800°C or carbon dioxide at higher temperatures. Micropores are formed during the activation process. The yield of activation process is in most cases below 50% and sometimes less than 10%.

2.2.6.2. Activated Carbon Characteristics

Micropores of activated carbon, where most adsorption takes place, are in the form of two-dimensional spaces between two graphite-like walls, two-dimensional crystalline planes composed of carbon atoms. The distance between the two neighboring planes of graphite is 0.376 nm, but in the case of activated carbons which have a rather disordered crystalline structure (turbostratic structure), this figure must be larger since adsorbate molecules are not accessible otherwise (Fig. 2.2).

Activated carbons generally contain some oxygen complexes which arise from either raw materials or from chemical adsorption of air during the activation process or during storage after activation. Surface oxides add a polar nature to activated carbons. Oxygen complexes on the activated carbon surface exist mainly in the form of four different acidic surface oxides; strong carboxylic groups, weak carboxylic groups, phenolic groups, and carbonyl groups. There are several other forms of oxides including basic groups such as cyclic ether groups. The basic character of activated carbon arises when activation is conducted at higher temperatures. Surface oxide groups can be removed by heat treatment of carbons in an inert atmosphere or under vacuum (8).

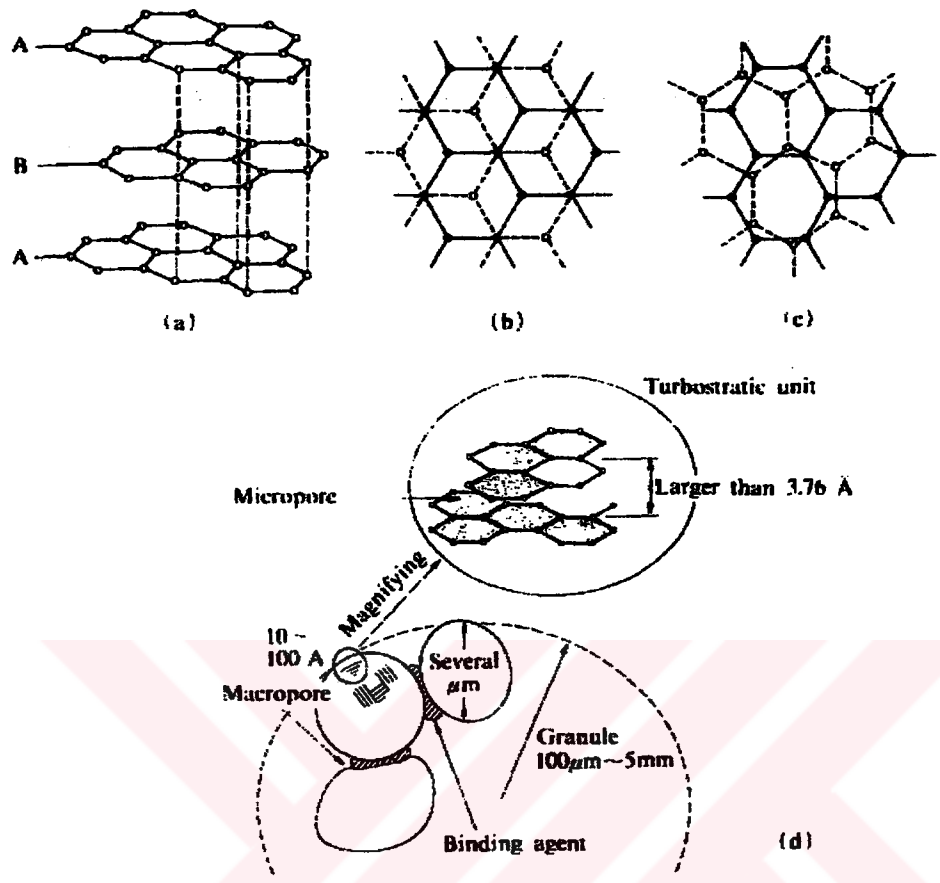


FIGURE 2.2. Graphite structure (a,b) and turbostratic structure (c) of activated carbon. Conceptual illustration of granular activated carbon (d) (8).

Chemical studies have shown that activated carbon may contain large quantities of mineral ions, mostly calcium, sulfate and phosphate ions. These groups influence surface properties in the same way as do acidic or basic organic surface functional groups (9).

Activated carbon also contains some ashes derived from the raw material. The amount of ash ranges from 1% to 12%. Ashes consist mainly of silica, alumina, iron, alkaline and alkaline earth metals. The ashes in activated carbon increase hydrophilicity of activated carbon And this is advantageous when PAC is used for water treatment because the PAC is more likely to stay inside the reactor rather than sticking on the reactor walls if ash content is high. Another function related with ash content is that the catalytic effects of alkaline-earth and some other metals during activation or regeneration process modifies pore size distribution to larger pore range.

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2.2.6.3. Powdered Activated Carbon

Powdered activated carbon (PAC) is generally produced from wood in the form of saw dust. The average size of PAC is in the range of 15-25 μm. Intraparticular diffusion is not the rate limiting step in PAC adsorption due to the very low particle sizes. PAC is considerably used in water treatment for both drinking water and watewater treatment. PAC is either added to activated sludge or contacted with the wastewater seperately. PAC is also used in chemical industry for decolorization in food processes such as sugar refinery, for oil production and sodium glutamate production as well as wine preparation.

Besides the adsorption characteristics of PAC, its surface charge may also cooperate as a coagulant for colloidal fractions in the liquid phase. Therefore the regeneration of PAC may become rather difficult, because seperation of colloidal particles will be required before regeneration. Spent PAC is generally dumped rather than regeneration for reuse.

2.2.6.4. Granular Activated Carbon

Granular activated carbons (GAC) are either in the form of crushed granules (coal or shell) or in the pelletized form prepared by granulation of pulverized powders using binders such as coal tar pitch. GAC produced from petroleum pitch is prepared by activation of the spherical beads prepared from the pitch. In liquid phase adsorption, the intraparticle diffusion often becomes the rate limiting step in GAC adsorption. Particle sizes in the range of 12/42 mesh are advantageous for liquid phase adsorption.

GAC filters are widely used in drinking water and wastewater purification processes as an advanced treatment method. In some GAC applications for wastewater treatment a microbiological film can form on the GAC particles for biological treatment combined with GAC adsorption. GAC is also used in industry for decolorization in sugar refinery. Spent GAC can be regenerated by a thermal method for reuse. Therefore the consumption of GAC is normally less than powdered activated carbon (10).

2.3. Treatment of Landfill Leachate in Activated Sludge

2.3.1. Activated Sludge Process

2.3.1.1. Basic Features

Activated sludge process is a biological treatment process, that involves the production of an activated mass of microorganisms capable of stabilizing a waste aerobically. The waste stream is contacted with a mixed culture of microorganisms, the microorganisms consume the organic matter in the waste stream and the individual organisms flocculate to form an active mass of microbial floc called activated sludge. The major objective is the removal of organic matter, and in many cases the removal of nutrients such as nitrogen and phosphorus. Trace concentrations of inorganics may be removed due to precipitation or adsorption onto microorganisms during biological treatment. Important microorganisms in biological treatment are bacteria, fungi, algae, protozoa and rotifiers (11).

The activated sludge process must provide optimum environmental conditions for enhanced degradation of organic wastes. The methods for optimizing the biological degradation include controlling the dissolved oxygen level, nutrient addition, increasing the concentration of microorganisms, and maintaining many environmental factors such as pH, temperature and mixing. The mixture of the activated sludge and wastewater in the aeration basin is called mixed liquor suspended solids (MLSS), and the volatile organic fraction is called mixed liquor volatile suspended solids (MLVSS) (1).

The MLSS flows from the aeration basin into a secondary carifier where the activated sludge is settled. A portion of the settled sludge is returned to the aeration basin to maintain the proper food-to-microorganism (F/M) ratio. Since more activated sludge is produced then that can be used in the process, some of it is wasted from the aeration basin or from the return sludge line to the sludge handling systems for further treatment and disposal (1).

The principle types of aeration basin are plug flow (PFR) and continuously stirred tank (CSTR) reactors. Design parameters such as aeration basin volume, effluent quality, rates

of return sludge and waste sludge, aeration period, oxygen utilization rates, F/M ratio,hydraulic residence time, and mean cell residence time can be calculated from equations that express biological growth and substrate removal rates in terms of biological kinetic coefficients (11).

2.3.1.2. Organic Matter Removal

In aerobic biological treatment processes, the organics are decomposed to carbon dioxide and water. Oxygen is essential for decomposition of organic matter. In the activated sludge reactor, the heterotrophic bacterial culture carries out the conversion in general accordance with the stoichometry shown in Equation 2.8 in which CHONS represents the organic substrates and $C_5H_7NO_2$ represents the new bacterial cells produced.

$$CHONS + O_2 + \text{nutrients} \rightarrow CO_2 + NH_3 + C_5H_7NO_2 + \text{other end products} \quad (2.8)$$

When the concentration of available organic substrate is at a minimum, the microorganisms are forced to metabolize their own protoplasm. This phenomenon is termed the endogenous respiration of activated sludge, which is stochiometrically shown in Equation 2.9.

$$C_5H_7NO_2 + 5\ O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O + \text{energy} \quad (2.9)$$

The organic matter in a wastewater may be subdivided into a number of categories based on the biodegradability and solubility. The distribution of organic fractions in a wastewater in terms of COD are shown in Figure 2.3. The total influent COD has two major components; the total nonbiodegradable or inert COD, and the total biodegradable COD (12).

Nonbiodegradable organic matter passes through an activated sludge system unchanged in form. Inert soluble organic matter leaves the system at the same concentration that it enters. Inert particulate organic matter becomes inmeshed in the activated sludge and thus is removed from the system through sludge wastage. Unbiodegradable organic compounds are also generated during activated sludge process, both in soluble form (metabolism-by-products) and in particulate form (unbiodegradable fraction of newly synthetized biomass).

Biodegradable organic matter can be divided into two fractions due to the rate of biodegradation; readily biodegradable and slowly biodegradable. For practical purposes, slowly biodegradable organics are treated as if they were particulate and can also be divided into two fractions due to the rate of hydrolysis; rapidly hydrolizable and slowly hydrolizable. The common feature of slowly biodegradable organics is that they cannot pass through the cell wall, and need to undergo extracellular hydrolysis before absorption. Readily biodegradable COD is mainly composed of soluble compounds such as volatile fatty acids, simple carbohydrates, alcohols, amino acids, etc., that can be directly absorbed for synthesis (12,13,14).

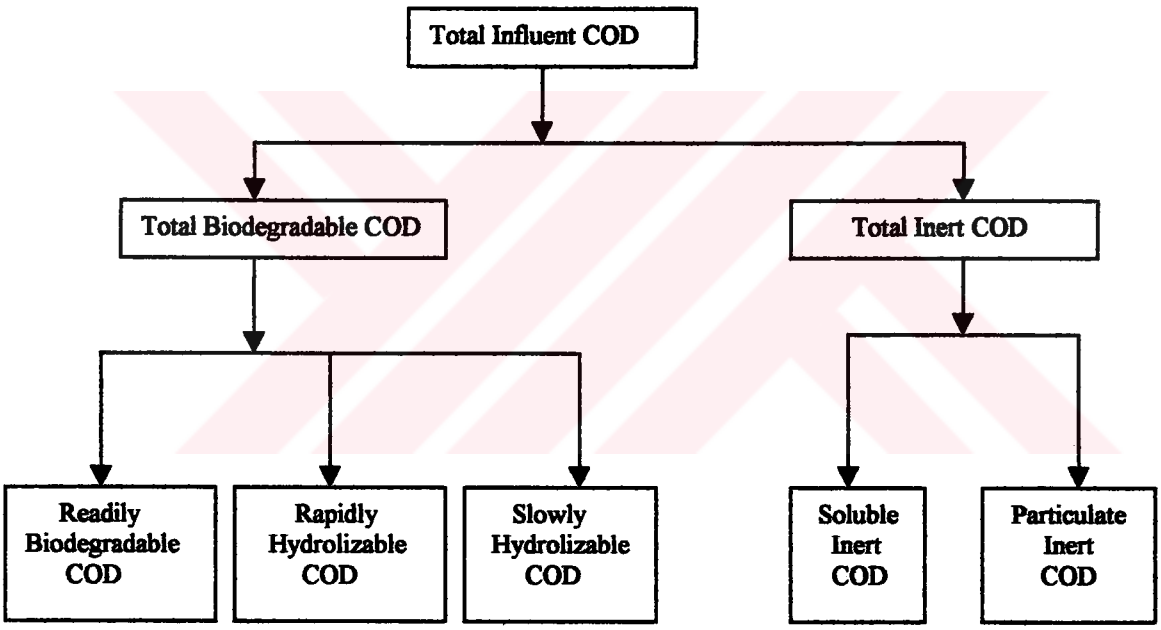


FIGURE 2.3. Distribution of COD fractions in wastewaters (12).

2.3.1.3. Nitrification

Nitrification is an autotrophic process in which energy for bacterial growth is derived from the oxidation of nitrogen compounds, primarily ammonia. Nitrification bacteria, or nitrifiers, use carbon dioxide rather than organic carbon for cell synthesis. Nitrification is a two step process that involves two kinds of autotrophic microorganism, namely *Nitrosomonas* and *Nitrobacter*. The two steps of oxidation reactions, which yield the energy required for the synthesis of new nitrifier cells, are shown in Equations 2.10-2.11.

$$NH_4^+ + \frac{3}{2}O_2 \xrightarrow{Nitrosomonas} NO_2^- + 2H^+ + H_2O \quad (2.10)$$

$$NO_2^- + \frac{1}{2}O_2 \xrightarrow{Nitrobacter} NO_3^- \quad (2.11)$$

Nitrogeneous matter in a wastewater, like carbonaceous matter, can be divided into two categories; nonbiodegradable and biodegradable, each with further subdivisions. Nonbiodegradable fraction is associated with the nonbiodegradable organic matter. The biodegradable fraction contains ammonia, soluble organic nitrogen and particulate organic nitrogen. Particulate organic nitrogen is hydrolized to soluble organic nitrogen in parallel with the hydrolysis of slowly biodegradable organic matter. The soluble organic nitrogen is acted on by heterotrophic bacteria and converted to ammonia (15).

2.3.1.4. Respirometry of Activated Sludge

Respirometry is the measurement of oxygen consumption rate of activated sludge under well defined experimental conditions. Respirometric measurements of activated sludge are based on the observations of the changes in dissolved oxygen concentration in the system. Oxygen uptake rate (OUR) indicates the amount of oxygen used by microorganisms as they utilize substrates. Changes in dissolved oxygen in the system are indicative of the respiration of activated sludge (endogenous oxygen uptake rate) and the uptake of substrate or wastewater (exogenous oxygen uptake rate).

The value of oxygen uptake rate is obtained by taking a sample of mixed liquor , saturated with dissolved oxygen (DO), and measuring the decrease in DO with time by using a DO probe. The slope of the line gives the OUR, and is typically reported as mg O_2/l.min or mg O_2/l.h. The combination of OUR with MLVSS concentration yields a value termed specific oxygen uptake rate (SOUR), or respiration rate. SOUR indicates the amount of oxygen used by microorganisms, and is reported as mg O_2/mg MLVSS.h (11).

OUR is successfully used as a means of monitoring and controlling the activated sludge process. The amount of oxygen to be transferred into the aeration tanks theoretically equals the amount of oxygen required by the microorganisms in the activated sludge system. When oxygen limits the growth of microorganisms, filamentous organisms may predominate and the settleability and the quality of the activated sludge may be poor. In practice, the DO concentration in the aeration tank should be maintained at about 1.5-4 mg/l; 2 mg/l is a commonly used value (11).

Respirometric measurements are also very widely used for the determination of biokinetic constants. In the aerobic batch tests, with the selection of an appropriate F/M ratio, the maximum growth rate of microorganisms can be obtained at the initial period when OUR stays constant. In this period, readily biodegradable organic matter is removed. After the depletion of readily biodegradable substrates, OUR drops to a level only correlated with the hydrolysis of slowly biodegradable organics and the endogenous respiration (14). Besides, cumulative OUR can successfully replace COD in the determination of biomass yield in batch tests if nitrification is prevented, since both are parameters incorporating the oxygen demand of microorganisms (16).

Respirometry eliminates the burden of chemical specific analyses associated with substrate depletion tests. In addition, the acquisition of dissolved oxygen data can be continuous and automated and the respiration of small substrate concentrations can be quantified due to the high sensitivity of DO measurements when compared to organic substrate measurements (17).

2.3.2. Application of Activated Sludge to Leachate Treatment

Leachate treatment has been successfully carried out by using the activated sludge processes in most cases (1). According to the laboratory data of many researchers, the following generalizations can be made in treating landfill leachate by the activated sludge process(1):

(1) BOD and COD removal: 90-99 percent

(2) Metal removal: 80-99 percent

(3) Operational range: (a) MLVSS concentration of 5000-10000 mg/l, (b) F/M ratio of 0.02-0.06 BOD_5 / MLVSS.day, (c) Hydraulic retention time of 1-10 days, (d) Solids retention time of 15-60 days.

The operational parameters with high biomass concentrations, low F/M ratios, high hydraulic and solids retention times indicate that extensive biological activity is required for the removal of organic matter in leachate that are not readily oxidizable. The problems reported for leachate treatment in activated sludge are: (1) foaming due to excessive aeration in conjunction with high metal concentrations, (2) requirement of antifoaming agents and mechanical mixing to reduce foaming, (3) inhibition of biological activity due to nutrient deficiency (particularly phosphorus concentration is often insufficient in leachate for biological treatment), (4) inhibition of biological treatment due to metals and other constituents in leachate.

Studies with leachate have resulted in four distinct and successive phases of substrate utilization by microorganisms: (1) carbohydrates, (2) fatty acids, (3) catabolites such as aminoacids, and (4) humic carbohydrate-like substances with molecular weight greater than 50000. The residual refractory organics remaining beyond the fourth phase consist mainly of fulvic acid-like materials with a molecular weight in the range of 500-10000 (1).

Leachate from a young landfill contains high amounts of volatile acids, and hence can be more easily treated by biological processes. The high BOD_5/COD ratios obtained in young landfills also prove the biological treatability of leachates from young landfills. In most cases, it is not convenient to treat leachate from old landfills which contains large proportions of refractory organic matter. Chemical-physical treatment processes should be applied to leachates from old landfills. Therefore the characterization and estimation of future changes in the characterictics of leachate is very essential for the applicability of activated sludge to leachate and also for the proper choose of the other treatment methods.

Organic nitrogen and ammonia concentrations in leachate are so high in most cases that removal of nitrogen is essential. Separate or one stage nitrification of leachate in activated sludge is one of the most promising methods for ammonia removal from leachate.

Activated sludge process can also remove metals from leachate by precipitation and adsorption on biomass. In the literature, 95 percent removal of aluminium, cadmium, chromium, iron and manganese has been reported (1). MLVSS/MLSS ratio decreases in an activated sludge reactor because of heavy metal precipitation. Inhibition of activated sludge due to the high metal concentrations in most landfill leachates results in the requirement of pretreatment to reduce metal concentrations prior to biological treatment.

2.3.3. Inhibition of Activated Sludge Process in Leachate Treatment

2.3.3.1. Inhibition of Organic Substrate Removal

Heavy metals and nonmetallic wastes in leachate, including organic compounds, may have an inhibitory or toxic effect upon the biological treatment process. A list of pollutants that have an inhibitory effect on the activated sludge process is presented in Table 2.2 (11).

TABLE 2.2. Threshold concentrations of pollutants inhibitory to the activated sludge process.(11)

Pollutant	Concentration (mg/l)	
	Carbonaceous Removal	Nitrification
Aluminium	15-26	-
Ammonia	480	-
Arsenic	0.1	-
Borate	0.05-100	-
Cadmium	10-100	-
Calcium	2500	-
Chromium (Hexavalent)	1-10	0.25
Chromium (Trivalent)	50	-
Copper	1.0	0.005-0.5
Cyanide	0.1-5	0.34
Iron	1000	-
Manganese	10	-
Magnesium	-	50
Mercury	0.1-5.0	-
Nickel	1.0-2.5	0.25
Silver	5	-
Sulfate	-	500
Zinc	0.8-10	0.08-0.5
Phenol	200	4-10
Cresol	-	4.16
2-4 Dinitrophenol	-	150

Heavy metals, such as copper, zinc, nickel, lead, cadmium, and chromium can react with the microbial enzymes to retard or completely inhibit metabolism. Heavy metals present as precipitates may be solubilized by a change in pH, causing a decrease in biological treatment efficiency. Biological degradation of certain organic compounds such as cyanide and humic acids, may cause the release of toxic metals from soluble complexes and retard biological activity. Nonmetallic compounds above specific threshold concentrations in leachate can also cause a temporary loss in biological process efficiency if sufficient acclimatization is not provided (11).

2.3.3.2. Inhibition of Nitrification

Nitrifiers are much more sensitive to toxic and inhibitory compounds than heterotrophs. Many substances which kill or inhibit the growth of nitrifiers have little or no effect on the heterotrophic bacteria responsible for carbonaceous removals. Threshold values for various inhibitory substances shown in Table 2.2 are much lower for nitrification than for carbonaceous removal. Several factors such as reduced temperature, limiting oxygen, elevated pH and presence of free ammonia and free nitrous acid were shown to inhibit nitrification (18).

Inhibition of nitrification generally is not a problem in the treatment of wastewaters with low ammonia (NH_4^+) and nitrite (NO_2^-) concentrations. When there is a high concentration of reduced nitrogen in the wastewater, both ammonia oxidation and nitrite oxidation may be inhibited. In many cases, the most important compounds that inhibit nitrification are the two substrates in nitrification; ammonia and nitrite. The unionized forms of ammonia and nitrite, namely free ammonia (FA) and free nitrous acid (FNA) are the inhibitory substances rather than ammonia or nitrite ions.

The concentrations of FA that inhibit *Nitrosomonas* are greater than those that inhibit *Nitrobacters*. FA concentrations in the range of 10 to 150 mg/l can inhibit ammonia oxidation, and FA concentrations in the range of 0.1 to 1 mg/l can inhibit nitrite oxidation. The inhibition of *Nitrobacters* starts at FNA concentrations between 0.22 and 2.8 mg/l, and severe inhibition is observed at higher values. Acclimation of nitrifiers to FA and FNA, temperature and the number of nitrifiers may effect the inhibitory concentrations of FA and

FNA (19). Since *Nitrobacter* species are much more exposed to inhibition than *Nitrosomonas*, nitrite accumulation is frequently observed in high strength wastewaters like leachate (18). Depending on the pH, the concentrations of FA and FNA can be calculated using the Equations 2.12 and 2.13 (19);

$$FA = \frac{(NH_4 - N).(10^{pH})}{(K_b / K_w) + 10^{pH}} \qquad (2.12)$$

where, FA = concentration of free ammonia nitrogen, mg NH_3-N/l

NH_4-N = concentration of ammonium nitrogen, mg NH_4^4-N/l

K_b = Ionization constant for ammonium

K_w = Ionization constant for water

$K_b / K_w = e^{(6344/273+°C)}$

$$FNA = \frac{NO_2 - N}{K_a.10^{pH}} \qquad (2.13)$$

where, FNA = concentration of free nitrous acid nitrogen, mg HNO_2-N/l

NO_2-N = concentration of nitrite nitrogen, mg NO_2^--N/l

K_a = Ionization constant for nitrite, $e^{(-2300/273+°C)}$

2.3.4. Combined Treatment of Leachate with Domestic Wastewater

Leachate generated in a landfill must be either hauled off-site for treatment and disposal or must be treated in an on-site treatment plant for direct discharge. The option of constructing an on-site treatment facility is costly because tertiary treatment is usually required for high strength leachates to meet established discharge standards. However if the landfill is located near a publicly owned sewer, direct discharge of leachate to sewer system, where it will be co-treated with domestic wastewater, is a cost-effective option. Landfill leachate can also be carried to the wastewater treatment plant where it can be subjected to biological processes combined with domestic sewage.

Combined treatment of landfill leachate and domestic sewage is a widely adopted practice (1,20,21,22,23). The requirements are: availability of sewer system, plant capacity to assimilate the waste, process compatibility with leachate characteristics, and facility to handle increased sludge production. However many concerns exist about the suitability of this leachate treatment option. Indeed the great leachate pollution load, particularly in terms of organic compounds with low biodegradability, high ammonia concentrations, and heavy metals, produces inhibition in the development of biomass with a possible worsening of plant efficiency.

Combined treatment may have certain advantages including better control of the influent characteristics. Since leachate pollutant loads and flowrates have in general significant variations in time, the adverse effects of these variations on activated sludge process can be minimized by applying proper volumetric leachates ratios to domestic wastewater with the knowledge of leachate characteristics. In order to realize the combined treatment option, the maximum adoptable leachate ratio must be defined at which no reduction in removal efficiency is observed. Due to the variable characteristics of leachate, determination of the proper volumetric ratio may be problematic. Leachate ratio can be better defined in terms of organic loading. However, the same doubt also remains because of the possible variation of leachate biodegradability during plant feeding (20).

High strength leachate with COD exceeding 10000 mg/l can be treated at a level of 5 percent by volume without seriously impairing the treatment process or the effluent quality. Beyond 5 percent by volume, leachate addition may result in substantial solids production, increased oxygen uptake rates, and poorer settling of biomass (1). Hence air supply and oxygen transfer must be sufficient in combined treatment practices. Increases in the sludge volume index and sludge bulking are potential problems that can be encountered (22). Many researchers have ended with different maximum adoptable leachate ratios depending on the quality of the leachate. Hence, the performance of a combined treatment process must be investigated on a case by case basis (1).

Besides reductions of efficiency, biomass alterations and foaming may be observed due to leachate addition. High leachate dosages may cause the dominance of filamentous microorganisms, as *Microthrix Parvicella*, that are stimulated by slowly biodegradable substrates. However, at low dosages leachate does not modify the biomass composition. In

addition high ammonia nitrogen concentrations in the leachate result in high nitrate concentrations in the effluent which requires further denitrification (20). Leachate addition also increases the sludge production significantly due to the precipitation of Fe, Cu and other metals present in leachate. The high concentrations of slowly biodegradable organic matter in leachate may require higher hydraulic residence time and sludge residence time for the complete removal of biodegradable organic matter. Hence the treatment plant to which leachate addition will be made should be suitable for such changes in design parameters or should be redesigned (1).

2.4. Powdered Activated Carbon Addition to Activated Sludge

2.4.1. Basic Features of PAC Added Activated Sludge Systems

Powdered Activated Carbon in conjunction with suspended growth biological reactor (under the name PACT) has been widely used for treatment of wastes containing nonbiodegradable and toxic organics over the past 25 years. PACT is applied in the treatment of highly polluted wastewaters contaminated with phenols, aromatics, volatile acids, aliphatics besides general BOD/COD reduction and color removal. Several authors have examined the effect of PAC on the activated sludge efficiency (24-35). All studies resulted in significant increases in the treatment efficiencies.

There is considerable evidence in the literature about the advantages gained by adding powdered activated carbon to activated sludge systems reporting that the addition of PAC to activated sludge helps stabilize the process through improved sludge settling characteristics, improved sludge thickening/dewatering characteristics, increased organics removal, removal of refractory and inhibitory organics, reducing the impact of organic shock loadings, increased color removal, suppressed aerator foaming, improved nitrification, increased solid residence times, and reduction in odor and sludge bulking over conventional systems (25, 26, 27).

The PAC addition to activated sludge is in fact a process modification of the activated sludge process. The addition of PAC to plug flow and complete mix suspended growth reactors is a more common process modification for industrial wastewater treatment, and has been applied to municipal systems in some instances. It can also be successfully applied to leachate treatment systems (4,28). For the design and operation of PACT systems, it is first necessary to establish the optimum adsorption conditions (carbon concentration, particle size and stirring rate) in the batch mode before applying to a full scale continuous flow system (29).

PAC is added to the aeration tank and it is here mixed with the biological solids. Besides adding PAC directly to the aeration tank, PAC can be mixed with the effluent from the primary settling tank and then introduced to the aeration tank together with the wastewater.

The mixed liquor solids are settled and separated from the treated effluent in a gravity clarifier. The PAC in the sludge can be either regenerated for further use or disposed with the biological sludge. The simple schematic diagram of PAC added activated sludge system is shown in Figure 2.4 (4).

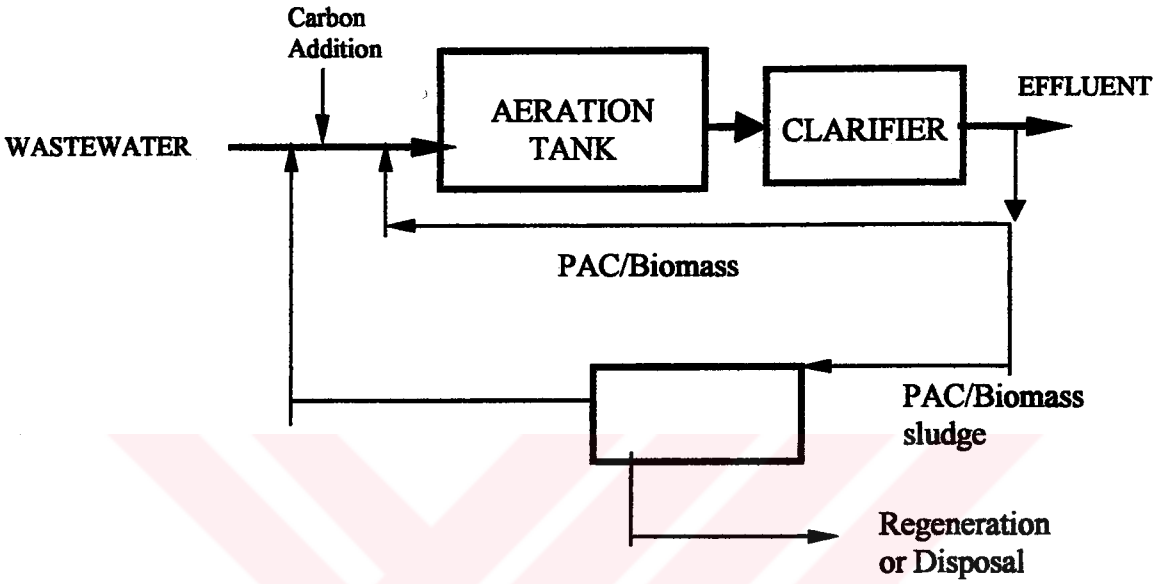


FIGURE 2.4. Schematic representation of a typical powdered activated carbon- activated sludge system (4).

The problem encountered in PAC-AS systems is the wastage of PAC with the excess biomass. Therefore virgin or regenerated PAC addition is required to maintain the desired concentration in the aeration tank. This represents a significant cost factor for the system. Also the inability to analytically differentiate PAC from background refractory volatile materials makes it difficult to quantify the value of the volatile suspended material recovered after regeneration (4).

Polyelectrolyte addition to the sedimentation tanks may be required in PAC-AS systems to enhance solid-liquid separation, because in the effluent PAC as well as biomass are not wanted. Even with polyelectrolyte addition, tertiary filtration is normally required to reduce the level of effluent suspended solids (4). The clarifier underflow solids are continuously returned to the aeration tank in order to keep the desired level of microorganisms in the reactor. A portion of the carbon-biomass mixture is wasted periodically to compensate for the virgin carbon added and the biomass produced within the system (See Figure 2.4).

The PAC concentration to be added to the aeration tank depends on the design solids retention time, the hydraulic retention time and the required PAC concentration in the reactor. The PAC concentration to be added can be determined by using the equation below;

$$PAC_i = (PAC_R \times \theta / \theta_c^d) + PAC_e \quad (2.14)$$

where;

PAC_i = Influent PAC concentration, mg/l

PAC_R = Mixed liquor PAC concentration, mg/l

PAC_e = Effluent PAC concentration, mg/l

θ = Hydraulic retention time

θ_c^d = Design solids retention time

The value of effluent PAC concentration can be estimated by assuming that the carbon fraction in the effluent total suspended solids is the same as the fraction of PAC in the MLSS.

2.4.2. Enhancement of Organic Matter Removal with PAC Addition

Organic matter removal in a PACT system is the combination of adsorption and biodegradation. Activated carbon, when used in conjunction with biological treatment is said to give higher degree of organic removal efficiency than separate adsorption and biological treatment. Many researchers suggest that a synergy exists between activated carbon activities and microorganism activities. PACT system can remove an organic compound more efficiently than would be expected from either biodegradation or adsorption alone. The mechanism consists of stimulation of biological activity by the action of PAC and bioregeneration (see Section 2.4.4) of PAC by microorganisms for further adsorption. Activated carbon provides the attachment surface for microorganisms and protects them from shock loadings of toxic and inhibitory materials, whereas microorganisms bioregenerate the activated carbon (25,29).

Activated carbon in conjunction with biological treatment increases the removal efficiency by adsorbing the nonbiodegradable organics and also the toxic and inhibitory organics and some metals. The adsorption of inhibitory and toxic organics and metals by PAC can stimulate the biological activity. The adsorption of inhibitory or toxic substance by PAC apparently restricts contact between the toxin and the microorganism. Stimulation of biological activity is generally the main mechanism in the enhancement of organic matter removal in PACT systems (25).

The activated carbon is widely used for the general BOD and COD removal, all aromatic compounds, aliphatics and halogenated aliphatics (See Table C1 in Appendix C) (4). In general, the activated carbon adsorption processes work best with organics that have a low water solubility and high molecular weight. Therefore a compound such as methanol can be poorly adsorbed while chlorinated aromatic compounds are very well adsorbed. The wastewater compounds that have a high BOD are generally less well adsorbed, because BOD represents the low molecular weight compounds. Therefore PAC is more suited to the removal of nonbiodegradable COD (4, 25, 36).

However preferential adsorption of high molecular weight organics is not always the case, because activated carbon can hardly adsorb organics with very high molecular weights (HMW). It is suggested that activated carbon preferentially adsorbs the refractory organics with lower molecular weights (LMW). However this does not mean that activated carbon preferentially adsorbs very low molecular weight organics that are more readily biodegradable. The LMW refractory organics in wastewaters are also more biodegradable than the HMW refractory organics in cases of bacterial acclimation and bioregeneration. Therefore the microorganisms also prefer LMW refractory organics for biodegradation during the bioregeneration of the activated carbon (36).

For a better evaluation of the adsorption effect of the PAC added activated sludge systems, separate adsorption studies should be conducted in order to predict the amount of organics removal due to adsorption by PAC when used in conjunction with activated sludge. Most of the activated carbon applications in wastewater treatment fit the Freundlich isotherms for organic matter (7,24).

Besides being very effective for its adsorption capacity, PAC may also provide an attachment surface for microorganisms (27, 30, 34). The property of providing an attachment surface for microorganisms is less possible than in the GAC filter processes. In fixed film processes or in fluidized bed processes, a biofilm forms on the attached media (GAC). Since in attached growth processes, the solids retention time is generally much higher than in activated sludge processes, this provides sufficient time for the microorganisms to attach on the activated carbon (GAC) surfaces. In an activated sludge process, microorganisms may have not enough time to attach on the PAC surfaces because of the lower sludge ages. Therefore, attachment efficiency is much lower in PAC added activated sludge systems compared to biologically activated GAC filter systems (36).

However, when activated carbon is used in a suspended medium, PAC is more advantageous than GAC, because PAC systems provide uniform distribution of solids with minimum energy requirements for mixing and arrive at an equilibrium of adsorption in a relatively short period of time. Regeneration technologies minimize the disposal problems associated with PAC and effective clarification in the presence of PAC makes continuous operation possible in some cases. Also the price of PAC is approximately one half that of GAC (26).

2.4.3. Enhancement of Nitrification with PAC Addition

Many studies in the literature show that nitrification is enhanced by PAC addition to the activated sludge (26, 27, 30, 31). Studies have demonstrated that ammonia removal is enhanced significantly by the addition of PAC. It is strange to have such a result, because adsorption of ammonia at the pH and concentrations found in wastewaters is very negligible.

The most probable reason for enhanced nitrification is the removal of toxic and inhibitory organics or inorganics by PAC. By adsorbing these materials, PAC decreases the amount of these materials that the nitrifiers are subject to. Inhibitory and toxic compounds are generally present in industrial wastewaters and landfill leachate rather than domestic wastewaters. Therefore PAC activated sludge nitrification systems are normally selected when the wastewater contains compounds originating from industrial operations or leachate. PAC enhancement due to the adsorption of inhibitors is more effective in

nitrification, because nitrifiers are more sensitive to inhibitors than heterotrophic bacteria. However not all of the inhibitory compounds are adsorbable on activated carbon. Therefore it is likely that the presence of activated carbon can protect nitrifiers from adsorbable inhibitory compounds (27, 30).

Acclimation of heterotrophs to refractory organics that can be inhibitory to nitrifiers may also increase the nitrification efficiency. Bioregeneration (see Section 2.4.4) may be important in the acclimation of heterotrophic organisms to certain slowly biodegradable inhibitors of nitrification. Adsorption of the inhibitory compounds increases the time available for heterotrophic acclimation and for the removal of nitrifier inhibition (30).

2.4.4. Bioregeneration Hypothesis in PAC Added Activated Sludge Systems

Bioregeneration is a term used to describe the synergism between PAC and microorganisms in a PACT system. Bioregeneration is the renewal of the adsorptive capacity of activated carbon by the activity of microorganisms in the activated sludge system for further adsorption. Several researchers state that the activated carbon is bioregenerated in PACT processes (25, 29, 30, 31, 32, 33, 34, 35). However recent studies have shown that the bioregeneration hypothesis is not always valid and PACT process is a simple combination of adsorption and biodegradation (24, 37).

Bioregeneration hypothesis is valid for slowly biodegradable and adsorbable organic compounds. Rapidly biodegradable organic matter is generally not adsorbable and can be removed by biological activity alone and the removal of nonbiodegradable and adsorbable compounds is through simple adsorption. Slowly biodegradable compounds can be biodegraded if a sufficient contact time is provided with the biomass. In a conventional activated sludge system, these slowly biodegradable compounds are in contact with the biomass for a length of time equal to the hydraulic retention time. However, in a PACT system these compounds are in contact with the biomass for a length of time equal to the sludge age if they are adsorbed by PAC. Therefore bioregeneration should increase with sludge age (25). The further adsorption of slowly biodegradable organics shows that bioregeneration of PAC promotes the degree of biodegradation. Hence it can be said that adsorption acts as a prerequisite step for biodegradation.

Proposed theories of bioregeneration require that a compound be adsorbed onto the carbon's surface where microorganisms reside, and that adsorption results in higher substrate concentrations than would be expected in the bulk solution. This increase in concentration stimulates biological growth and replenishes the carbon surface for further adsorption.

One of the main theories regarding bioregeneration is the desorption of organic matter according to exoenzymatic reactions (25, 32, 33). According to this theory, bacteria are too large to migrate into the micropores of PAC. However some enzymes excreted by the bacteria could easily diffuse into the micropores and react with the adsorbed substrates and further desorption may take place due to the weak adsorbability of enzyme reacted organic matter. On the other hand, it is also suggested that the molecules of enzymes are larger than the sizes of micropores, so that bioregeneration cannot occur due to enzymatic reactions (37).

The second theory is that adsorption concentration rises more than the equilibrium adsorption concentration through the decrease of bulk concentration by biological activity and the adsorbed organic matters are desorbed due to the concentration gradient between the PAC surface and bulk liquid (32, 33, 35). However for some complex substrates bioregeneration seems to be limited, because complex substrates are likely to be irreversibly adsorbed. Hence bioregeneration is controlled by the reversibility of adsorption (33, 35).

The extent of bioregeneration is normally uncertain in such systems like PAC added activated sludge systems. It is difficult to measure bioregeneration experimentally, since bioregeneration, biodegradation and adsorption occur simultaneously within these systems (32). The maximal extent of bioregeneration is dependent on the type of activated carbon. This fraction is considerably larger with the chemically activated-wood based PAC than with the thermally activated-peat based PAC (33).

The activated carbon when used alone (GAC filters) represents a large capital investment and operating costs mainly due to the need for regeneration of activated carbon. However, bioregeneration possibly occurring in PAC added activated sludge systems may decrease the costs related with regeneration. The adsorption capacity of PAC is extended by the

regeneration of adsorption sites by biodegradation of previously adsorbed organic matter. The bioregeneration process increases the service period of PAC.

Bioregeneration hypothesis is close to be more valid in biologically activated GAC filters than in PAC added activated sludge processes. The first reason for this is that the sludge age is much higher in attached growth processes than in activated sludge, and microorganisms often have enough time to degrade the refractory organisms that the activated carbon has adsorbed. The second reason which is also related to the first one is that GAC provides an intimate contact between the activated carbon pores and the microorganisms by providing suitable attachment sites for them (36).

Adsorption induced acclimation of microorganisms is another mechanism proposed for bioregeneration (36). Adsorption of refractory organics on activated carbon which is in intimate contact with the microorganisms induces the acclimation of attached microorganisms to these refractory organics. This idea differs from the previous ones by suggesting that the nature of the bacterial culture changes to use the refractory organics as substrates. This suggestion does not seem to be valid for PAC added activated sludge systems at low sludge ages. However, in nitrification systems at higher sludge ages with respect to systems that primarily aim carbonaceous BOD removal, the hypothesis of bioregeneration is more likely to be valid.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Landfill Leachate

Leachate generated from the Kemerburgaz Sanitary Landfill Site located on the European side of Istanbul was used throughout the experimental path of this study. Leachate samples were taken from the leachate storage lagoon on 15 July 1998, and were stored at 4°C in closed plastic barrels. The characteristics of the leachate sample are given in Table 3.1. The concentrations given in Table 3.1 are the averages of multiple analyses.

TABLE 3.1. Characteristics of Landfill Leachate used throughout the study.

pH	8.2
TCOD (mg/l)*	10750
SCOD (mg/l)*	9070
BOD_5 (mg/l)	6380
TKN (mg/l)	2031
NH_4-N (mg/l)	2002
NO_x-N (mg/l)	128
Total P (mg/l)	6.8
Cl^- (mg/l)	4322
Alkalinity (mg $CaCO_3$/l)	10600
Total Solids (mg/l)	17326
TSS (mg/l)	1013
VSS (mg(l)	786
Salinity (%)	18.2
Conductivity (mS)	29.5

*See Section 3.2 for the difference between TCOD and SCOD.

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Kemerburgaz Landfill Site was projected by the Municipality of Istanbul. In the scope of the project two landfill sites and six transfer stations were constructed. The landfill receives solid wastes from the three transfer stations on the European side and three stations on the Asian side. The landfill receives only municipal solid wastes.

The soil in the area of landfill is rich in clay which gives an impermeable character to the soil and no groundwater is reported in the landfill area. High density membrane liners are used to prevent leachate leakage. The solid wastes are landfilled by the cell method and they are covered daily by soil. Leachate generated in the landfill is collected by special pipes and the generated gas is collected by gas collection chimneys.

3.1.2. Synthetic Domestic Wastewater

Synthetic domestic wastewater is a synthetically prepared solution used for the purpose of representing the characteristics of domestic wastewater. Synthetic domestic wastewater was prepared as a stock solution having a COD 10000 mg/l, TKN 1060 mg/l, phosphorus 812 mg/l and pH 7.1. It was diluted 20 folds before use throughout the experimental work. The composition of synthetic domestic wastewater is shown in Table 3.2. Phosphorus was used in excess amounts in the synthetic domestic wastewater to compensate for the phosphorus deficiency in the leachate in order to provide enough phosphorus as nutrient for biological treatment and to buffer severe pH decreases.

TABLE 3.2. Composition of Synthetic Domestic Wastewater Stock Solution.

Component	Concentration (mg/l)
CH_3COONa	6000
Glucose	5600
Peptone	2000
$(NH_4)_2SO_4$	5000
KH_2PO_4	2000
K_2HPO_4	2000
$MgSO_4.7H_2O$	2000
$CaCl_2.2H_2O$	600
$FeCl_3.6H_2O$	200

3.1.3. Activated Carbon

The activated carbon used throughout the study was Norit SA 4 in powdered form. PAC was dried at 103°C before using in experiments. The properties of activated carbon are shown in Table 3.3.

TABLE 3.3. Properties of activated carbon used in the experiments.

Apparent density (g/l)	190
Moisture (%)	5
Ash content (%)	6
Phenol Adsorption (%)	4
Molasses Number	525
Methylene Blue adsorption (g/100g)	10
Iodine number (mg/g)	750
Internal Surface Area (m^2/g)	650
Particle Size	
>10 micron (%)	80
>44 micron (%)	37
>79 micron (%)	20
>150 micron (%)	5

3.1.4. Activated Sludge

A five liter reactor was inoculated with the sludge taken from the recirculation line of an activated sludge treatment unit of a meat processing plant, and it had been fed with the synthetic domestic wastewater for two years. During the last two months before the experiments were started and during the experimental period of eight months, 1/20 of the sludge was daily wasted from the reactor to have a sludge age of 20 days. In this period, the reactor was fed with the synthetic domestic wastewater daily to have a loading rate of 500 mg COD/l.day. The activated sludges used in the batch, semi-continuously fed batch and continuous-flow operations were all taken from this five liter mother reactor.

3.2. Analytical Methods

The analytical methods used in the experiments followed the *Standard Methods for the Examination of Water and Wastewater* (38) except biomass-MLVSS analysis in PAC added activated sludge reactors. Analytical methods are explained below:

a) COD Analysis: For chemical oxygen demand (COD) analysis the dichromate closed reflux method was employed. Samples were refluxed with Potassium Dichromate ($K_2Cr_2O_7$) and H_2SO_4 for two hours at 150°C in the Hach COD digester, in the presence of Ag_2SO_4 as catalyst and $HgSO_4$ to prevent chloride interference. COD measurements were done colorimetrically by measuring the absorbance of samples at 600 nm with Hach DR/3 Spectrophotometer. Calibration curves were prepared by using standard KHP (Potassium Hydrogen Phthalate) solutions with correctly estimated COD values. All COD values, except Batch Run 1, were corrected for nitrite interference and reported with correction throughout the study. In a former study, it has been reported that 1 mg/l NO_2-N led to a positive interference in COD about 1.1 mg/l (6). Hence, 1.1 mg/l COD was subtracted from the measured COD values for each 1 mg/l NO_2-N measured.

Total COD (TCOD) is the COD of the supernatant. Soluble COD (SCOD) is the COD of the supernatant filtered through 0.45 μ Millipore filter. SCOD was taken as the main organic parameter throughout the study. Mixed Liquor COD (MLCOD) is the total COD of the sample taken from the agitated activated sludge. MLCOD includes both the total COD of the bulk liquid and the COD caused by the biomass in the reactor. MLCOD calculations were performed to observe the changes in biomass concentration in reactors and to calculate yield coefficients in batch reactors. MLCOD calculations were not performed in PAC added reactors since PAC is itself mainly organic in nature and would exert a strong positive interference in the measured COD values.

b) NH_4-N Analysis: Preliminary Distillation Method using Gerhardt Vapodest 12 Distillation Apparatus was employed. Samples were buffered to a pH of about 9.5 and then distilled into boric acid solution for 15 minutes. The concentration of NH_4-N in the distillate was measured by titration with a standard sulfuric acid solution.

c) NO_x-N Analysis: NO_x-N is equal to the sum of NO_2-N (nitrite) and NO_3-N (nitrate) which are the oxidized forms of nitrogen. Devarda's Alloy Reduction Method was employed for NO_x-N measurements. Devarda's Alloy was added to the samples after the NH_4-N analysis. Under hot alkaline conditions, nitrite and nitrate were reduced to ammonia in the Gerhardt Vapodest 12 Distillation Apparatus. Ammonia was distilled into boric acid solution for 15 minutes and the concentration of NH_4-N in the distillate was measured by titration with a standard sulfuric acid solution. The obtained value was equal to the NO_x-N concentration in the sample.

d) NO_2-N Analysis: Nitrite concentrations were measured by colorimetric methods. Nitriver 2 test kits were added to samples and the absorbance at 560 nm were measured by Hach DR/3 Spectrophotometer. Calibration curves were prepared by using $NaNO_2$ solutions with known concentrations of NO_2-N.

e) TKN Analysis: TKN (Total Kjeldahl Nitrogen) involves the organic nitrogen in the tri-negative oxidation state and ammonia nitrogen. Kjeldahl Method involves the conversion of organic nitrogen to ammonium sulfate in the presence of digestion reagent (concentrated sulfuric acid as oxidizing agent, mercuric sulfate as catalyst and potassium sulfate). The digestion is applied slightly above the boiling point of sulfuric acid (340°C). Mercury-ammonium complex formed during digestion is decomposed by adding sodium thiosulfate in order to prevent negative interference. After digestion, all of the organic nitrogen is converted to ammonia nitrogen, and the concentration of NH_4-N was measured by the distillation and titration method as explained for NH_4-N analysis.

f) pH Analysis: Orion SAS20 pH meter was used.

g) OUR Analysis: Oxygen Uptake Rates in the activated sludge reactors were measured automatically by WTW Microprocessor Oximeter Oxi 3000. OUR (mgO_2/l.min) measurement is based on the dissolved oxygen consumption in the 300 ml BOD bottle per minute. Sample taken from the mixed liquor of an activated sludge reactor is placed in a BOD bottle and stirred with a magnetic stirrer. Dissolved oxygen concentration in the BOD bottle declines with respect to time. The slope of the dissolved oxygen decline curve gives OUR. Oximeter Oxi 3000 calculates the slope automatically and gives the OUR value. Oximeter Oxi 3000 is very sensitive to low dissolved oxygen concentrations. It does

not calculate OUR values if the dissolved oxygen concentration drops to below 1 mg/l, because OUR measurements are not reliable below 1 mg/l. Below 1 mg/l, the dissolved oxygen concentration becomes the rate limiting substrate and the activity of microorganisms decreases.

h) MLSS Analysis: Mixed Liquor Suspended Solids analysis were carried out by drying residue on filter paper (Millipore 0.45 μ) for one hour at 103°C.

i) MLVSS Analysis: Mixed Liquor Volatile Suspended Solids analysis were carried out by igniting residue from MLSS analysis for 30 minutes at 600°C.

Since PAC also contributes to the MLVSS measurements, determination of the biomass-MLVSS was required in PAC added activated sludge reactors. The biomass-MLVSS of PAC added sludges in the continuous reactor were determined according to the procedure proposed by Arbuckle et al., 1982 (39). In this procedure, basically MLSS, MLVSS at 400°C, MLVSS at 550°C tests are performed on both the PAC added sludge and the PAC used. By incorporating the volatile suspended solids amount of PAC, the biomass-MLVSS is estimated using the calculated values with small errors.

j) BOD_5 Analysis : Biochemical Oxygen Demand analysis were performed by the dilution method. The method consists of filling an airtight BOD bottle and incubating at 20°C for 5 days. Dissolved oxygen is measured initially and after incubation, and the BOD is calculated from the difference between initial and final dissolved oxygen. Dissolved oxygen concentrations were either determined by Hach Portable DO Apparatus with membrane electrode or by titration with sodium thiosulfate.

3.3. Experimental Work

3.3.1. Adsorption Tests with Activated Carbon

Adsorption tests with activated carbon were performed to investigate the adsorption characteristics of PAC and to estimate the COD removal due to activated carbon adsorption in PAC added activated sludge reactors. The estimation of COD removal due to PAC adsorption helps to find out whether a synergistic relationship is present between PAC and activated sludge by comparing the COD removals in PAC added activated sludge and activated sludge reactors as explained in Section 2.4.

The adsorption characteristics of PAC used throughout the study was determined through shaker flask experiments. Shaker flask experiments consists of shaking PAC added wastewater samples at about 80 rpm at room temperature in 250 ml stoppered flasks. The SCOD of the final liquids were determined after filtering through 0.45 μ Millipore filters to remove PAC particles.

The time required for reaching an equilibrium SCOD concentration is the equilibrium time for adsorption. Equilibrium time was obtained to determine the shaking time required for adsorption isotherm tests. For this purpose, the SCOD values of 20-folds diluted leachate in flasks with different PAC concentrations were analyzed with respect to time until reaching equilibrium concentrations. Equilibrium time was described as the time when the SCOD concentrations reached constant values. Adsorption tests were performed with 20-folds diluted leachate at different PAC concentrations and with the leachate combined with synthetic domestic wastewater (volumetric ratio: 5% leachate in total wastewater).

3.3.2. Experiments in Batch Reactors

Biological treatment and activated carbon addition were first performed in two liter plexiglass batch activated sludge reactors. Batch runs were performed in order to investigate the biological treatability of leachate when combined with the synthetic domestic wastewater and the effect of PAC addition on COD removal and nitrification. Aeration and mixing within the reactors were achieved by the air supplied from a

compressor. Ten batch runs were performed. The first six runs lasted for several days and the last four runs lasted for 24 hours.

In batch runs, the reactors were fed with the leachate combined with synthetic domestic wastewater at a volumetric ratio of 5% in the first 8 runs, 15% in the 9th run, and 10% in the 10th run. The change in parameters like COD, NH_4-N, NO_x-N and OUR were monitored with respect to time. Most of the reactors were inoculated with activated sludge taken from the 5 liter mother reactor.

The reactors to which activated sludge was added were named as AS (Activated Sludge) reactors and the reactors to which both activated sludge and PAC were added were named as AS+PAC reactors throughout the thesis. In the first two runs one reactor was fed only with wastewater and PAC, and no AS was added to reactors to observe the difference from the case of AS addition. In BATCH RUN 3, in one of the reactors the feed was only aerated and no AS and PAC were added to observe the biological treatability of aerated leachate combined with the synthetic domestic wastewater due to the activity of microorganisms in the leachate.

3.3.3. Experiments in Semi-Continuously Fed Batch Reactors

Semi Continuously Fed Batch (SCFB) operation is a semicontinuous operation in batch reactors or in other words a simulation of the continuous-flow operation in batch type reactors. The main reason for applying SCFB operation was to maintain simultaneous operation of AS and AS+PAC reactors under the same working conditions in order to be able to monitor the differences between these two reactors in terms of COD removal, nitrification, OUR and pH simultaneously. In batch reactors it is easier to control working conditions like aeration, agitation, feeding, sludge age and hydraulic residence time than in continuous reactors. SCFB operation can also be used to determine the optimum working conditions for a subsequent continuous-flow operation. In the scope of this study, it helped in gaining an opinion about the application of continuous-flow operation and it served us to see whether batch reactors can successfully be used to simulate continuous-flow operation.

Two liter plexiglass batch reactors were employed in SCFB runs. Aeration and mixing was achieved by air supplied from a compressor. Semi Continuously Fed Batch runs were

performed by applying once-a-day feeding of influent and once-a-day wasting of sludge to operate the system at a predetermined sludge age and by the discharge of effluent at an amount equal to the predetermined hydraulic residence time. Since PAC was wasted daily with the wasted sludge, the wasted amount of PAC was added to the reactors daily. Only in SCFB RUN 1, no sludge wastage and no PAC addition were performed. The hydraulic residence time was adjusted to 32 hours in all the runs by discharging 1.5 liter of effluent daily from the reactors. In SCFB RUN 1 , the sludge age was not controlled. Sludge age was adjusted to 20 days in SCFB RUNS 2 and 4, and to 10 days in SCFB RUN 3 which was fed with a high influent COD. The sludge age was adjusted to 20 days by discharging 1/20 of sludge from the reactors daily. It is important to regulate the sludge age to prevent excessive microbial growth in reactors, or in other words to keep the MLVSS level constant.

3.3.4. Experiments in the Continuous-Flow Stirred Tank Reactor (CFSTR)

A lab-scale continuous-flow reactor gives more chance to simulate the situations in a full-scale operation than lab-scale batch and SCFB reactors. Hence, in order to estimate the biological treatability of leachate and to observe the effect of PAC addition to activated sludge, a lab-scale continuous-flow stirred tank reactor (CFSTR) was employed. The aeration tank and the settling tank of the reactor had a volume of 3.6 L and 2.5 L, respectively. The sludge was recycled to the aeration tank by means of an air lift. Air lift for sludge recycle and aeration and mixing in the aeration tank were achieved by air supplied from a compressor.

The lab-scale continuous-flow stirred tank reactor that had been previosly used in another study (24) was also used in this study during the continuous-flow experiments. The reactor is illustrated in Figure 3.1. It was fed with leachate combined with the synthetic domestic wastewater at a volumetric ratio of 6.7 per cent for 27 days. In the CFSTR, neither daily PAC dosages were made to the reactor, nor sludge and PAC were discharged from the reactor. However, some sludge and PAC which did not settle in the settling tank escaped from the reactor with the effluent. In addition, some sludge and PAC left the system through spillages from the aeration tank due to the high turbulence. At the 19^{th} day, PAC was added to the reactor to have 2000 mg/l PAC in the reactor. In the succeeding days, the effect of PAC was observed. At the 27^{th} day of operation, the leachate ratio in the influent

was increased to 13.3 per cent. After the reactor came to a steady-state at the 36th day, a new PAC addition was made to have 2000 mg/l virgin PAC in the reactor. The effect of new PAC addition was observed in the succeeding days. The operation was stopped at the 44th day when the effect of the added PAC disappeared.

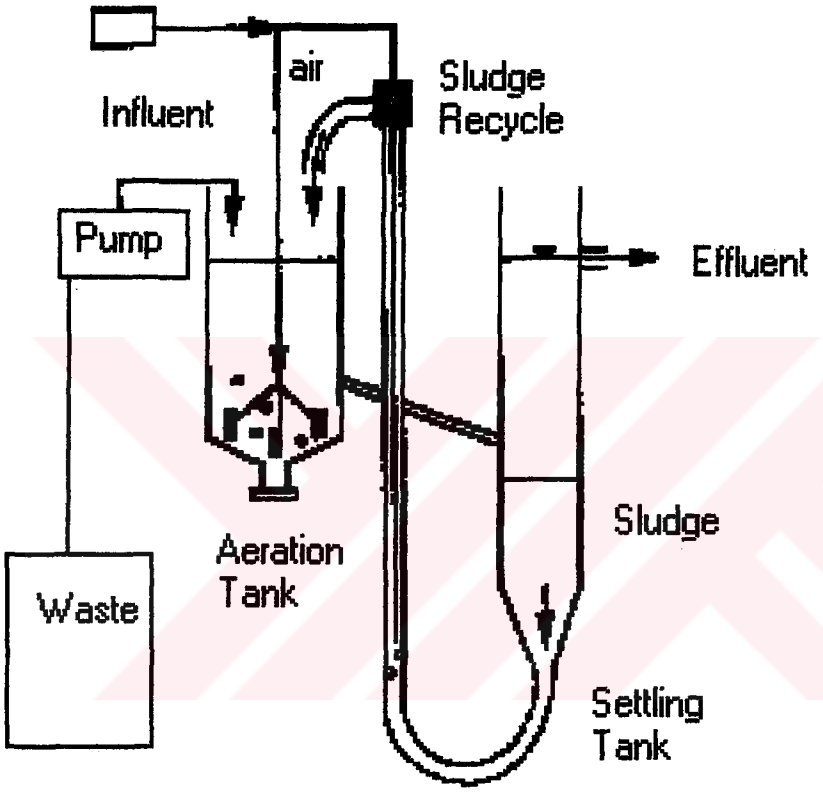


FIGURE 3.1. Set-up for the continuous-flow experiments.

4. RESULTS AND DISCUSSIONS

4.1.Determination of Adsorption Isotherms

In order to investigate the adsorption characteristics of the activated carbon used throughout the study and to identify its effect on the treatability of the leachate when combined with the synthetic domestic wastewater, adsorption tests in shaker flasks were performed as explained in Section 3.3.1.

In adsorption studies, the equilibrium time is of critical importance , because not every type of adsorbate is adsorbed on the adsorbent at the same rate. For example adsorption equilibrium time for metals and COD would probably be not equal (40). Three different PAC concentrations (1000mg/l, 5000 mg/l, 15000 mg/l) were used, and the soluble COD (SCOD) of the final liquids were analyzed with respect to time for four days until reaching an equilibrium concentration. The results of the equilibrium time determination when the leachate was diluted 20 times with distilled water are illustrated in Table A1 in Appendix A. The results show that the SCOD stayed constant between the third and fourth days, showing that an equilibrium time of three days was needed for SCOD adsorption onto activated carbon.

Adsorption isotherms were determined both with diluted leachate (dilution:20 folds) and the leachate and synthetic domestic wastewater mixture in which the volumetric ratio of leachate was 5%. The equilibrium data were fitted into the Freundlich equation of the following form:

$$q = K_f . S_e^{1/n} \qquad (4.1)$$

q = adsorption capacity of the activated carbon (mg SCOD adsorbed / mg PAC)

S_e = the equilibrium SCOD concentration after 72 hours (mg SCOD/l).

K_f and 1/n are the Freundlich constants (Freundlich exponent and slope).

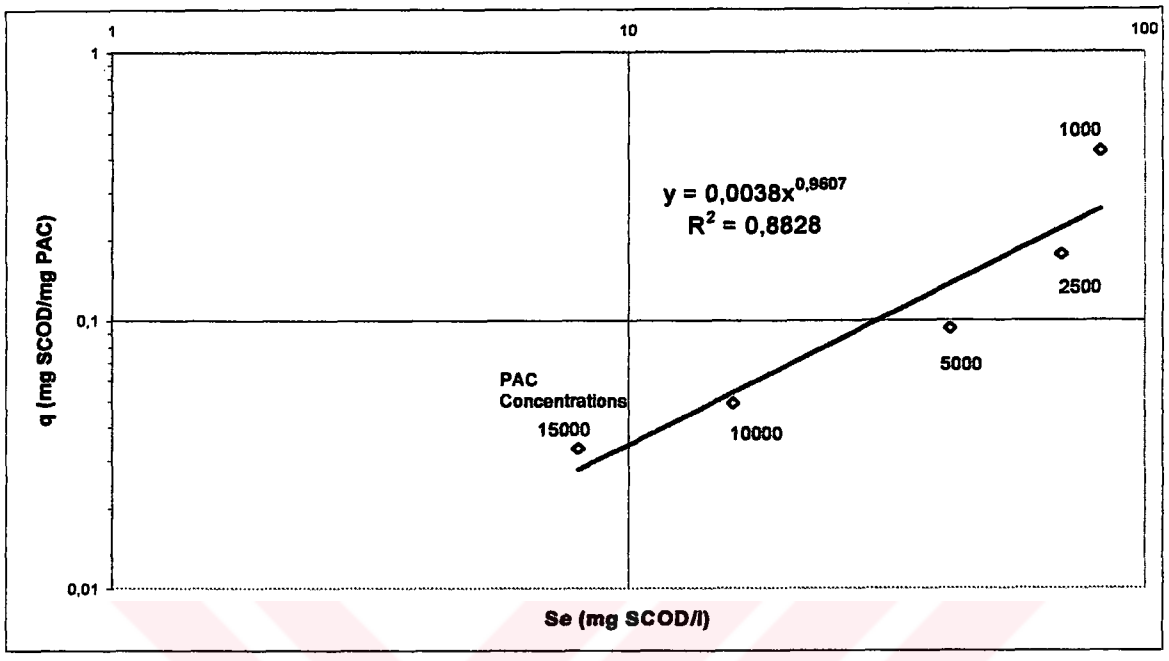


FIGURE 4.1. Freundlich adsorption isotherm for diluted leachate (5%) at high PAC concentrations

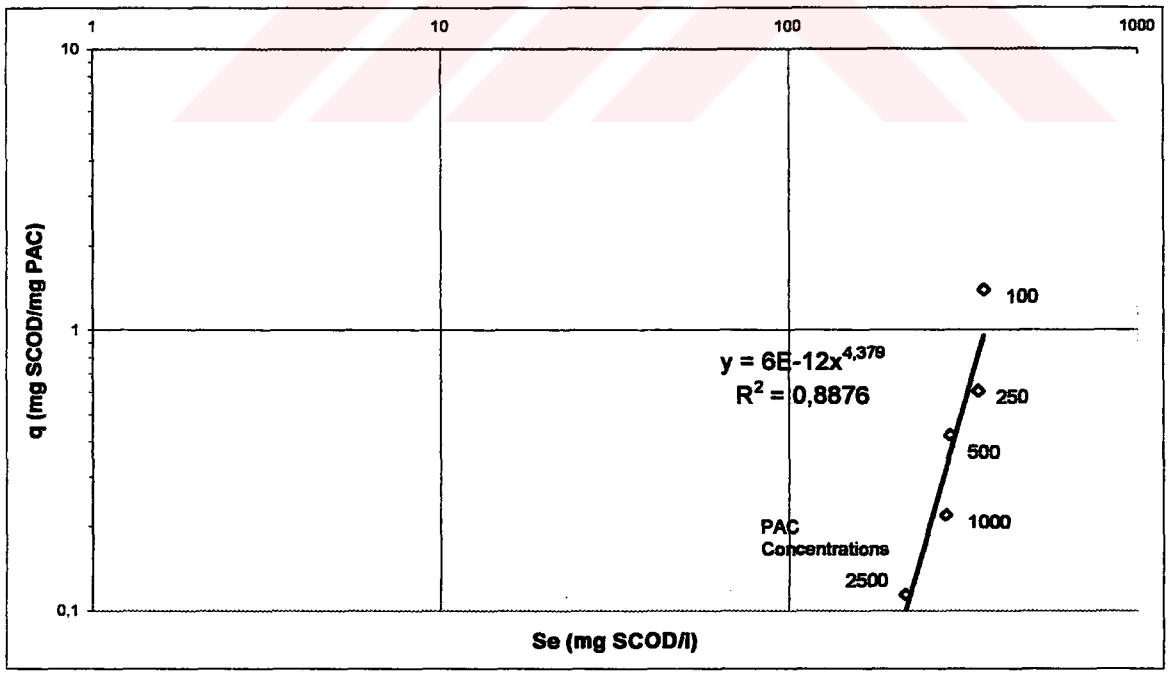


FIGURE 4.2. Freundlich adsorption isotherm for diluted leachate (5%) at low PAC concentrations.

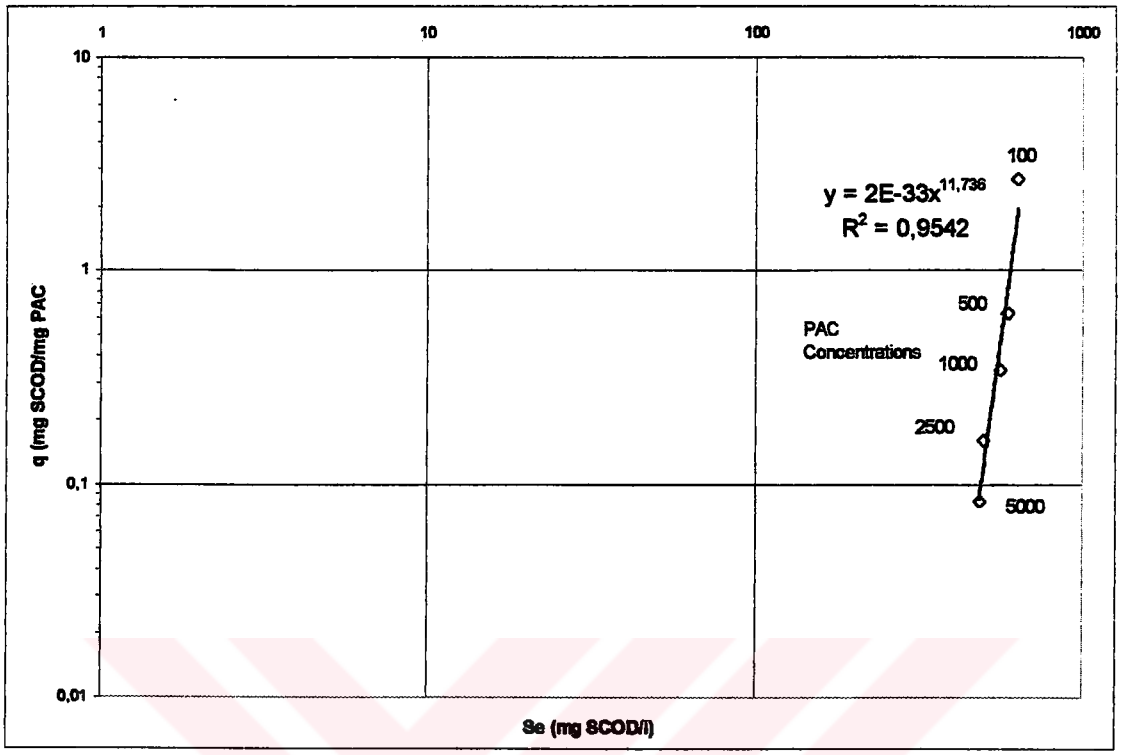


FIGURE 4.3. Freundlich adsorption isotherm for combined leachate and synthetic domestic wastewater (Leachate ratio: 5% by volume).

The Freundlich adsorption constants obtained are shown below in Table 4.1. The K_F values, an indicator of sorption capacity, are quite low, hence they propose a low adsorption capacity of the activated carbon used in the studies. The adsorption intensity, 1/n, is the slope of the adsorption isotherm in logarithmic scale. High slopes show that the amounts of adsorption at different PAC concentrations are not significantly different from each other. The isotherm at higher PAC concentrations gave a lower 1/n value (0.96) compared to isotherm at lower PAC concentrations (4.38), because adsorption intensity at higher PAC concentrations are greater. At low PAC concentrations, the easily adsorbable compunds fill the activated carbon sites, and poorly adsorbable compunds cannot be adsorbed (41). Therefore a steeper isotherm was determined at low PAC concentrations.

The 1/n value for the isotherm when leachate and the synthetic domestic wastewater were combined was found to be higher than the one for the diluted leachate only. This shows that the organic matter in the synthetic domestic wastewater is less adsorbable on activated carbon than that in the leachate. A steeper isotherm arises due to a smaller fraction of adsorbable organic compounds in the wastewater. The readily biodegradable organic

compounds; glucose and sodium acetate which are present in the synthetic domestic wastewater are not well adsorbed on activated carbon (25).

TABLE 4.1. Freundlich adsorption constants obtained from adsorption isotherms.

Wastewater	K_F (mg COD / mg PAC)	1/n
Diluted Leachate (5%) High PAC Concentrations	0.0038	0.96
Diluted Leachate (5%) Low PAC Concentrations	6×10^{-12}	4.38
Combined Leachate and Synthetic Domestic Wastewater (Leachate Ratio: 5% by volume)	2×10^{-33}	11.74

Effect of Adsorption on pH:

A considerable pH decrease with respect to time was observed in the determination of equilibrium time and in isotherm studies (Appendix A) . For example, the pH of the diluted leachate decreased from 8.46 to 7.47 within three days in the batch experiments at 1000 mg/l PAC concentration in equilibrium time determination experiments. This decrease may be due to the adsorption of organic molecules with basic properties, resulting in a pH decrease in the bulk liquid (8).

Acidic or basic organic surface functional groups of activated carbon surface also play a vital role in the final pH of the bulk liquid. Some of the surface functional groups can be freed by simple contact with the wastewater (9). In the activated carbon adsorption studies, the pH of the bulk liquid appeared to be higher for higher PAC concentrations (Appendix A). This shows that the basic surface functional groups dominate over the acidic surface functional groups for the activated carbon used throughout the study.

4.2. Activated Carbon Addition to Activated Sludge in Batch Reactors

Batch runs were initially performed with synthetic domestic wastewater in the mother reactor which was explained in Section 3.1.4. The results obtained from these runs (Table B1 in Appendix B) served as a guidance for the batch runs in which leachate was added to the feed and PAC was added to the reactors. The batch runs, in which leachate in combination with synthetic domestic wastewater was treated, were performed as explaned in Section 3.3.2. The results of the batch runs are displayed in Table B2 in Appendix B.

4.2.1. Removal of Organic Substrates

4.2.1.1. COD Profiles in Batch Runs

In the batch runs, a considerable amount of the organic substrates was removed by biological treatment only. More than 85 per cent removal was achieved in the AS (Activated Sludge only) reactors in the runs when the leachate was combined with the synthetic domestic wastewater at a volumetric ratio of 5 per cent showing that the leachate used in the experiments was highly biodegradable. PAC addition increased COD removal efficiencies to more than 90 per cent in most of the runs (Table 4.2). The total removal efficiencies in Table 4.2 were based on the final COD concentrations after reaching equilibrium conditions.

The COD profiles of the BATCH RUNS 1, 2 and 3 resulted in small differences between the AS reactor and the AS+PAC reactor, because of the low concentrations of PAC used (Fig. 4.4, 4.5, 4.6). Also the removal efficiencies did not significantly differ from each other in the AS and AS+PAC reactors. However, in all of the batch runs, AS+PAC reactors gave the highest removal efficiencies. In all of the batch runs, COD removal was mainly achieved within the first 24 hours. Especially in the first few hours, the readily biodegradable organic substances, which constituted the largest portion in the wastewater, were removed. After 24 hours a small removal occurred in all reactors.

The smallest removal efficiencies were achieved in reactors to which only PAC was added and in the reactors in which the feed was aerated only and no PAC or activated sludge was added. Removal efficiencies of 80-90 per cent, a considerable amount of removal, were achieved in the first three runs in the reactors to which AS from the mother reactor was not added (Table 4.2). In these reactors, COD removal was achieved mainly due to the activity of microorganisms in the leachate and probably due to the adsorption of soluble organic molecules on particulate substances in the leachate.

TABLE 4.2. COD removal efficiencies in batch reactors.

Run No	Leachate Ratio (Vol. %)	Reactor	Initial So/Xo Ratio (gCOD/gVSS)	Estimated Removal due to PAC Adsorption Isotherms (%)	Total Observed Removal (%)
1	5	AS	3.06	-	85
		AS+PAC(100 mg/l)		17	92
		PAC(100 mg/l)		18	80
2	5	AS	2.98	-	90
		AS+PAC(100 mg/l)		15	92
		PAC(100 mg/l)		15	87
3	5	AS	5.35	-	92
		AS+PAC(250 mg/l)		23	94
		Aerated Feed		-	90
4	5	AS	-	-	88
		AS+PAC(500 mg/l)		22	92
		AS+PAC(2500 mg/l)		25	95
5	5	AS	3.66	-	88
		AS+PAC(1000 mg/l)		23	96
		AS+PAC(3500 mg/l)		29	96
6	5	AS	0.43	-	89
		AS+PAC(500 mg/l)		33	94
		AS+PAC(1000 mg/l)		38	94
7	5	AS	0.55	-	84
		AS+PAC(1000 mg/l)		-	92
8	5	AS	0.59	-	84
		AS+PAC(1000 mg/l)		-	91
9	20	AS	1.24	-	75
		AS+PAC(2000 mg/l)		-	82
10	15	AS	0.85	-	81
		AS+PAC(2000 mg/l)		-	88

PAC addition at low concentrations did not have any positive effect on COD removal in these reactors. The removal efficiencies due to PAC adsorption (Table 4.2) were estimated according to the adsorption isotherm for the leachate and synthetic domestic wastewater combination which was previously determined in Section 4.1. The relationship between PAC concentration, initial COD concentration (S_o) and the final equilibrium COD concentration (S_e) was obtained from the adsorption isotherm (Fig. 4.3) and this relationship is shown in equation 4.2.

$$\frac{S_o - S_e}{PAC} = 2.10^{-33}.S_e^{11.736} \qquad (4.2)$$

S_o = Initial COD concentration (mg/l)
S_e = Equilibrium COD concentration due to PAC adsorption (mg/l)
PAC = PAC concentration in the batch reactor (mg/l)

The final equilibrium COD concentrations (S_e) due to PAC adsorption that would have been obtained if biodegradation had not occurred, were estimated using equation 4.2. The estimated S_e values were not shown in Table 4.2. The removal efficiencies due to PAC adsorption were calculated by using the known values of S_o and estimated values of S_e. Removal due to PAC adsorption were not calculated for BATCH RUNS 7-10, because these runs lasted for 24 hours which is less than the equilibrium time (3 days) required for adsorption as obtained in Section 4.1.

It was seen that the the total COD removal in PAC reactors exceeded the removal predicted by the adsorption isotherms (Table 4.2). A factor contributing to this unexpected COD removal could be the volatilization of volatile organic acids that might be at high concentrations in a leachate from a young landfill (3). A batch run was performed to find out if a significant amount of COD was removed from the reactors due to volatilization. One of the reactors was inhibited with $HgSO_4$ for 24 hours keeping the oxygen uptake rate at zero. Also two control reactors were operated. One of them contained only the feed and to the other 250 mg/l PAC was added (Table B3). The control reactors gave high COD removals (83-84 per cent) as in the first three batch runs as expected. But the inhibited reactor showed a very small COD removal (6 per cent) in the first 24 hours. It is highly probable that this amount of removal was due to the adsorption of organics onto the

particulate matters, and the effect of volatilization on COD removal was disregarded. The main mechanism of removal in the "aerated feed" reactors was biodegradation due to the presence of microorganisms in the leachate. This showed that the leachate used throughout the study was quite rich in terms of microorganisms.

In BATCH RUN 1, a slight increase in the COD concentrations at 72 hours was observed (Fig. 4.4). In this run, nitrite concentrations were not measured and therefore the COD concentrations were not corrected for nitrite interference. Hence these small increases in COD profiles may be due to nitrite interference or to the hydrolysis of slowly biodegradable particulate organics at about 72 hours (6). In BATCH RUNS 2 and 3, the COD values were corrected for nitrite interference and the increase observed in BATCH RUN 1 was not observed in any of these runs (Fig. 4.5 and 4.6). The removal efficiencies of the three reactors in BATCH RUN 1 were less than the ones of the succeeding runs, probably because of the nitrite interference. This shows that correcting COD values for nitrite interference is very important in order to obtain the correct COD profiles. This is especially important in the case of inhibitory wastewaters in which nitrification is incomplete and NO_2 accumulation takes place because of the inhibition of *Nitrobacter* species.

In BATCH RUNS 4, 5 and 6 higher PAC concentrations were used (500-3500 mg/l) which led to more significant differences between the AS reactors (Fig. 4.7, 4.8 and 4.9). The final COD values in these runs with PAC addition were below 60 mg/l. In BATCH RUNS 5 and 6, no difference in COD removals was observed between the reactors with different PAC concentrations (Table 4.2). This shows that additional PAC does not always result in higher COD removals. Some of the nonbiodegradable organic matter can also be nonadsorbable on activated carbon. Therefore the amount of PAC concentration to be applied should be well determined in order to avoid excessive usage of PAC.

In BATCH RUN 4, a new feeding was made to the reactors at the 15^{th} day (Fig. 4.7). In the succeeding days after new feeding, the final COD values in AS+PAC reactors were much lower than the final COD values in the AS reactor. Since no PAC addition was made at the day of new feeding, the difference between final COD values was not due to adsorption on PAC, but probabaly it was due to previously increased microbial activities in the AS+PAC reactors.

The difference between total COD (TCOD) and soluble COD (SCOD) (see Section 3.2 for the difference between TCOD and SCOD) decreased very rigorously with time through all batch runs resulting in effluent TCOD and SCOD values with very small differences. This was because the leachate and the stock synthetic domestic wastewater were kept at about 4°C and contained significant amounts of organic matter in particulate form that was hydrolized or solubilized with time by the enzymatic actions of the microorganisms and agitation in the reactors (12,13).

In BATCH RUNS 4-10, mixed liquor COD (MLCOD) (see Section 3.2) was determined in order to obtain an idea about the microorganism concentration in the reactors. MLCOD contains both the TCOD of the wastewater and the COD exerted by the microorganisms in the mixed liquor. MLCOD measurements are less amenable to significant experimental errors. On the other hand, MLVSS measurement may be very errorenous and there is a considerable amount of inert suspended matter in the leachate that may be misleading in using MLVSS values to estimate biomass concentrations. Using the MLCOD measurements, yield coefficients were determined according to the procedure described by Copp et al. (16). The procedure was based on the assumptions that there is no production of soluble COD as a by-product of metabolism and the experiment occurs over a short period of time so that endogenous decay can be neglected. The difference between MLCOD and SCOD was accepted as cell-COD and the yield (Y) was calculated as the ratio of biomass COD produced to SCOD consumed. The yield calculated in terms of mg cell-COD/mg SCOD can be converted into mg MLVSS/mg SCOD by dividing through the theoretical coefficient of 1.42 mg COD/mg MLVSS. The observed yield coefficients for BATCH RUN 4 and BATCH RUN 5 were found as 0.212 mg MLVSS/mgSCOD and 0.42 mgMLVSS/mgSCOD respectively. These values are not very far from the typical values of 0.4-0.8 mgMLVSS/mgBOD_5 given in the literature for domestic wastewater (11).

Batch runs have proved that MLVSS concentration throughout this study does not play a vital role in COD removal. In BATCH RUNS 1-5, MLVSS concentrations were kept very low(200-500 mg/l) and the initial COD/MLVSS ratios (So/Xo) were above 3 (Table 4.2). In BATCH RUNS 6-10, MLVSS concentrations were kept at higher levels (about 2000 mg/l) and the So/Xo ratios were as low as 0.5. But no significant difference was observed

in terms of COD removal at different So/Xo ratios (Table 4.2). The COD profiles of BATCH RUNS 6,9 and 10 are shown in Figures 4.9, 4.10 and 4.11.

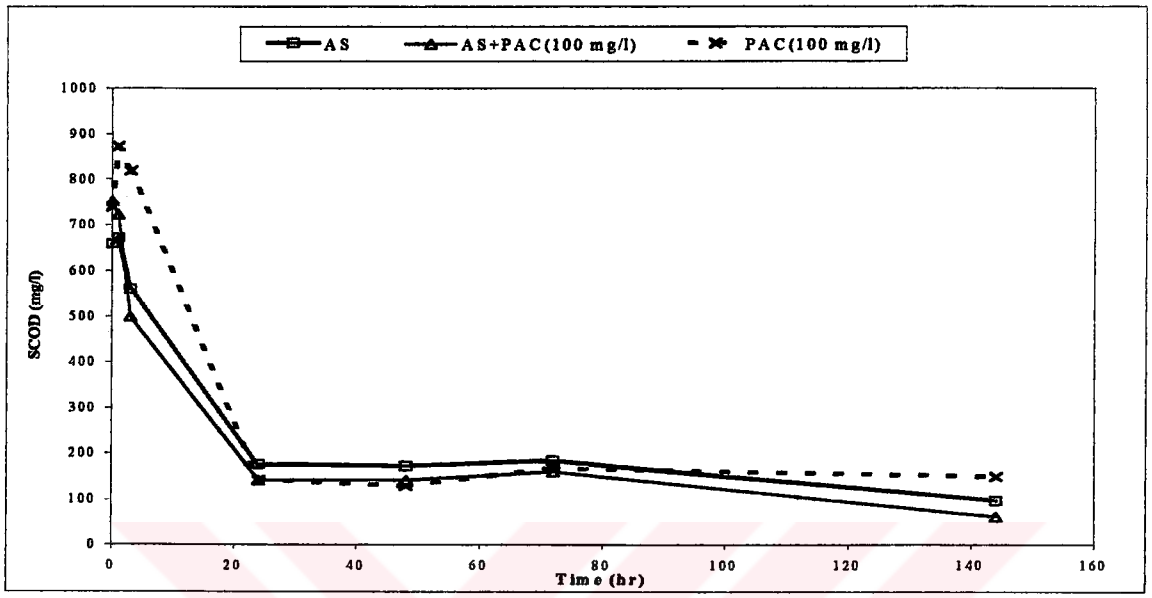


FIGURE 4.4. COD Profiles in BATCH RUN 1.

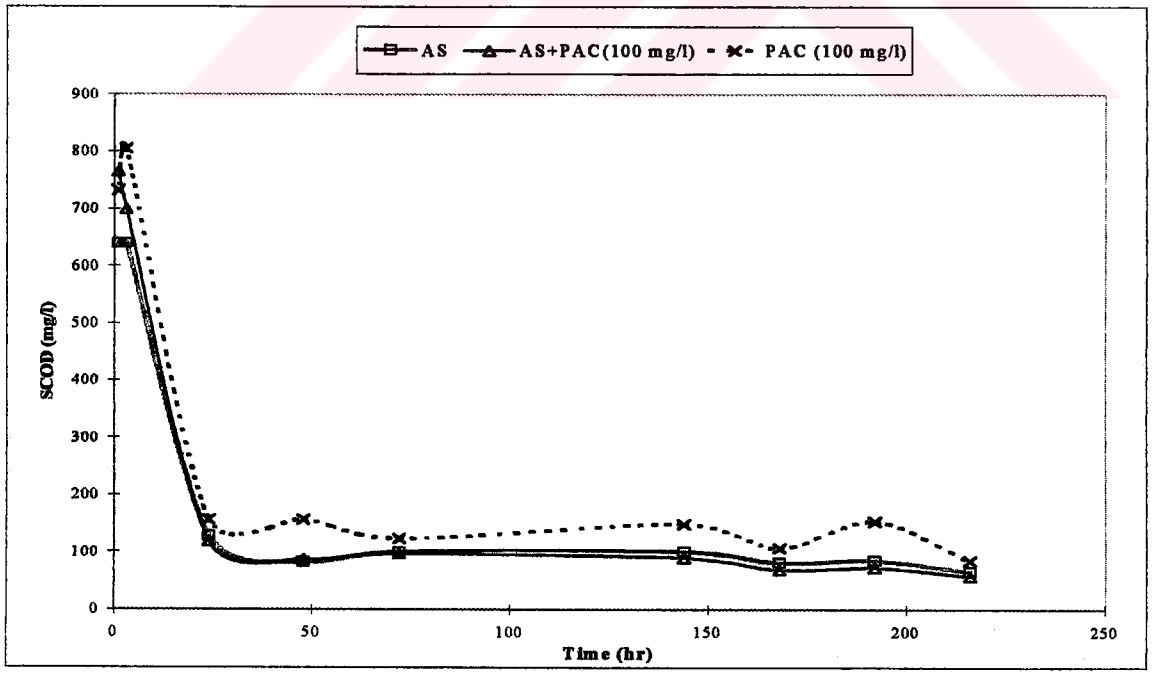


FIGURE 4.5. COD Profiles in BATCH RUN 2.

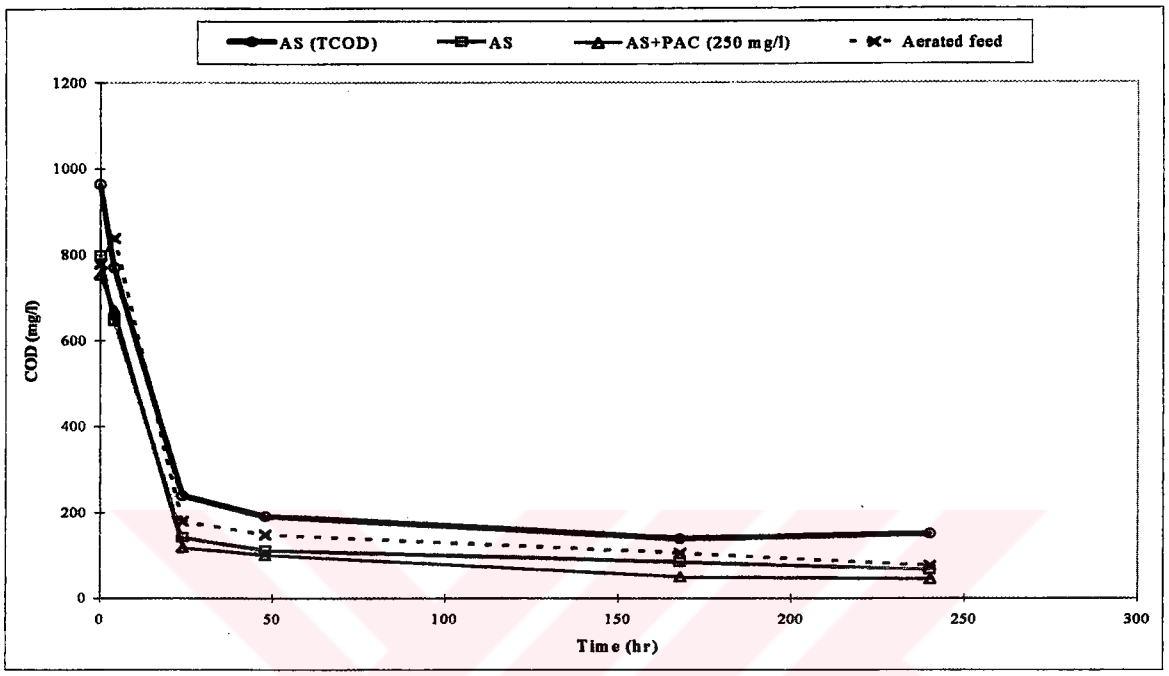


FIGURE 4.6. COD Profiles in BATCH RUN 3.

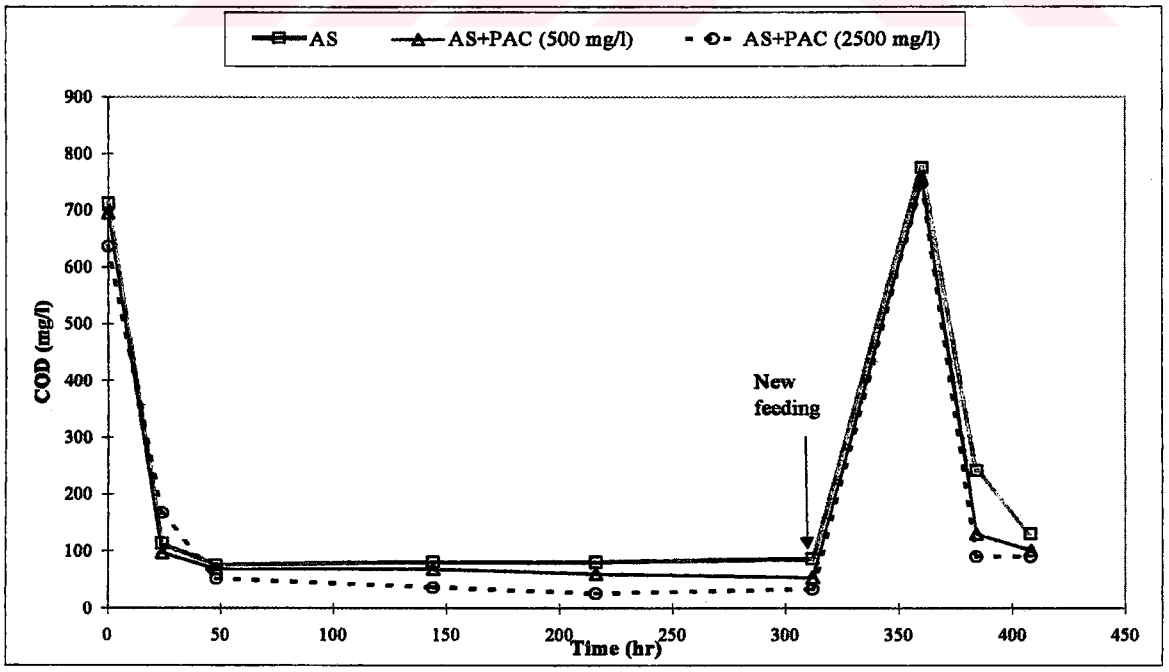


FIGURE 4.7. COD Profiles in BATCH RUN 4.

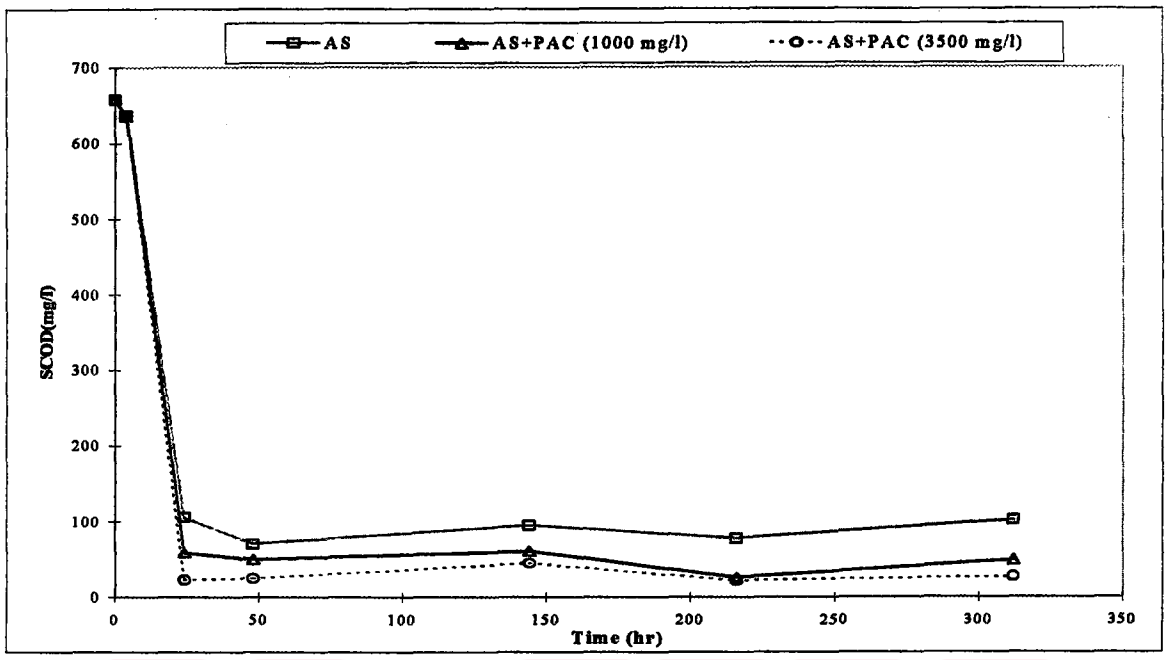


FIGURE 4.8. COD Profiles in BATCH RUN 5.

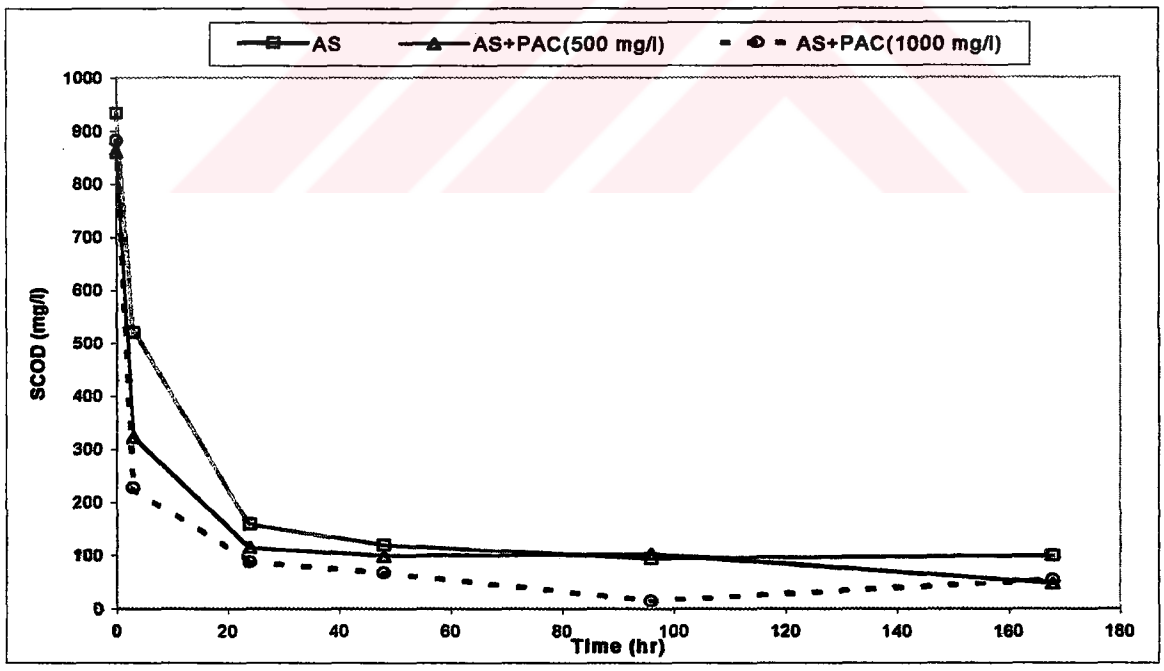


FIGURE 4.9. COD Profiles in BATCH RUN 6.

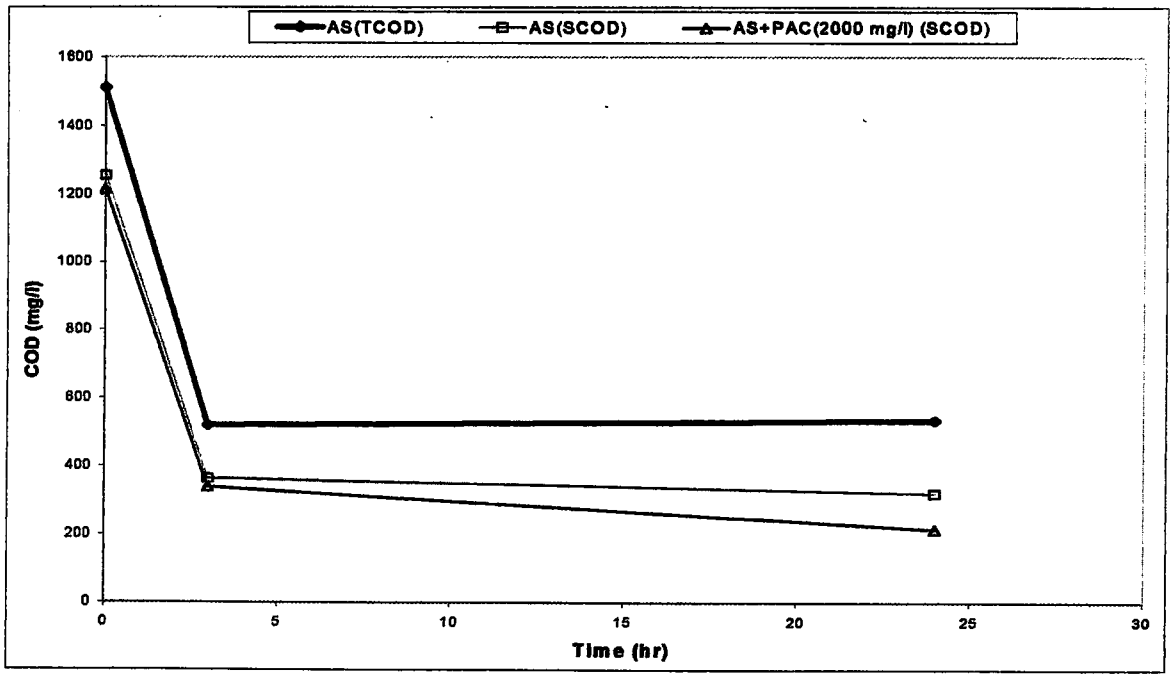


FIGURE 4.10. COD Profiles in BATCH RUN 9.

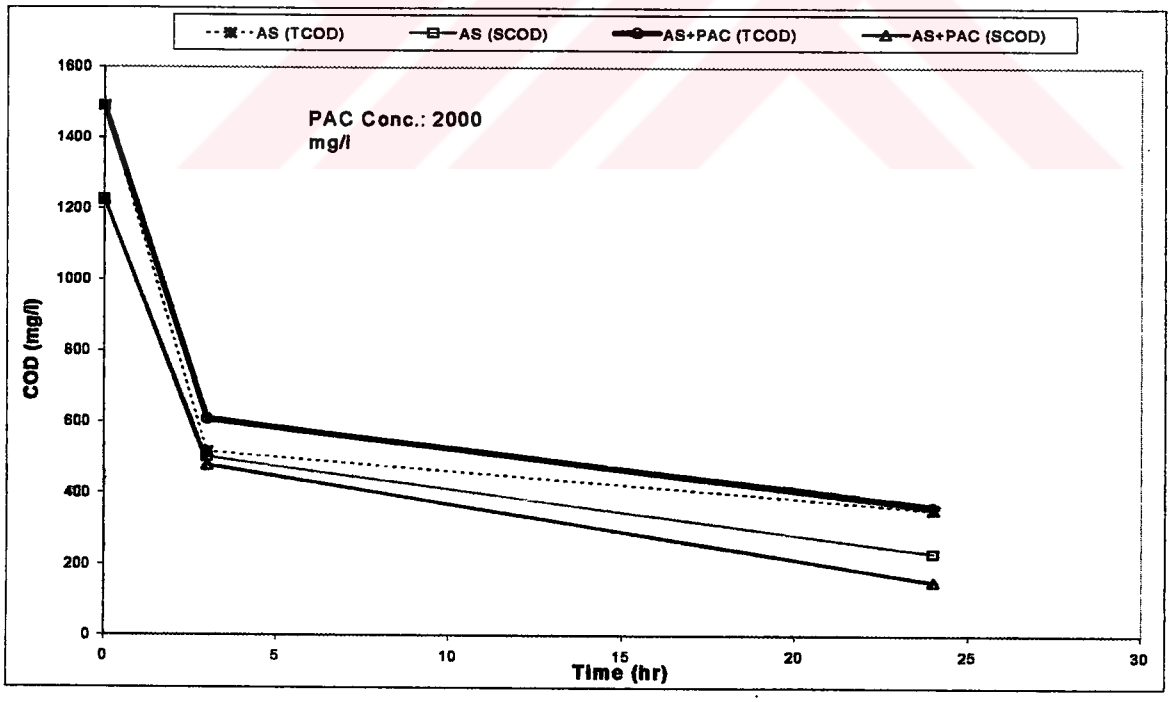


FIGURE 4.11. COD Profiles in BATCH RUN 10.

4.2.1.2. Kinetic Evaluation of Organic Substrate Removal in Batch Runs

The Monod kinetic model for activated sludge systems states that if the substrate concentration is much higher than the half-velocity constant, the Monod equation reduces to a zero-order equation (Eq. 4.2). A zero-order model proposes a substrate removal kinetics independent of the substrate concentration, i.e. substrate concentration is not rate limiting.

$$r_S = -\frac{dS}{dt} = qX = k \tag{4.3}$$

S = Substrate concentration, mass COD/volume
X = Average biomass concentration in the reactor, mass MLVSS/volume
q = Zero order specific substrate removal rate, mass COD/ mass MLVSS/time
k = Zero order substrate removal rate, mass COD/volume/time

In the batch runs of this study, the initial substrate concentrations were high so that substrate concentration was not likely to be rate limiting in the first hours (3-4 hours). Therefore the reaction kinetics is closer to a zero-order model during the first hours. The high zero order reaction rates for TCOD for the first hours (Table 4.3) favors the zero-order assumption for the first hours. But, the zero order model is not applicable to SCOD removal in the first hours because the exact COD removal can not be observed due to the solubilization of the particulate organics during these first hours. Therefore, the zero-order assumption for batch runs was extended to 24 hours to observe an apparent zero-order rate constant for SCOD. A 24 hours period is also comparable with the 32 hours of hydraulic retention time in semi-continuously fed batch runs and continuous-flow operations.

After the utilization of readily biodegradable organics, substrate concentration becomes rate limiting and the substrate removal kinetics approaches a first-order reaction. But the presence of soluble and particulate nonbiodegradable organics in the leachate make the first order model inapplicable to the batch runs of this study. A model which takes the nonbiodegradable COD (final COD concentration in batch reactors) into account was used in a previous study (6). The model was proposed by Braha (Ref. in Çakıroğlu, 1998). According to this model, substrate utilization can be expressed as follows;

$$\frac{-dS}{dt} = q'X(S - Si) = k'(S - Si) \qquad (4.4)$$

where, Si = Nonbiodegradable substrate concentration, mass COD/volume

q′ = First order specific substrate removal rate, volume/mass MLVSS/time

k′ = First order substrate removal rate, $time^{-1}$

First order rate constants for Braha's model were estimated by a trial and error procedure until reaching a suitable k′ value that best fits the actual profile. Braha's model fits the experimental COD profiles in the period after 24 hours when the substrate concentration becomes rate limiting. Figures 4.12-4.17 show that Braha's model is applicable to the evaluation of reaction kinetics in a batch reactor when leachate was combined with synthetic domestic wastewater. Low standard deviations from the mean in the case of Braha's model prove that the analysis of a series of batch runs can provide an acceptable rate constant for the removal of slowly biodegradable organic compounds in this leachate-synthetic domestic wastewater combination (Table 4.3). Braha's model was not applied to BATCH RUNS 7-10 which lasted for only 24 hours.

The zero-order assumption for the period of the first 24 hours can also give a plausible reaction rate constant for the readily biodegradable organic compounds in the leachate-domestic wastewater combination. Also the low standard deviations from the mean values favor the validity of the zero-order assumption within the first 24 hours. Although it is clear that reaction is not actually zero-order during the whole period of 24 hours, the mean values for the batch runs with 5 per cent leachate ratio are in accordance with rate constants determined for the semi-continuosly fed batch runs and the continuous flow operation at an hydraulic detention time of about 32 hours and leachate ratio of 6.7 per cent (Sections 4.3 and 4.4).

Throughout the BATCH RUNS 6-8, higher MLVSS concentrations were maintained compared to the first five runs (see Table B2). However, these runs gave only slightly higher zero-order rate constants within the period of first 24 hours compared to other runs. Very high standard deviations for specific substrate removal rates (q) both in the case of Braha's model and the zero-order assumption show that specific substrate removal rate

(substrate removal rate divided by MLVSS) was not a plausible indicator to define COD removal kinetics for this wastewater. The substrate removal rate (k) gives a better idea about the kinetics of COD utilization.

TABLE 4.3. Kinetic rate constants for AS reactors in Batch Runs.

				Braha's Model		Zero Order (First hours)		Zero Order (24 hours)	
Run	Leachate Ratio (Volume%)	X mgVSS/l	Basis	k' 1/h	q' l/mgVSS.h	k mgCOD/ l.h	q mgCOD/ mgVSS.h	k mgCOD/ l.h	q mgCOD/ mgVSS.h
1	5	563	TCOD	0.10	$1.78x10^{-4}$	128.7	0.229	34	0.060
			SCOD	0.08	$1.42x10^{-4}$	33.33	0.059	20.12	0.036
2	5	467	TCOD	0.09	$1.92x10^{-4}$	95.33	0.204	35.83	0.077
			SCOD	0.09	$1.92x10^{-4}$	0	0	21.25	0.046
3	5	439	TCOD	0.087	$1.98x10^{-4}$	48.25	0.110	30.13	0.069
			SCOD	0.095	$2.16x10^{-4}$	38	0.087	27.29	0.062
4	5	-	SCOD	0.12	-	-	-	24.92	-
5	5	250	SCOD	0.12	$4.8x10^{-4}$	5.25	0.021	23	0.092
6	5	1980	SCOD	0.105	$0.53x10^{-4}$	137.67	0.069	32.29	0.016
7	5	1525	SCOD	-	-	-	-	29.29	0.019
8	5	1390	SCOD	-	-	-	-	29	0.021
Mean	5		TCOD	0.092 ±0.007	$1.89x10^{-4}$ $\pm0.1x10^{-4}$	-	-	33.32 ±2.91	0.069 ±0.008
			SCOD	0.102 ±0.007	$2.17x10^{-4}$ $\pm1.6x10^{-4}$	-	-	25.97 ±4.19	0.042 ±0.028
9	15	1225	TCOD	-	-	331	0.270	40.67	0.0332
			SCOD	-	-	296.67	0.242	38.96	0.0318
10	10	1760	TCOD	-	-	324.67	0.185	47.29	0.0268
			SCOD	-	-	241.33	0.137	41.42	0.0235

TABLE 4.4. "Apparent" kinetic rate constants for AS+PAC reactors in Batch Runs.

				Braha's Model	Zero Order (First hours)	Zero Order (24 hours)
Run	Leachate Ratio (Volume %)	PAC Conc. (mg/l)	Basis	k' (1/h)	k (mgCOD/l.h)	k (mgCOD/l.h)
1	5	100	SCOD	0,090	84.33	25.46
2	5	100	SCOD	0.095	33	24.38
3	5	250	SCOD	0.095	20.75	26.46
4	5	500	SCOD	0,118	-	24.92
4	5	2500	SCOD	0.065	-	19.54
5	5	1000	SCOD	0.123	5.75	25
5	5	3500	SCOD	0.268	5.5	26.46
6	5	500	SCOD	0.105	179	31.08
6	5	1000	SCOD	0.103	218	33.08
7	5	1000	SCOD	-	-	32.25
8	5	1000	SCOD	-	-	31.21
9	15	2000	SCOD	-	272.33	41.71
10	10	2000	TCOD	-	294	47
			SCOD	-	248.67	44.71

"Apparent" kinetic rate constants were also determined for the AS+PAC reactors for comparison purposes (Table 4.4). The "apparent" rate constants for the AS+PAC reactors were found to be equal or greater than the rate constants determined in the case of AS reactors. These apparent rate constants do not actually define the removal rates due to biodegradation, because here also an adsorption takes place.

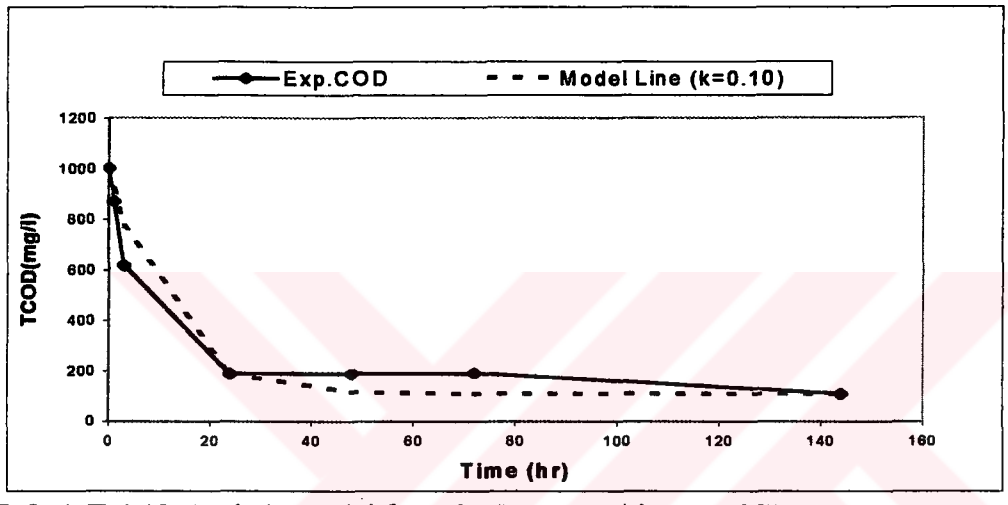


FIGURE 4.12. Braha's model for TCOD removal in BATCH RUN 1.

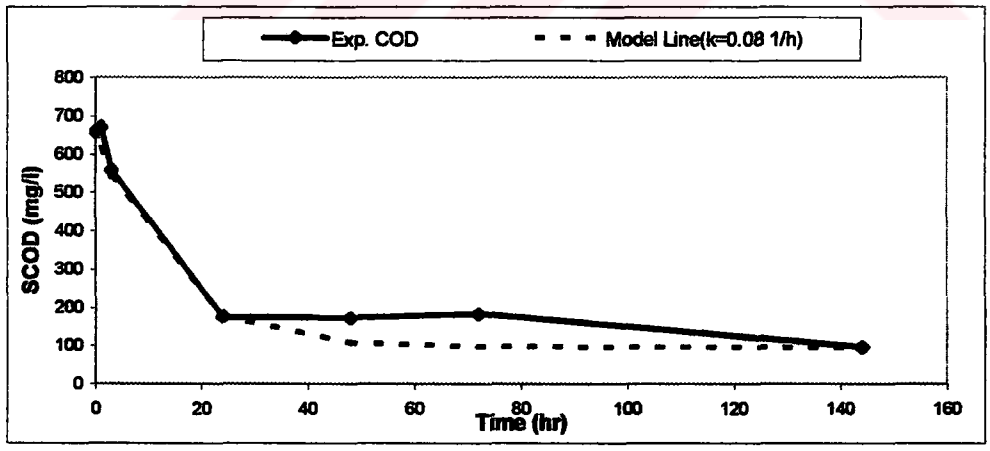


FIGURE 4.13. Braha's model for SCOD removal in BATCH RUN 1

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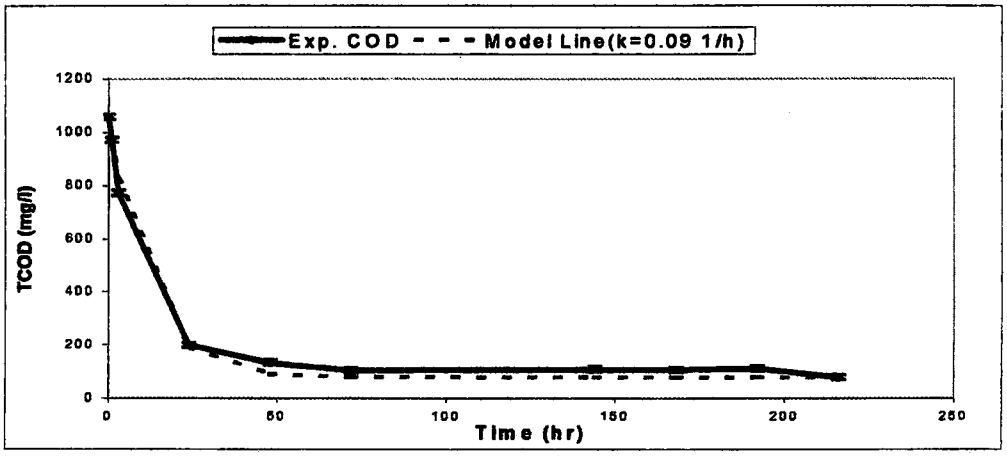


FIGURE 4.14. Braha's model for TCOD removal in BATCH RUN 2.

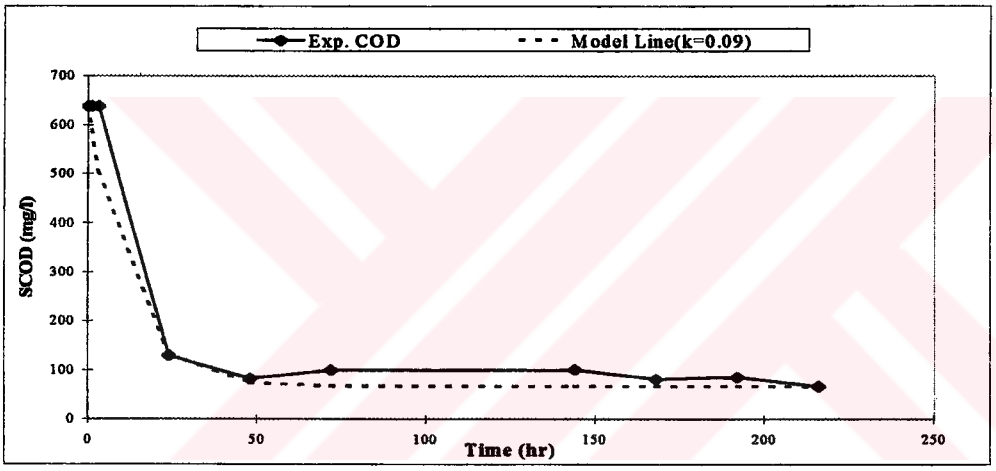


FIGURE 4.15. Braha's model for SCOD removal in BATCH RUN 2.

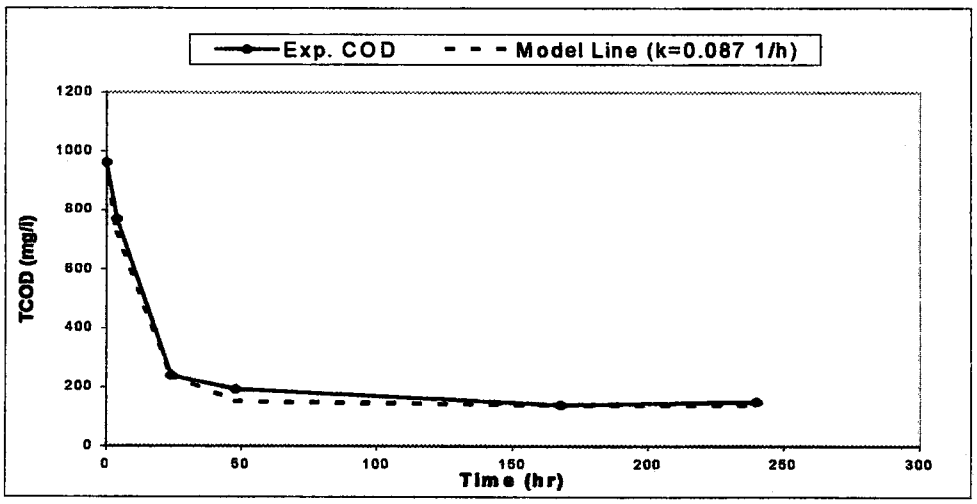


FIGURE 4.16. Braha's model for TCOD removal in BATCH RUN 3.

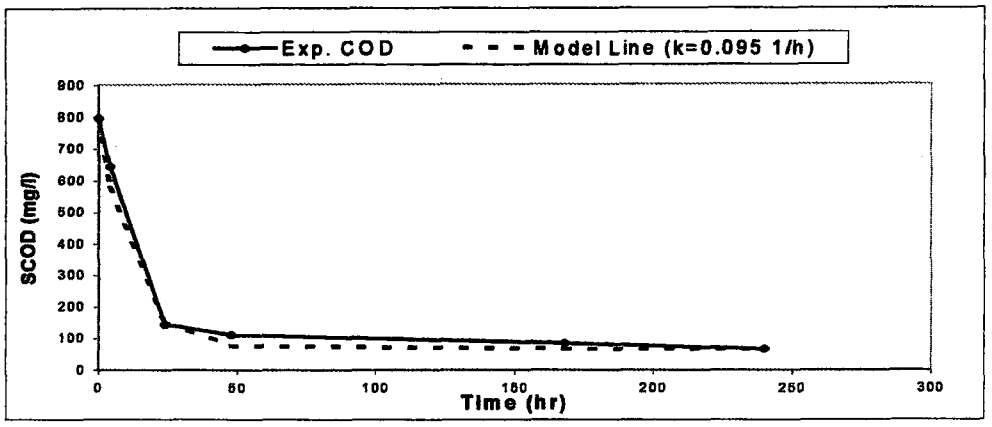


FIGURE 4.17. Braha's model for SCOD removal in BATCH RUN 3.

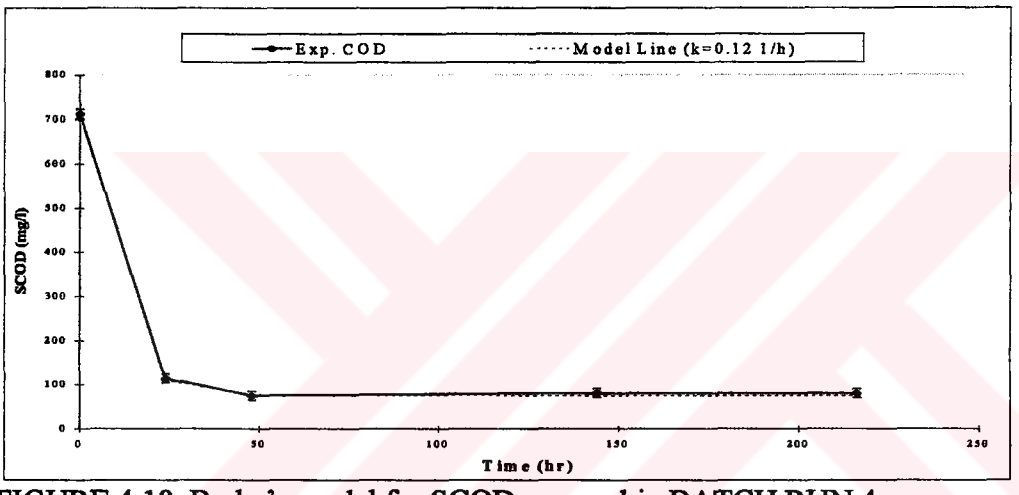


FIGURE 4.18. Braha's model for SCOD removal in BATCH RUN 4.

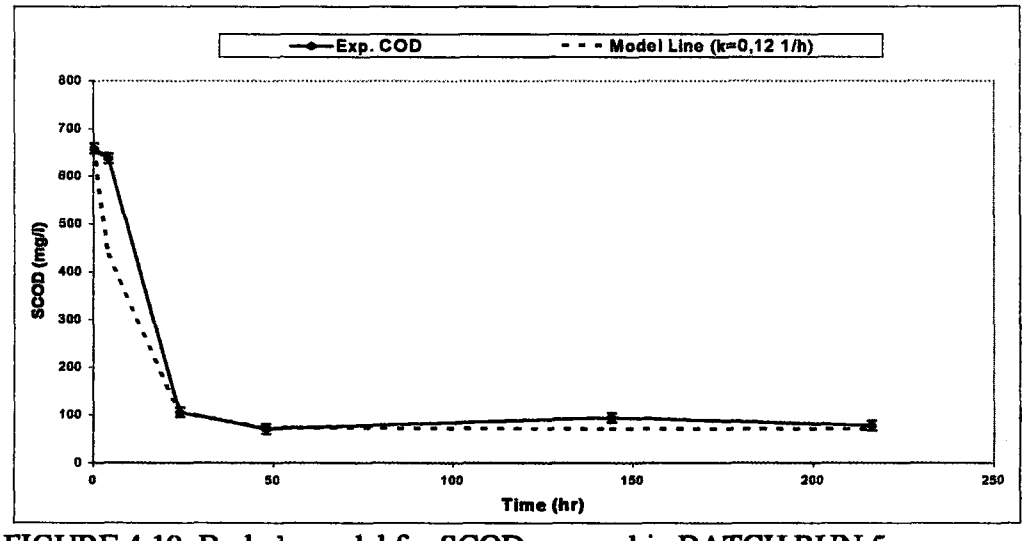


FIGURE 4.19. Braha's model for SCOD removal in BATCH RUN 5.

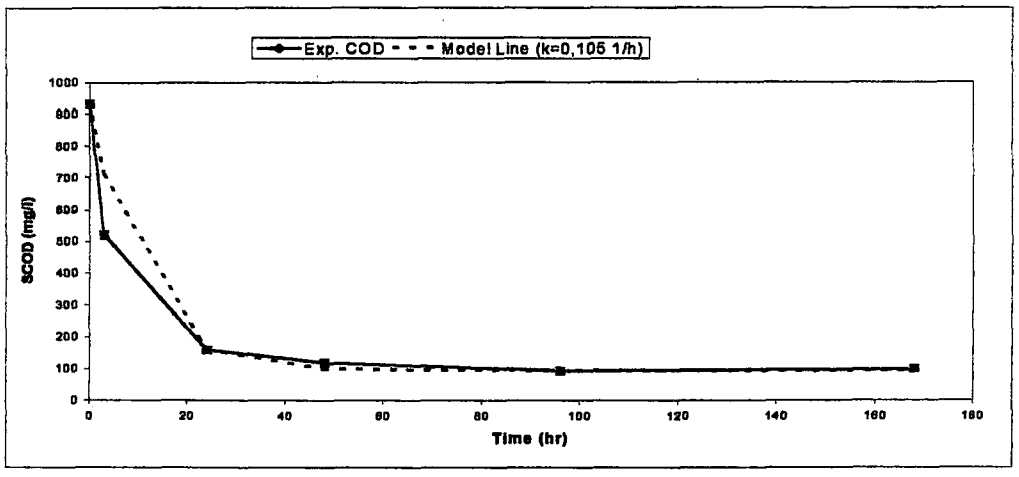


FIGURE 4.20. Braha's model for SCOD removal in BATCH RUN 6.

Batch Runs with Synthetic Domestic Wastewater:

Also batch runs were conducted by feeding a reactor with synthetic domestic wastewater in order to have an idea about the COD removal in the absence of leachate (Table B1). The reaction rate constants based on the zero-order assumption within the first 24 hours are displayed in Table 4.5. The mean value obtained is higher than the mean value obtained for the runs with leachate addition even though the COD values were not corrected for nitrite interference in these runs. The decrease in reaction rate constants in leachate systems proves the inhibitory character of leachate when it is added to the domestic wastewater. A previous study focused on the differences of COD removal between leachate-added reactors and the reactors fed with synthetic domestic wastewater only (6).

TABLE 4.5. Zero order reaction rate constants for batch reactors fed with synthetic domestic wastewater.

Run No	X (mgMLVSS/l)	k (mgCOD/l.h)*	q (mgCOD/mgVSS.h)*
1	2225	32.62	0.0145
6	2580	36.08	0.0140
8	2720	46.25	0.0170
10	3045	30.67	0.0101
12	3705	38.67	0.0104
Mean		36.86±6.09	0.0132±0.0029

* Rate constants are based on a 24 hours time span.

4.2.2. Nitrification in Batch Runs

Nitrification microorganisms are much more sensitive to the inhibitory compounds in the leachate than the heterogenous microorganisms (11,27). Hence PAC addition to the activated sludge can also increase nitrification rates (26,27,30). In order to observe this effect, NH_4^+-N, NO_2-N and NO_x-N concentrations were monitored throughout the batch runs. The true measure for nitrification is the NO_x-N production.

Nitrification profiles showed that nitrification starts after the depletion of readily biodegradable organics by heterotrophs in the first 24 hours and the decrease of COD/ NH_4^+-N ratio. At high COD/ NH_4^+-N ratios, heterotrophs which compete for substrates (O_2 and NH_4^+-N for cell synthesis) retard the activity of nitrifiers (42).

In BATCH RUN 2, only the NO_2-N concentrations were monitored and nitritification (conversion to nitrite only) was observed in AS and AS+PAC reactors, and no nitritification was observed in the PAC reactor. In the AS and AS+PAC reactors, nitrite accumulation increased until 72 hours and then started to decrease (Figure 4.21). This profile shows that conversion of nitrite to nitrate was inhibited during the first days, and in the succeeding days complete nitrification could start to some extent. However this tendency was not observed in any of the other runs in which nitrite accumulation increased by time and nitrite and nitrate concentrations were very close to each other showing that the activity of *Nitrobacter* species was completely inhibited by leachate (Table B2). Free ammonia concentrations were calculated to be above 1 mg/l at pH values above 8 throughout the batch runs. Therefore another important inhibitor for *Nitrobacter* was free ammonia (Section 2.3.3.2).

In the reactors with PAC addition only or simple aeration of the feed (no activated sludge and PAC addition), nitrification was not observed to any extent (BATCH RUNS 2 and 3) contrary to the high COD removals in such reactors (Section 4.2.1.1). Only in the reactors with activated sludge addition, nitrification occurred. This may have arised since in the microbial population of the leachate nitrifiers were not in sufficient amounts or were not present at all.

In BATCH RUNS 2,3 and 4 the positive effect of PAC addition on nitrification was not seen. Nitrification profiles were similar for AS and AS+PAC reactors in these runs (Figures 4.21-4.23). Moreover, even worse nitrification profiles were observed with PAC additions at concentrations of 2500 and 3500 mg/l in BATCH RUNS 4 and 5, respectively. This undesired effect of PAC was highly probably because of increased settling of biomass at high PAC concentrations. In these reactors the MLVSS concentrations were kept quite low resulting in very high PAC/MLVSS ratios. Therefore the nitrifiers could have been settled and surrounded by PAC particles hindering the contact of nitrifiers with ammonium ions in the bulk liquid. This handicap could be overcome by applying a more severe agitation by mechanical means instead of aeration mixing only. Undesired settling in aeration tanks because of PAC addition is a problem encountered in reactors with aerator mixing (43). The positive effect of PAC addition to nitrification was observed better in BATCH RUNS 5 and 6 at PAC concentrations of 500 and 1000 mg/l, which caused less settling problems in the reactors (Figures 4.24-4.26).

The removal efficiencies presented in Table 4.6 show that nitrification is not the main mechanism for NH_4^+-N removal. NH_4^+-N profiles display a decreasing slope of NH_4^+-N removal by time (Figure 4.24). During the first periods of the batch runs, activity of heterotrophs is the highest and hence mainly COD removal takes place. Heterotrophs that oxidize organic matter also use some of the carbonaceous organic matter for growth and they also use NH_4^+-N for cell synthesis. Therefore the high slopes at the initial periods may be because of heterotrophic growth in this period. Another possible mechanism for high NH_4^+-N removal in this period may be air stripping of ammonia at pH values of 8.5-9.0.

TABLE 4.6. NH_4^+-N Removal Efficiencies in Batch Reactors.

Run No	Reactor	Total NH_4^+-N Removal %	NH_4^+-N Removal % due to NOx-N Production
3	AS	95	16
	AS+PAC (250 mg/l)	95	28
	Aerated Feed	95	0
4	AS	98	13
	AS+PAC (500 mg/l)	98	14
	AS+PAC (2500 mg/l)	89	1
5	AS	92	24
	AS+PAC (1000 mg/l)	97	26
	AS+PAC (3500 mg/l)	89	11
6	AS	44	0
	AS+PAC (500 mg/l)	52	15
	AS+PAC (1000 mg/l)	54	27

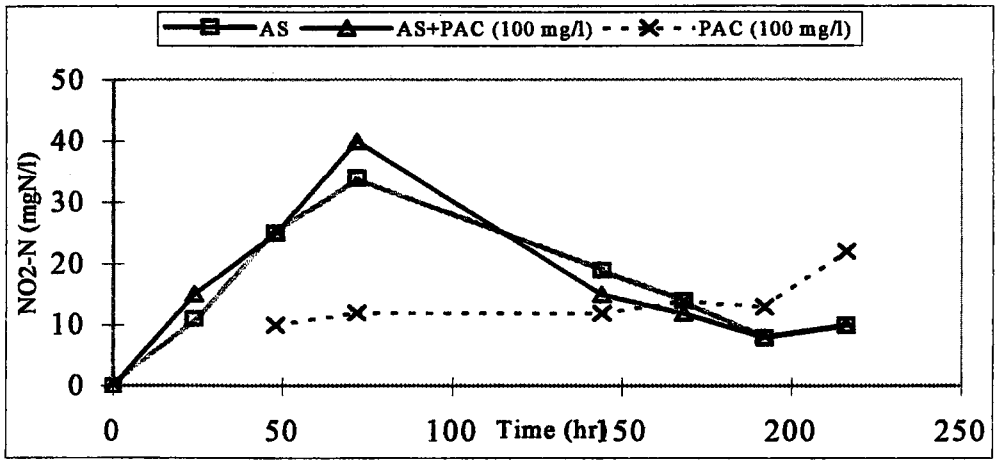


FIGURE 4.21. NO_2-N Profiles in BATCH RUN 2.

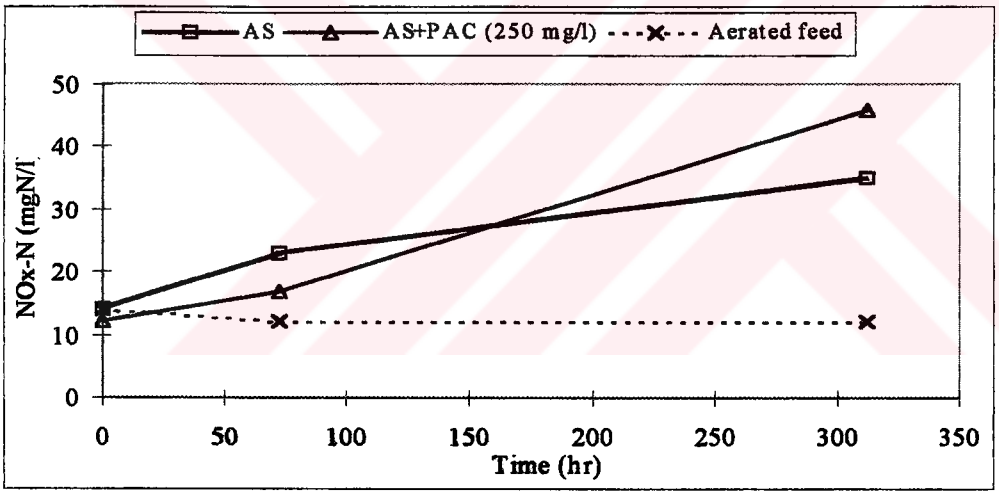


FIGURE 4.22. NO_x-N Profiles in BATCH RUN 3.

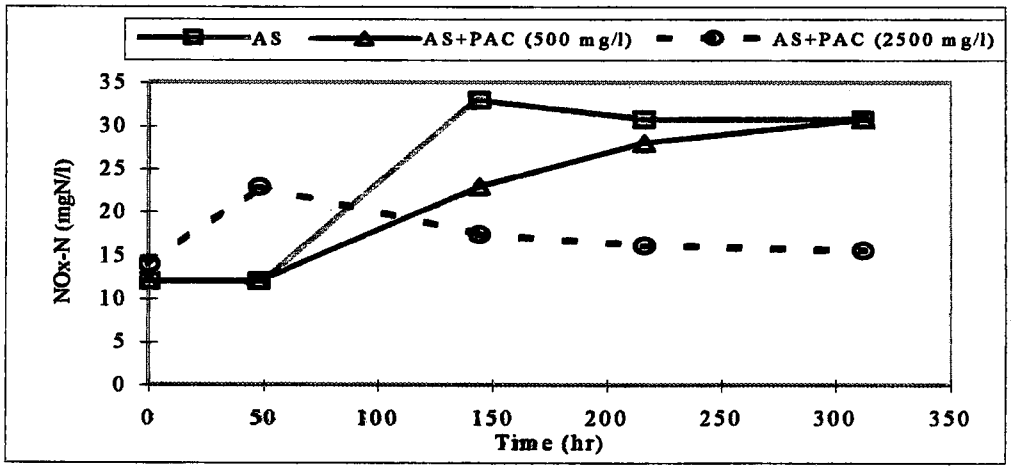


FIGURE 4.23. NO_x-N Profiles in BATCH RUN 4.

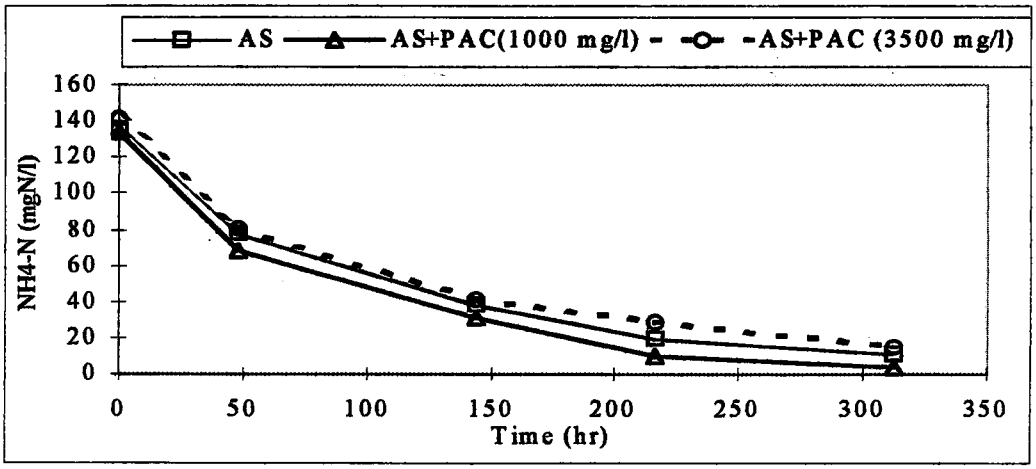


FIGURE 4.24. NH_4-N Profiles in BATCH RUN 5.

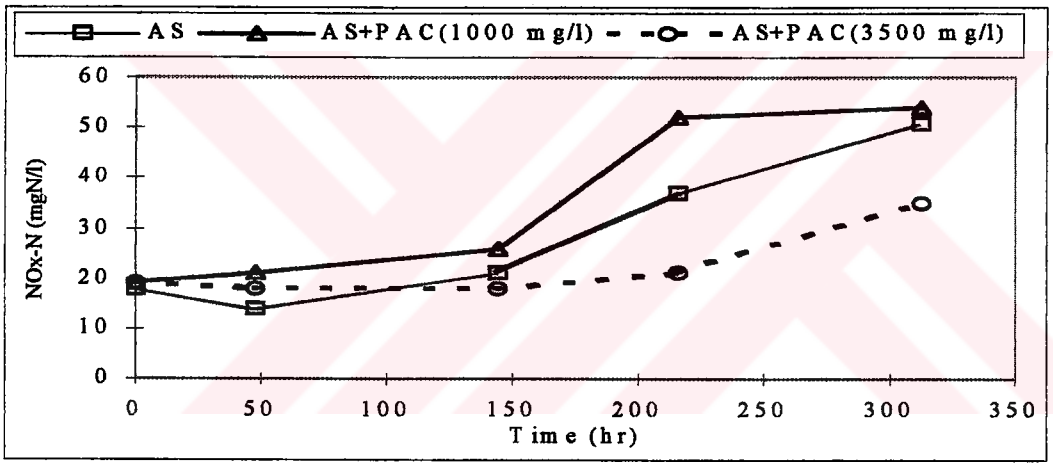


FIGURE 4.25. NO_x-N Profiles in BATCH RUN 5.

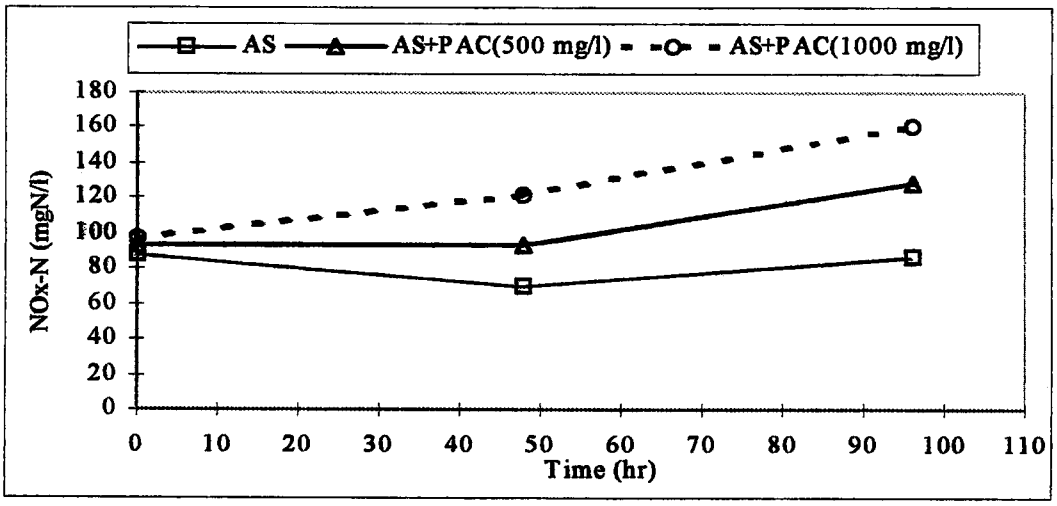


FIGURE 4.26. NO_x-N Profiles in BATCH RUN 6.

4.2.3. Oxygen Uptake Rates in Batch Runs

Throughout the batch runs, the respirometric properties of the activated sludge in the batch reactors were monitored besides COD removal and nitrification measurements in order to investigate the relationship between OUR (Oxygen Uptake Rate) and substrate removal. OUR is related to both the microbial activity and the presence of biodegradable substrates.

Initially the OUR is due to the utilization of readily biodegradable substrate present in the wastewater and due to the hydrolysis of particulate substrate derived from the wastewater. In BATCH RUNS 1, 2 and 3 a significant decrease in OUR takes place in the first 24 hours (Fig. 4.27, 4.28 and 4.29). The initial high OUR is due to the utilization of readily biodegradable COD which constitutes the largest portion of COD in the wastewater. After this sharp decrease, increases in OUR values were detected in the 48^{th} or 72^{nd} hours in the first 3 runs. This increase may be due to oxygen consumption through nitrification, which starts at about this period after the depletion of readily biodegradable COD (Section 4.2.2). Another probable reason for this unexpected increase may be due to the oxidation of hydrolyzed particulate organic substrates in this period (14,44).

In BATCH RUN 4, OUR values stayed constant for the first few hours (Fig. 4.30). This plateau occurs at the maximum specific growth rate during the removal of readily biodegradable COD provided that nitrification does not take place in the first hours (44). The first 48 hours of BATCH RUN 4 were plotted in Figure 4.30, and the full data may be seen in Table B2.

In BATCH RUNS 5 and 6, increases in OUR values in the first hours are observed (Fig. 4.31, 4.32). The reason for this increase may be the hydrolysis of some particulate COD in this period besides the removal of readily biodegradable COD in the influent wastewater (44). Since the synthetic domestic wastewater is kept as a concentrated stock solution at 4°C, some of the organic compounds appear as particulate COD at time zero and during the succeeding hours they can be easily solubilized in the turbulent batch reactor. Another probable reason for the increase in OUR in the first hours may be due to the growth of microorganisms in this period when the substrate concentration is high with respect to the biomass(16).

The OUR in the reactors which were not inoculated with activated sludge appeared to be much lower than the OUR in AS and AS+PAC reactors (Fig. 4.28 and 4.29). Particularly in the first hours, very low OUR values were detected in reactors to which AS was not added, and OUR increased after some period in these reactors (Fig. 4.29). This delay in the OUR increase was due to the acclimation of leachate microorganisms to the new aerobic environment.

PAC addition to AS seems to increase OUR in considerable amounts. Particularly the high concentrations of PAC (2500 and 3500 mg/l) resulted in high OUR values. However this foundation is very misleading, because the COD removal and nitrification profiles for BATCH RUNS 4 and 5 offer that OUR values should not be much higher than the AS reactors. The reason for this unexpectedly high OUR values, particularly in BATCH RUN 4, may be due to the settling problems encountered with high PAC concentrations. In OUR measurements, the sample to be used in OUR measurement is taken from the reactor after a severe mixing and the OUR measurement bottle is mixed mechanically during measurement. Therefore the hindering of contact between microorganisms and substrate is prevented during the measurement resulting in higher OUR values detected than the actual OUR values inside the batch reactors.

OUR values decreased to values as low as 1-4 mg O_2/l.h in the late periods in all of the batch runs (see Table B2). These very low OUR values represent the endogenous decay of microorganisms after the depletion of organic substrates in the reactors (44). Very low values of OUR were observed after 48 or 72 hours throughout the batch runs. However it is not correct to say that these values show exactly the endogenous respiration rates, because also nitrification took place in this period (see section 4.2.2).

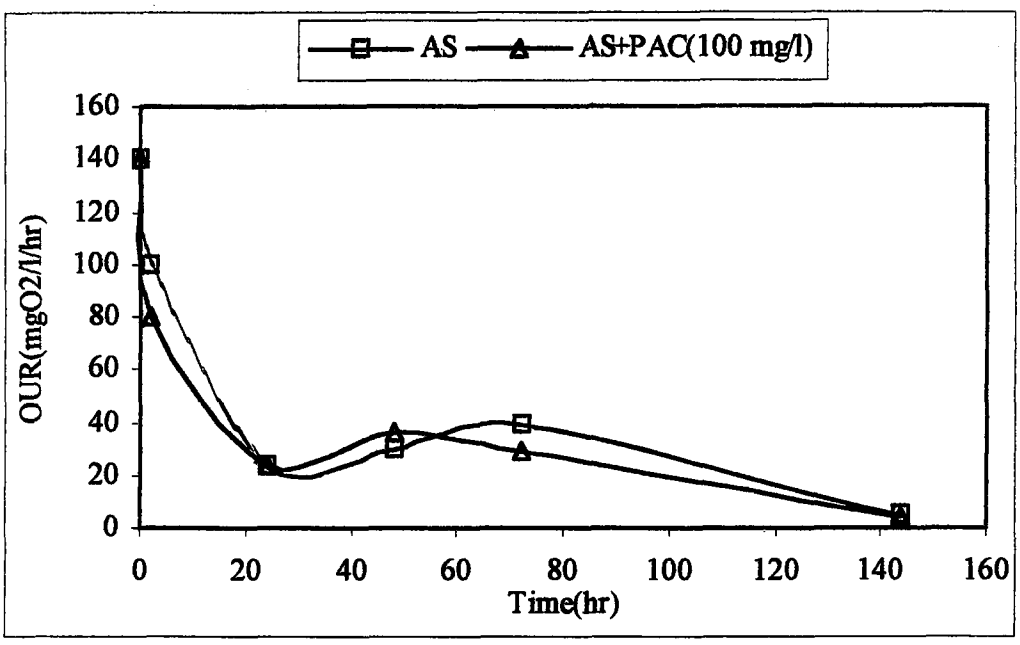


FIGURE 4.27. OUR Profiles in BATCH RUN 1.

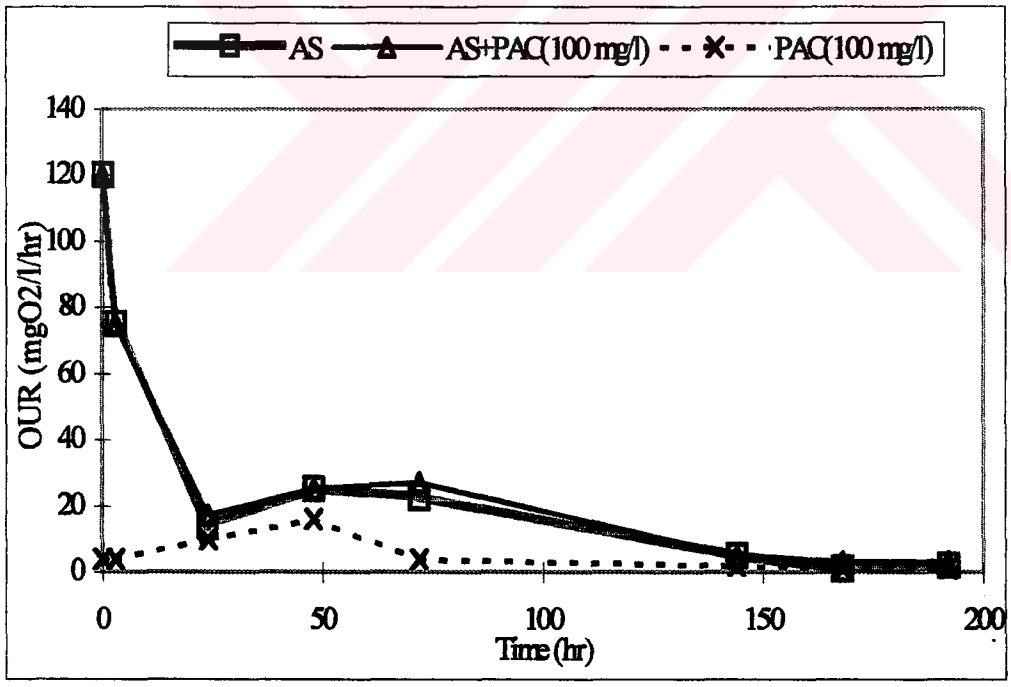


FIGURE 4.28. OUR Profiles in BATCH RUN 2.

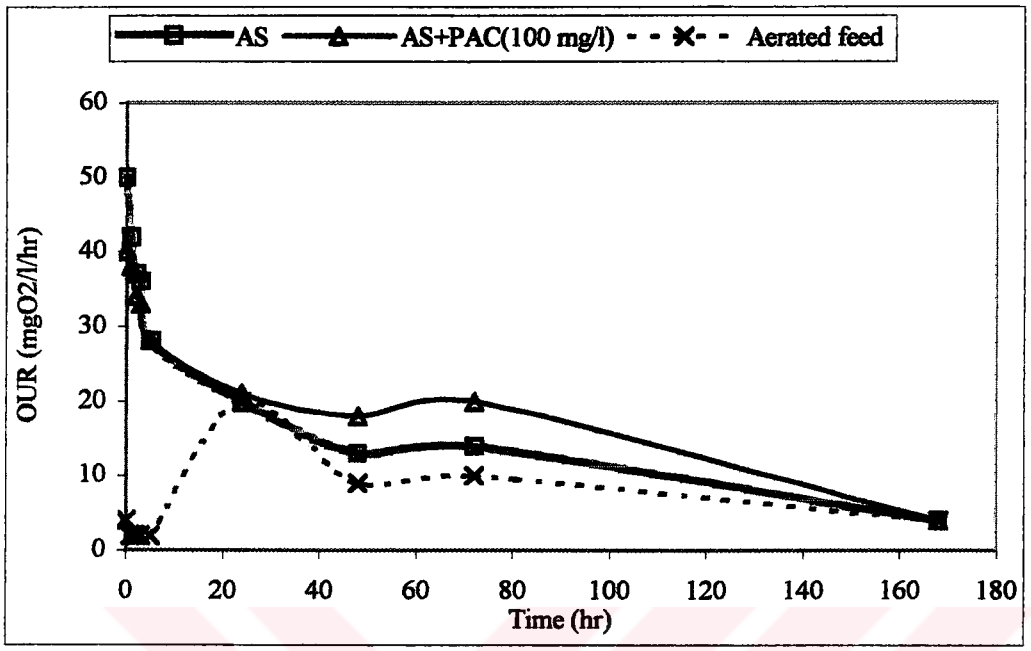


FIGURE 4.29. OUR Profiles in BATCH RUN 3.

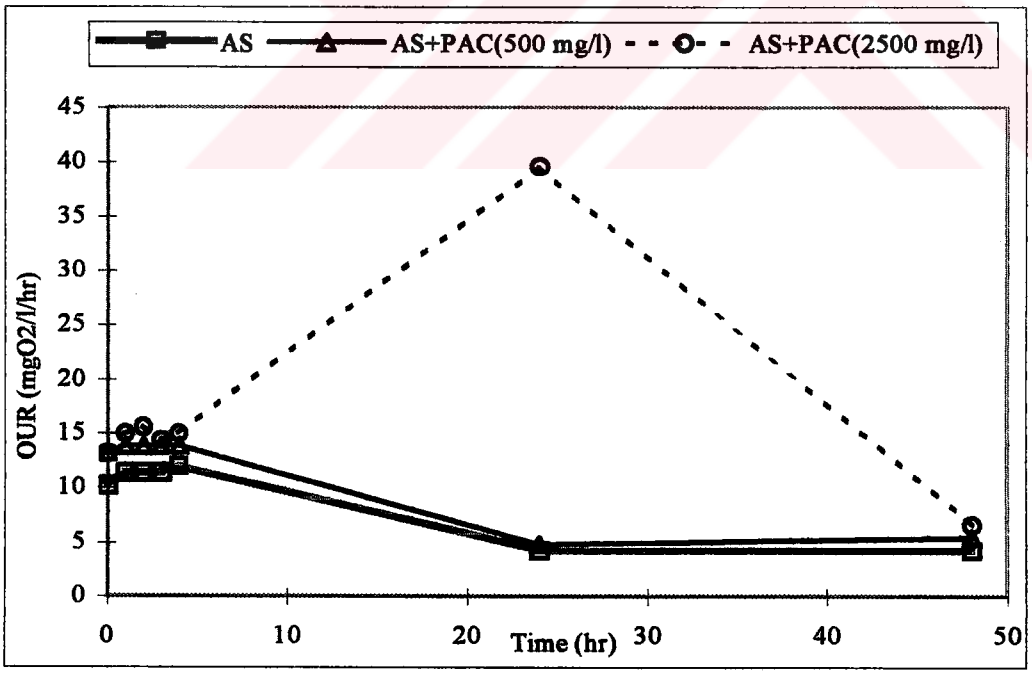


FIGURE 4.30. OUR Profiles in BATCH RUN 4.

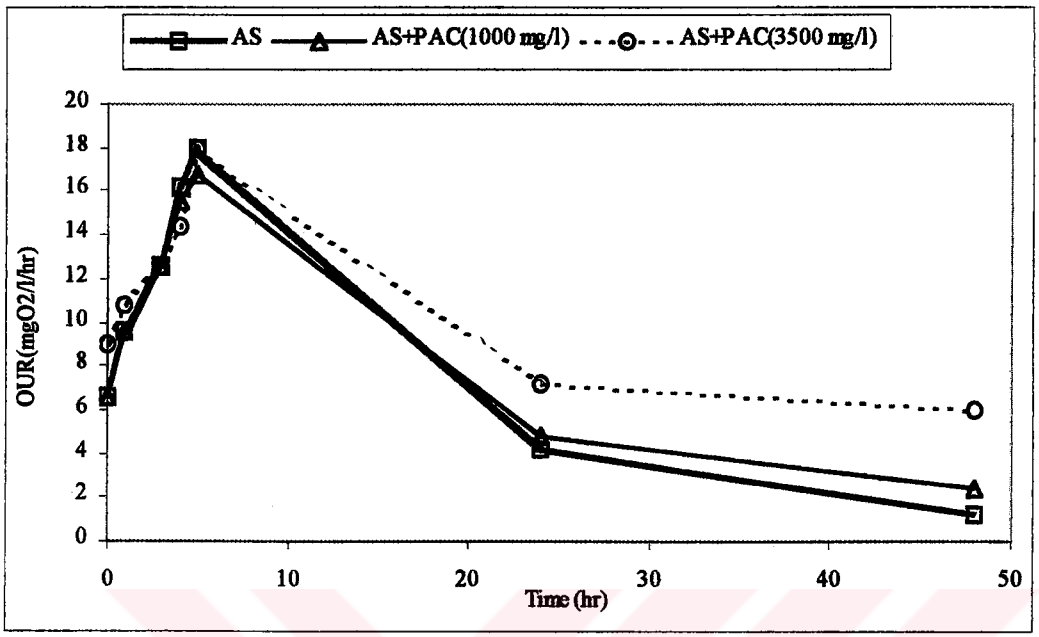


FIGURE 4.31 OUR Profiles in BATCH RUN 5.

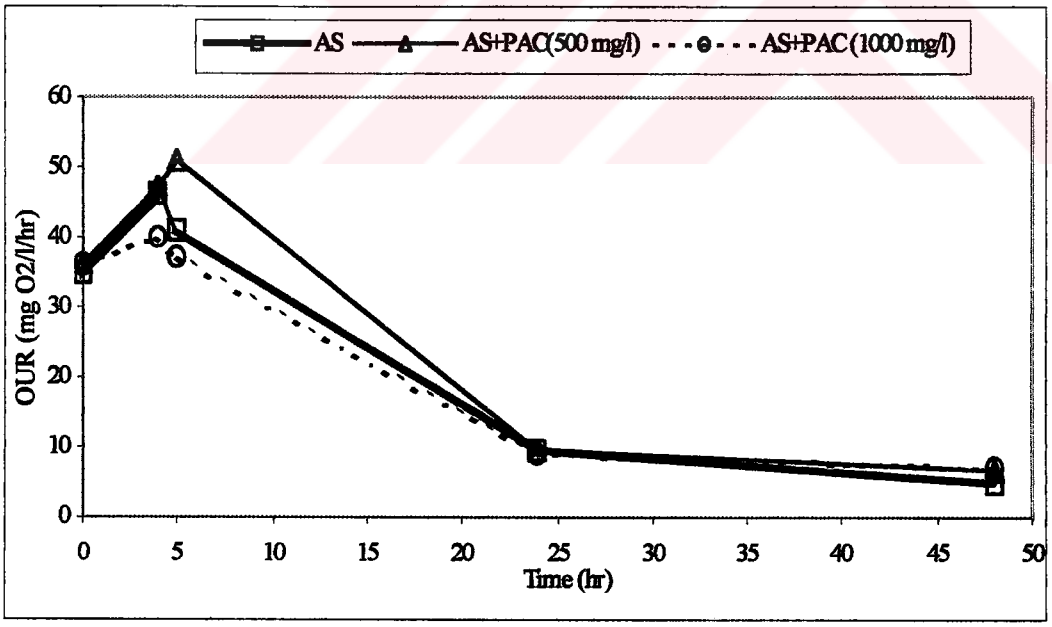


FIGURE 4.32. OUR Profiles in BATCH RUN 6.

4.3. Activated Carbon Addition to Activated Sludge in Semi-Continuously Fed Batch (SCFB) Reactors

Semi-Continuously Fed Batch (SCFB) Runs were performed in two-liter batch reactors as explained in detail in Section 3.3.3.

4.3.1. Removal of Organic Substrates in SCFB Runs

4.3.1.1. COD and OUR Profiles

SCFB RUN 1:

In the first day of SCFB RUN 1, a considerable difference between AS and AS+PAC reactors was observed in terms of COD removal. However in the succeeding days, this difference disappeared giving equal effluent COD values for AS and AS+PAC reactors (Fig. 4.33). This shows that the active sites of activated carbon became saturated in the first day and the initially added PAC did not improve the COD removal when no further PAC was added. OUR in AS+PAC reactor of SCFB RUN 1 is apparently greater than the OUR of AS reactors throughout this run although this much difference can not be expected considering the COD and nitrification profiles (see Section 4.3.2) of this run (Fig. 4.34). The reason for this unexpected observation may be because of the misleading OUR measurements due to settling in AS+PAC reactors as explained in Section 4.2.3.

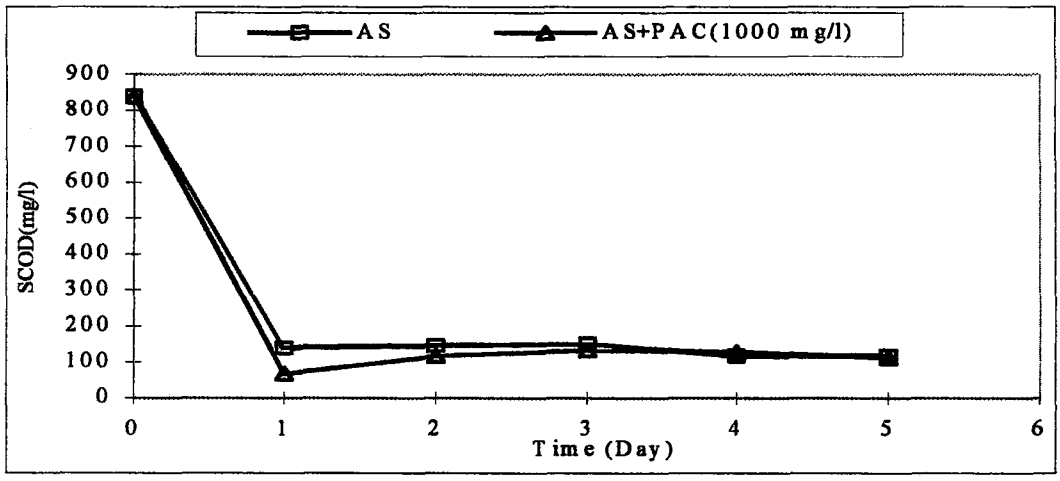


FIGURE 4.33. COD Profiles in SCFB RUN 1.

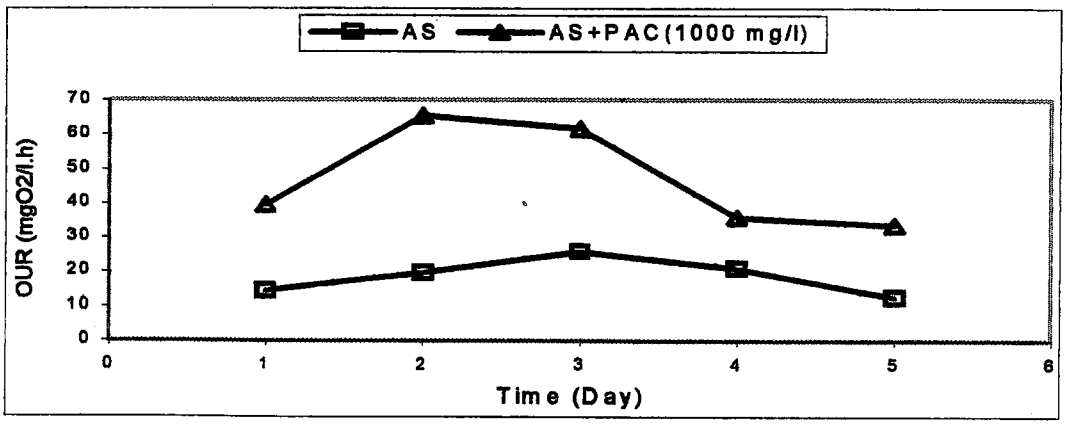


FIGURE 4.34. OUR Profiles in SCFB RUN 1.

SCFB RUN 2:

SCFB RUN 2 lasted for 35 days. As in SCFB RUN 1, in SCFB RUN 2, the only detectable difference between two reactors was observed in the 1st and 15th days at which 1000 mg/l shock PAC additions were performed besides the daily addition of PAC to keep PAC concentration constant in the AS+PAC reactor (Fig. 4.35). In other days of the run throughout the 35 days, no considerable enhancement in COD removal due to PAC addition was observed. The statistical analysis of the effluent SCOD data obtained in this run using the *Paired t-test* (45) showed that there was no significant difference between the two reactors at a level of 95% confidence.This shows that the saturated activated carbon was not effectively bioregenerated by the activity of microorganisms under the current circumstances (see Section 2.4.4).

SCFB RUN 3:

In SCFB RUN 3, significant differences between TCOD and SCOD concentrations in the effluents of AS and AS+PAC reactors were achieved (Fig. 4.36). The statistical analysis of the effluent COD data obtained in this run using the *Paired t-test* (45) showed that there was significant difference between the two reactors at a level of 95% confidence. The difference between two reactors in terms of effluent TCOD was more apparent. One reason for this may be the higher adsorbability of insoluble organic compounds by PAC. But besides adsorption, PAC also improves the settleability of activated sludge and hence decreases the concentration of microorganisms and other particulate organic substrates that contribute to TCOD in the effluent. In all the batch runs and SCFB runs a clearer effluent was observed in the PAC-added reactors. Additionally, sludge volume indexes (SVI) were

measured for two reactors at the end of the run. SVI values were obtained as 38.3 ml/g for the AS reactor, and 22.9 ml/g for the AS+PAC reactor. Lower SVI values imply better settling characteristics for the sludge (11).

The effluent SCOD concentrations also proceeded at lower values for the AS+PAC reactor in SCFB RUN 3, particularly after the addition of a shock PAC concentration (2000 mg/l) at the 1st day and 16th day of operation as in SCFB RUN 2. OUR values proceeded at higher values for AS+PAC reactor parallel to the COD profiles except for the 7th and 8th days (Fig. 4.37). This unexpected observation was probably due to an aeration-agitation related problem encountered in these days in the AS reactor.

SCFB RUN 4:

The most significant differences between two reactors in terms of COD removals were achieved in SCFB RUN 4 in which the leachate ratio was kept as high as 13.3 per cent. The statistical analysis of the effluent COD data obtained in this run using the *Paired t-test* (45) showed that there was significant difference between the two reactors at a level of 95% confidence. The difference between the two reactors in terms of effluent TCOD until the shock PAC addition at the 9th day, increased progressively (Fig. 4.38). The reason for this was the better settling of activated carbon particles in the succeding days and hence the contribution of activated carbon particles to TCOD of the effluent decreased by time in addition to the increased settling characteristics of sludge due to PAC addition. Throughout batch and SCFB runs, it was observed that PAC did not settle well in the reactors during the first few days after PAC addition.

After the shock PAC addition at the 9th day of SCFB RUN 4, very important decreases in both effluent TCOD and SCOD were observed in the AS+PAC reactor whereas the ones for AS reactor remained the same in this period. After this shock carbon addition, TCOD in AS+PAC reactor decreased to about 100 mg/l whereas TCOD in the AS reactor stayed at about 400 mg/l, and SCOD of the AS+PAC reactor decreased to 27 mg/l whereas the SCOD in the AS reactor decreased to about 300 mg/l. This shows that if significant decreases in COD concentration are aimed, the amount of PAC addition should also be high enough to obtain the desired concentrations. The OUR profiles in the SCFB RUN 4 showed higher OUR values for the AS+PAC reactor because of the higher microbial activity in this reactor (Fig. 4.39).

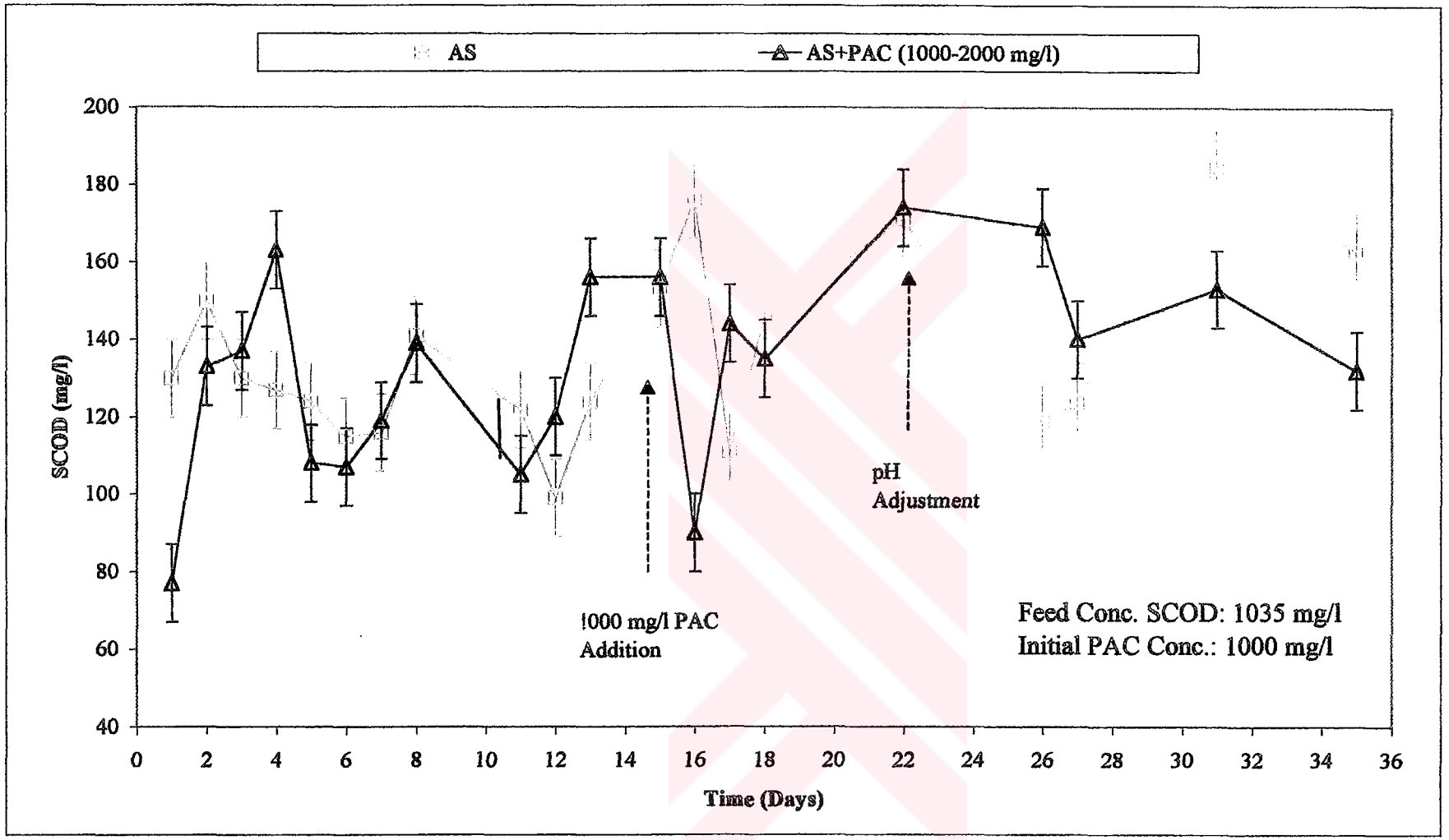


FIGURE 4.35. COD Profiles in SCFB RUN 2.

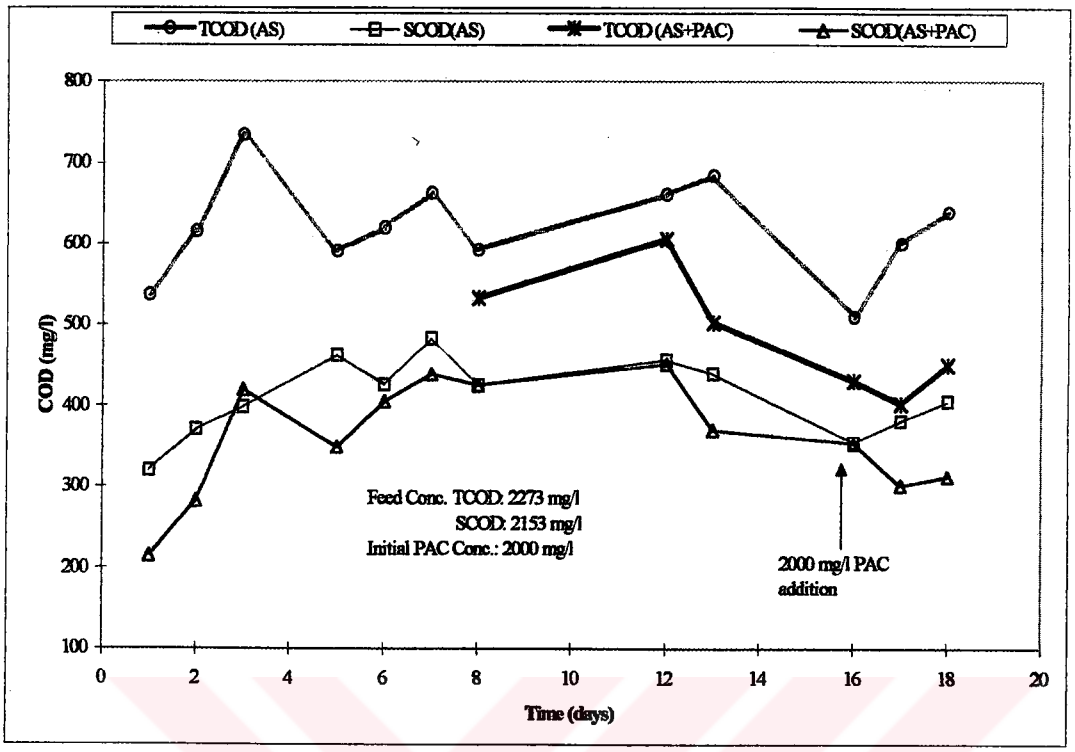


FIGURE 4.36. COD Profiles in SCFB RUN 3.

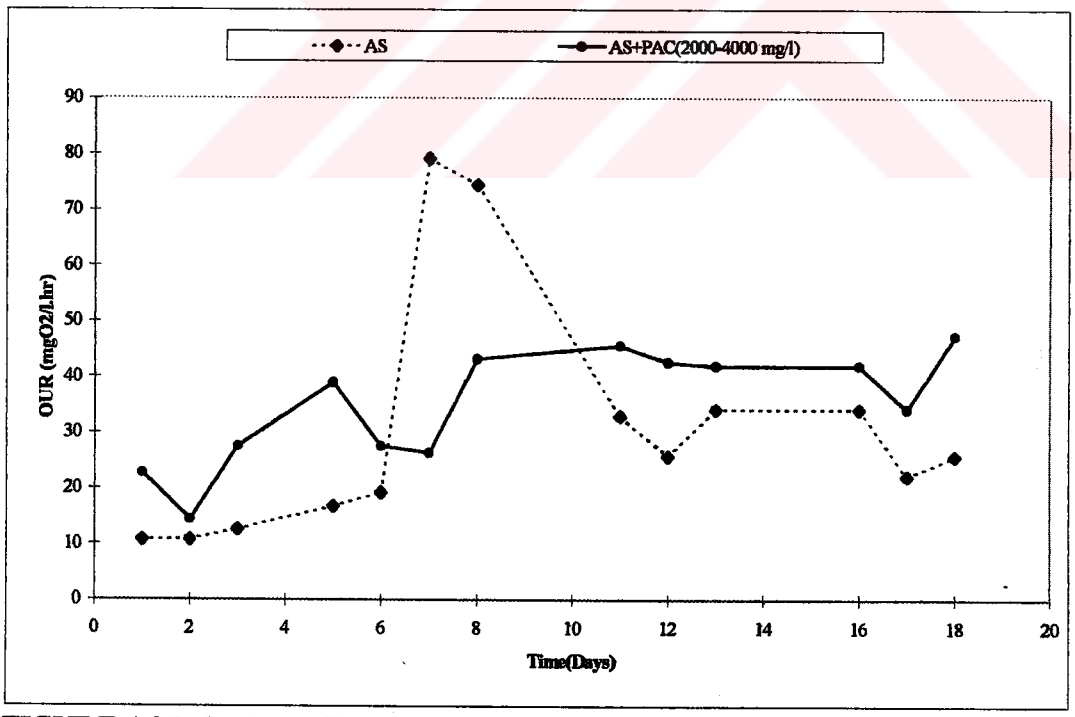


FIGURE 4.37. OUR Profiles in SCFB RUN 3.

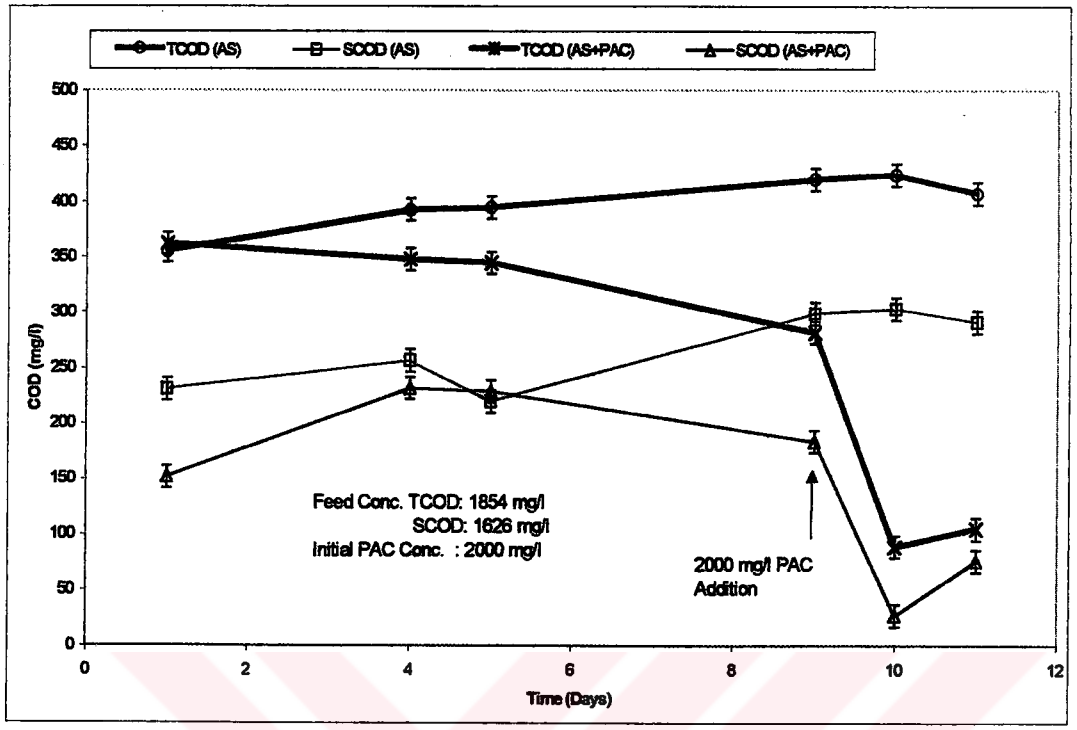


FIGURE 4.38. COD Profiles in SCFB RUN 4.

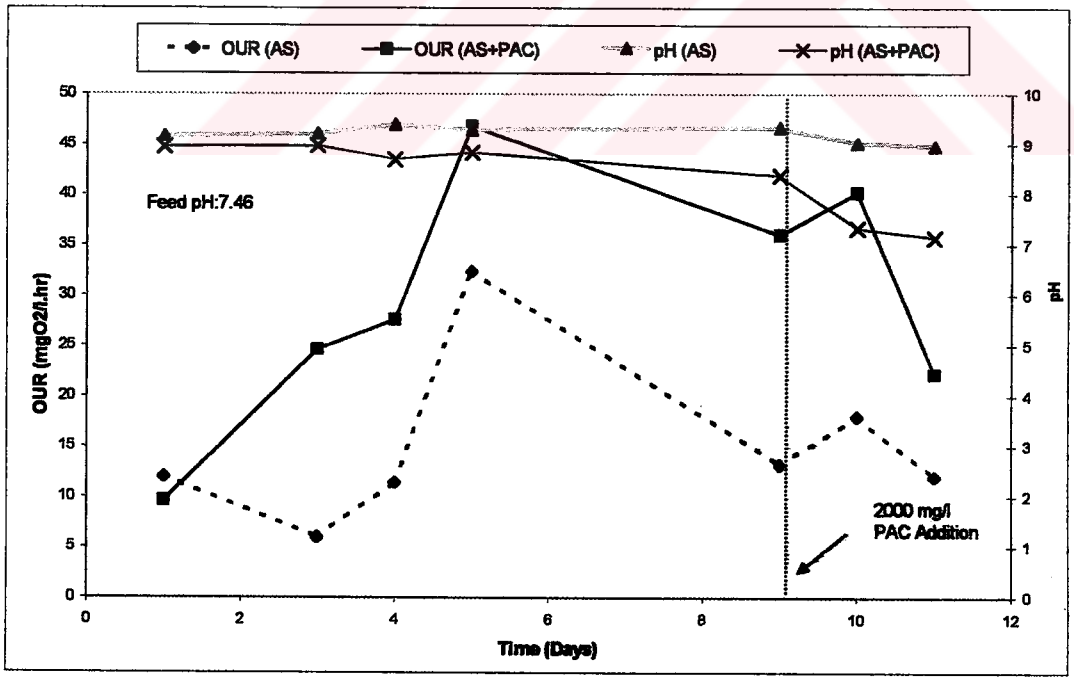


FIGURE 4.39. OUR and pH Profiles in SCFB RUN 4.

4.3.1.2. Kinetic Evaluation of COD Removal

The specific substrate removal rate (q) can be calculated by equation 4.5 in SCFB Runs in which a steady state effluent is obtained as in a continuous reactor.

$$q = \frac{S_o - S}{\theta . X} \tag{4.5}$$

where

So = Influent concentration (mg COD/l)

S = Effluent concentration (mg COD/l)

θ = Hydraulic retention time (hr)

X = Average biomass concentration in the reactor (mg MLVSS/l)

The substrate removal rate ($-r_{su}$) is equal to the product of q and X. The removal rates obtained for SCFB runs are illustrated in Table 4.7. The "apparent" rate constants for AS+PAC reactors were also calculated for comparison purposes. The removal efficiencies were calculated based on the mean COD values which were obtained after reaching pseudo steady-state conditions. The measure of reaching steady-state was to reach constant COD values. All the reactors came to steady-state at the 3rd or 4th days after two or three hydraulic residence times (1.33 days) passed.

In SCFB RUNS 1 and 2 in which the leachate ratio was 6.7 per cent, no difference between AS and AS+PAC reactors in terms of COD removal efficiency was observed (Table 4.7). The apparent substrate utilization rates were also similar for these two reactors indicating no bioenhancement due to PAC addition to activated sludge. But the rate constants obtained with 6.7 per cent leachate were similar to the mean value of zero order rate constants (based on 24 hours) in batch runs with 5 per cent leachate. This foundation favors the applicability of the zero order assumption (based on 24 hours). In SCFB RUNS 3 and 4 higher removal efficiencies and rate constants were obtained in AS+PAC reactors than in AS reactors (Table 4.7). But in these reactors, the PAC concentrations were kept higher (2000 mg/l) until the second shock PAC additions. In SCFB RUN 4 with 13.3 per cent leachate, an increase of 4 % in both TCOD and SCOD removal was observed in the period in which PAC concentration was kept constant at 2000 mg/l.

TABLE 4.7. Evaluation of SCFB runs in terms of COD removal efficiencies and COD utilization rates.

Run	Reactor	Leachate Ratio (Vol.%)	X' (mgMLVSS/l)	PAC Conc. (mg/l)	θ (hr)	θc (day)	Basis	So (mgCOD/l)	S (mgCOD/l)	COD Removal (%)	F/M (mg/mg.h)	q (mg/mg.h)	$-r_{su}$ (mgCOD/l.h)
SCFB 1	AS	6.7	2003	-	32	-	SCOD	1035	116	89	0.0161	0.0143	28.68
	AS+PAC	6.7	-	1000	32	-	SCOD	1035	110	89	-	-	28.91
SCFB 2	AS	6.7	2082	-	32	20	SCOD	1035	125±15	88	0.0155	0.0137	28.44
	AS+PAC			1000	32	20	SCOD	1035	130±23	87	-	-	28.28
SCFB 3	AS	20	1738	-	32	10	TCOD	2277	618±23	73	0.0409	0.0298	51.84
							SCOD	2153	435±15	80	0.0387	0.0309	53.69
	AS+PAC	20	-	2000	32	10	TCOD	2277	519±73	77	-	-	54.94
							SCOD	2153	399±16	81	-	-	54.81
SCFB 4	AS	13.3	2083	-	32	20	TCOD	1854	408±14	78	0.0278	0.0217	45.19
							SCOD	1626	274±35	83	0.0244	0.0203	42.25
	AS+PAC	13.3	-	2000		20	TCOD	1854	325±37	82	-	-	47.78
							SCOD	1626	215±27	87	-	-	44.09

4.3.2. Nitrification in SCFB Runs

The nitrification profiles in the SCFB Runs were monitored in order to observe the effect of PAC addition to activated sludge and to compare the results with the results of the Batch Runs and the Continuous-Flow Operation.

SCFB RUN 1:

The NH_4-N and NO_x-N concentrations in the AS and AS+PAC reactors of SCFB RUN 1 reached the same values at the 5th day of run. But until the 5th day the nitrogen profiles in terms of ammonia, nitrite and nitrate concentrations showed a better nitrification in the AS reactor (Fig. 4.40 and 4.41). The reason for this observation was probably the settling problem encountered in the PAC added reactor that decreased nitrification efficiency as explained in Section 4.2.2. In this run, the maximum free ammonia concentration was calculated as 6 mg/l, which may have contributed to the inhibition of *Nitrobacter* resulting in no NO_3 production.

SCFB RUN 2:

In SCFB RUN 2, PAC addition did not improve nitrification as in SCFB RUN 1. The statistical analysis of the NH_4-N and NO_x-N data obtained in this run using *Paired t-test* (45) showed that there was no significant difference between the two reactors at a level of 95% confidence. But a pH adjustment significantly increased nitrification. In order to prevent free ammonia inhibition at high pH values, the pH of the leachate was decreased by sulfuric acid before feeding in SCFB RUNS 1 and 2. But in this case, the pH values decreased to very low pH values (as low as 5) at which nitrification was not possible. Hence at the 23rd day of SCFB RUN 2, the pH regulation was given up and the nitrification performance increased very apparently (Fig. 4-42 and 4.43). The NH_4-N concentrations decreased from about 80 to about 25 mg/l for both reactors (Table 4.8). Also, NH_4-N removal due to nitrification increased from about 30 per cent to about 55 percent in the reactors.

In SCFB RUN 2, free nitrous acid (FNA) concentrations up to 3.25 mg/l were observed at pH values below 5 in the period before pH adjustment. This amount of FNA is inhibitory to both *Nitrosomonas* and *Nitrobacter* species (Section 2.3.3.1). Hence no nitrification was observed after the decrease of pH to about 5. After pH adjustment, lower FNA

concentrations were detected (about 0.6 mg/l) that were not inhibitory to *Nitrosomonas* but may be inhibitory to *Nitrobacter*. This shows that nitrifiers are very sensitive to pH, whereas COD utilizing heterotrophs are not as much, because COD profiles did not change apparently in SCFB Run 2 after the pH adjustment.

SCFB RUN 3:

The reason why PAC additions did not improve nitrification in SCFB RUNS 1 and 2 may be that the PAC concentrations were not sufficient to remove nitrification inhibitors in the wastewater. Therefore PAC concentrations were increased in SCFB RUNS 3 and 4. In SCFB RUN 3, no recordable nitrification was observed in both reactors (Fig 4.44) contrary to SCFB RUNS 1 and 2. Since the leachate ratio in the total feed was much higher (20 % by volume), the amount of inhibitory organic matter and heavy metals were much higher than the first two runs resulting in a severe inhibition in nitrification. Besides this, very high free ammonia (FA) concentrations were calculated throughout the run (as high as 55-75 mg/l) for both reactors with pH values about 9 and FA inhibition might have contributed to the inhibition of *Nitrosomonas* resulting in no NO_x formation.

NH_4-N profiles of SCFB RUN 3 resulted in higher effluent NH_4-N concentrations in the AS+PAC reactor. The statistical analysis of the NH_4-N data obtained in this run with *Paired t-test* (45) showed that there was significant difference between AS and AS+PAC reactors in terms of NH_4-N effluent concentrations at a 95% confidence level. The reason for this may be that more ammonia stripping occurred in AS reactor in which the pH proceeded a bit higher than the pH in AS+PAC reactor. The ammonia removal efficiencies were found to be lower in the first two runs in which leachate ratio was 6.7 per cent due to total nitrification inhibition in SCFB RUN 3. However the NH_4-N utilization rates were found to be greater than the ones for the first two runs. The main reason for this was that the COD concentration in the feed in SCFB RUN 3 was much greater resulting in a higher heterotroph growth as biomass growth is directly related to substrate concentration. Hence, heterotrophs should have utilized more NH_4-N for growth. Another reason for higher NH_4-N utilization rates in SCFB RUN 3 may be the higher rate of ammonia stripping at the high pH values observed throughout this run.

SCFB RUN 4:

PAC concentration was kept at 2000 mg/l in the AS+PAC reactor during the first 9 days of operation in SCFB Run 4. During the first 5 days, no nitrification was observed in both reactors. But at the 9th day an extreme increase in NO_x concentration was detected in the AS+PAC reactor showing an extreme nitrification (Figure 4.45). In this run, the effect of PAC on COD removal had been observed apparently starting already from the first day of run (Section 4.3.1). The late improvement in nitrification by PAC proposes that nitrifiers are much more sensitive to toxic and inhibitory shocks than heterotrophs, so that their inhibition is more long lasting.

The activated sludge used in this study had been fed with the synthetic domestic wastewater and was not acclimated to the leachate addition. Since the reactor was initially fed with leachate and PAC simultaneously, it was probable that the activity of nitrifiers were inhibited by leachate components before they were adsorbed on activated carbon. This shows that addition of 2000 mg/l PAC will stimulate nitrification in a CSTR operation after reaching steady state and nitrifiers are acclimated to the new conditions. Addition of 2000 mg/l PAC at the 9th day did not improve NO_x production in the first two days after addition.

However, In SCFB RUN 4, nitrification proceeded to the stage of only NO_2 production in the AS+PAC reactor and no NO_3 production was obtained (see Table B4). PAC addition did not prevent the inhibition of *Nitrobacter* species. Throughout the run, FA concentrations in the AS reactor were found to be high (38-69 mg/l) and this might have contributed to the inhibition of N*itrosomonas* in this reactor. Also in the AS+PAC reactor, FA concentrations were calculated to be high (32-42 mg/l) during the first five days of operation where no nitrification was observed. But after the 9th day FA and also FNA concentrations decreased to very low values such that they did not contribute to inhibition of nitrifiers. Therefore inhibition of *Nitrobacter* after the 9th day was totally due to the inhibitory components in the leachate. On the other hand, the pH profiles in SCFB RUN 3 very apparently shows that nitrification decreased the pH significantly (Fig. 4.39).

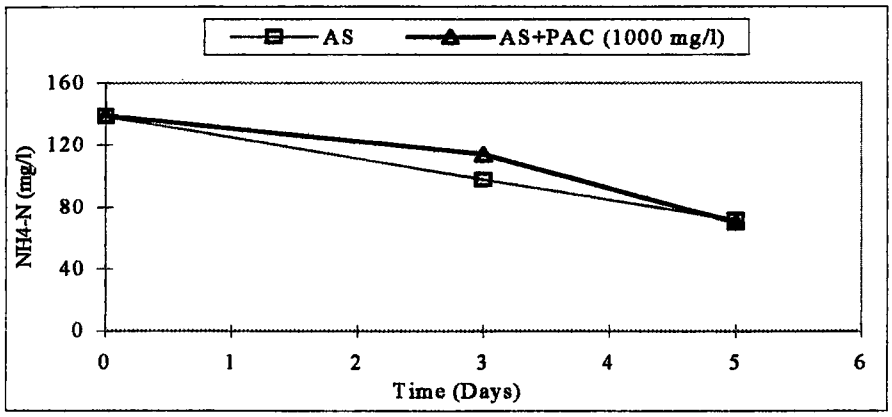


FIGURE 4.40. NH_4-N Profiles in SCFB RUN1.

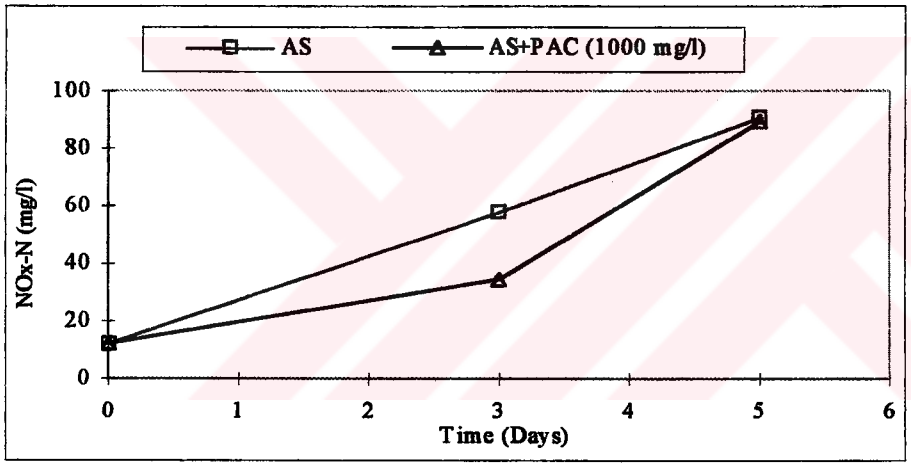


FIGURE 4.41. NO_X-N Profiles in SCFB RUN 1.

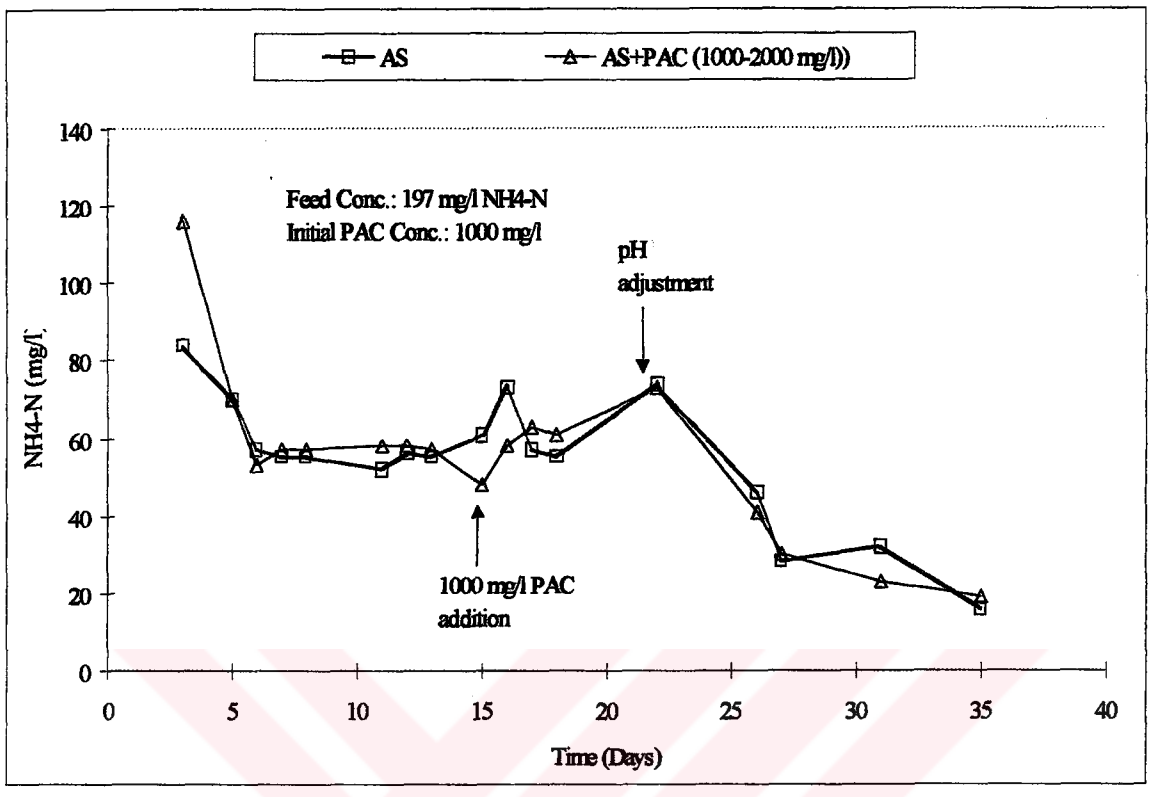


FIGURE 4.42. NH_4-N Profiles in SCFB RUN 2.

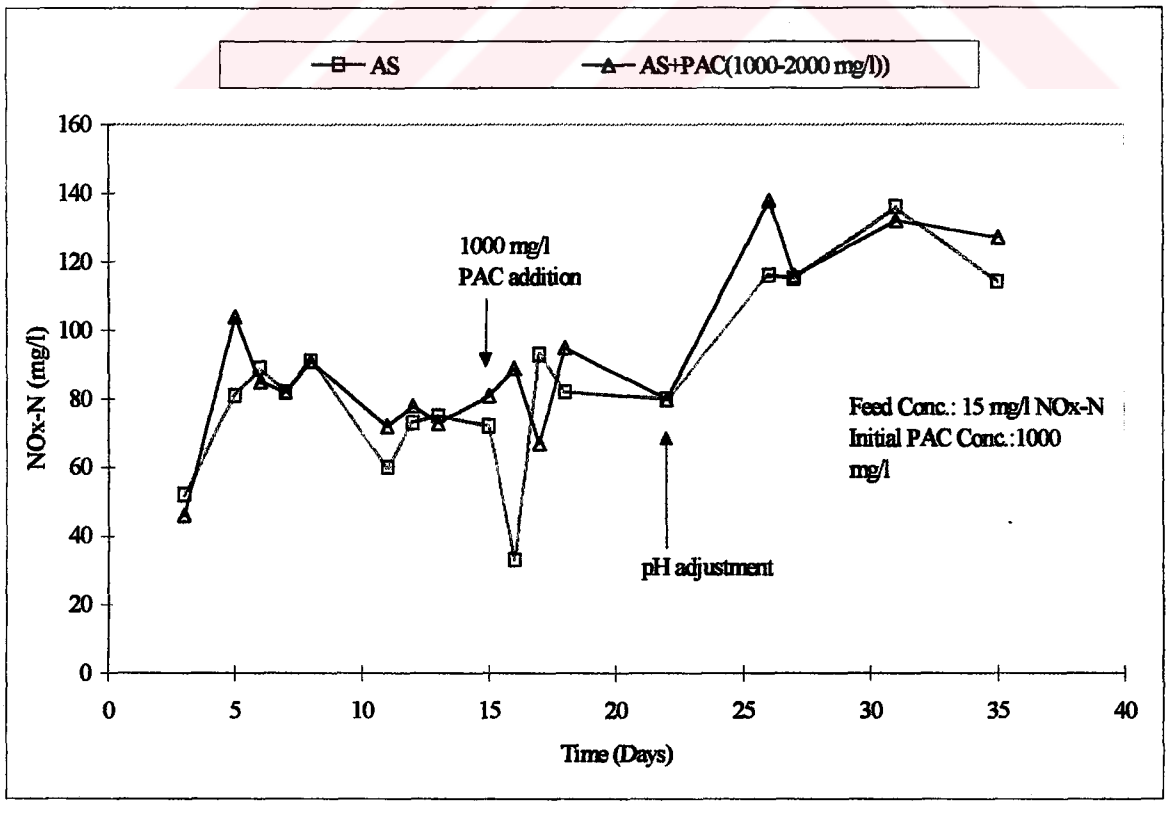


FIGURE 4.43. NO_X-N Profiles in SCFB RUN 2.

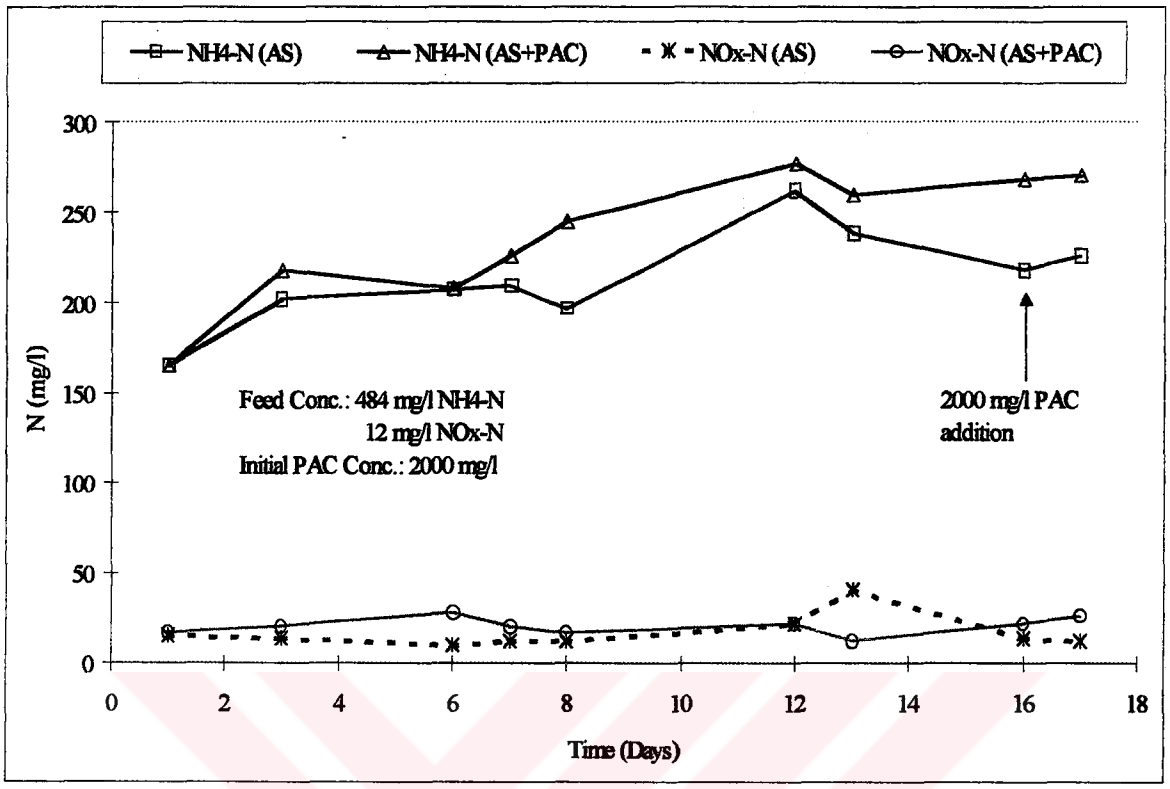


FIGURE 4.44. Nitrogen Profiles in SCFB RUN 3.

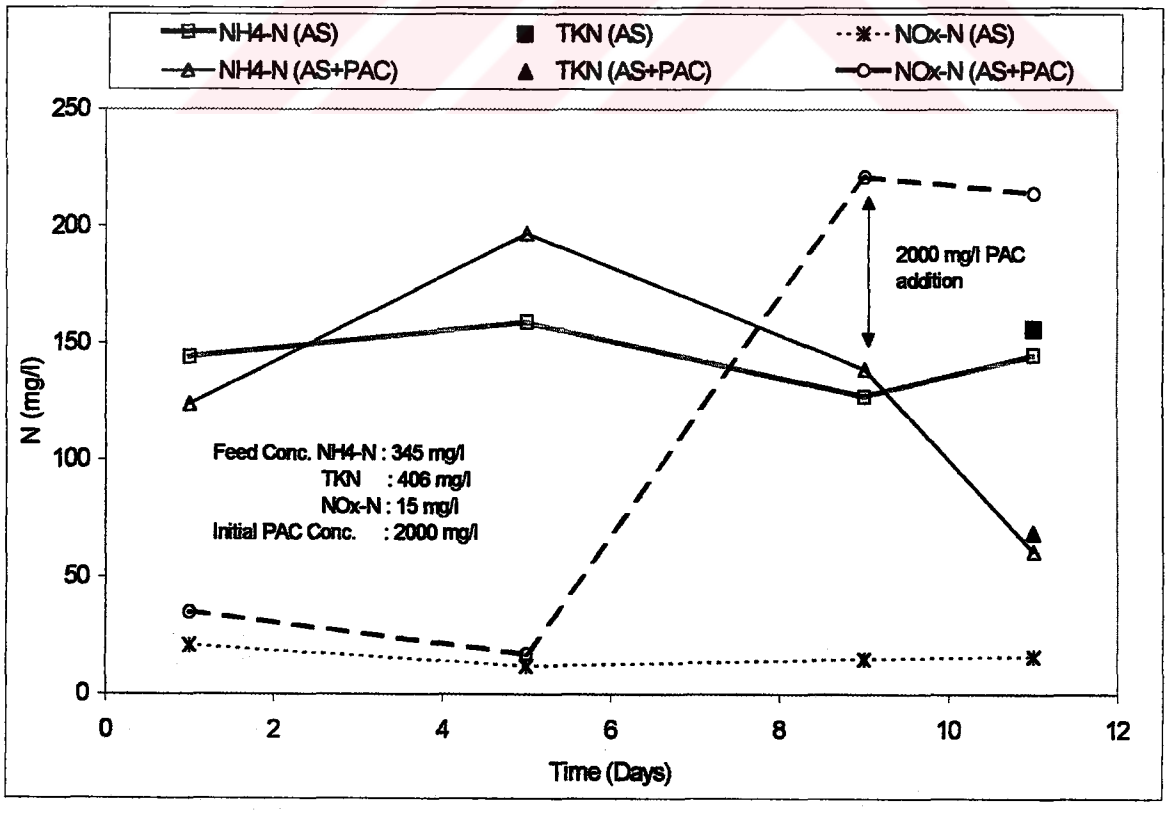


FIGURE 4.45. Nitrogen Profiles in SCFB RUN 4.

TABLE 4.8. Evaluation of SCFB Runs in terms of NH_4-N removal efficiencies and utilization rates.

Run	Reactor	Leachate Ratio (Vol. %)	X' (mgMLVSS/l)	PAC Conc. (mg/l)	θ (hr)	θc (day)	So ($mgNH_4/l$)	S ($mgNH_4/l$)	TKN Removal (%)	NH_4-N Removal (%)	NH_4-N Removal due to NO_x-N Production (%)	$-r_{su}$ ($mgNH_4$-N/l.h)
SCFB 1	AS	6.7	2003	-	32	-	197	72	68	63	39	3.91
	AS+PAC	6.7	-	1000	32	-	197	70	70	64	38	3.97
SCFB 2	AS	6.7	2082	-	32	20	197	75±17	-	70	30	4.31
	AS+PAC	6.7		1000	32	20	197	81±9	-	70	34	4.34
(pH adjust.)	AS	6.7	2082	-	32	20	197	25±8	84	88	54	5.41
	AS+PAC	6.7		1000	32	20	197	24±6	84	88	56	5.41
SCFB 3	AS	20	1738	-	32	10	484	222±22	-	54	1	8.18
	AS+PAC	20	-	2000	32	10	484	247±26	-	49	1	7.41
SCFB 4	AS	13.3	2083	-	32	20	345	144	62	59	0	6.28
	AS+PAC	13.3	-	2000	32	20	345	61	83	82	58	8.88

4.4. Activated Carbon Addition to Activated Sludge in a Continuous-Flow Stirred Tank Reactor (CFSTR)

The lab-scale Continuous-Flow Stirred Tank Reactor illustrated in Section 3.3.4, was fed with leachate in combination with the synthetic domestic wastewater at a volumetric ratio of 6.7 per cent for 27 days. At the 19th day of continuous-flow operation, 2000 mg/l PAC was added to the reactor to observe its effect in the following days. In the CFSTR, neither daily PAC dosages were made to the reactor, nor sludge and PAC were discharged form the reactor except the sludge and PAC escaping with the effluent and spillages from the reactor. At the 27th day of operation, the leachate ratio in the influent was increased to 13.3 per cent. After the reactor came to a steady state at the 36th day, a new 2000 mg/l PAC was added to the reactor and the operation was stopped at the 44th day when the effect of the added PAC disappeared.

4.4.1. Organic Substrate Removal in the CFSTR

The COD removal efficiencies (Table 4.9) were calculated based on the steady-state effluent COD concentrations. Steady-state effluent COD concentrations were calculated using the data in Table B5. Steady-state effluent COD concentrations are shown in Table 4.9 with their standard deviations. The relatively low standard deviations show that a steady-state operation was maintained in the reactor.

During the first period of CFSTR operation before PAC addition to the reactor, the COD removal efficiencies and removal rates were found to be very similar to the ones obtained in the AS reactors in SCFB RUNS 1 and 2 which were fed with the same feed (Tables 4.7 and 4.9). This shows that simulation of a CFSTR by the SCFB reactors was a practical option under the conditions of this study.

However, PAC addition at the 19th day increased COD removal efficiencies by 6 and 8 per cent for TCOD and SCOD respectively, whereas in the AS+PAC reactors in SCFB RUNS 1 and 2 no increase in COD removal efficiency and rate had been obtained. PAC addition also increased COD removal rates significantly in the CFSTR. This shows that simulation of a continuous-flow operation as a SCFB reactor was not successful for PAC added

activated sludge systems. This is due to the different operating conditions of the two reactors. In an ideal CFSTR, the substrate concentration inside the reactor is theoretically equal to the effluent concentration (11). Hence the PAC added to the CFSTR is always exposed to effluent concentrations which are much lower than the influent concentrations. On the other hand, due to the once-a-day feeding characteristic of the SCFB reactor, the daily added PAC is exposed to very high COD concentrations and it becomes probably saturated with biodegradable COD and therefore not a high effect of PAC was observed in AS+PAC reactors. This shows that bioregeneration hypothesis was not valid for the combined leachate (6.7 % by volume) and synthetic wastewater feeding in SCFB reactors.

In the CFSTR, the PAC added is exposed only to the nonbiodegradable COD, because for systems under steady-state at sludge ages greater than 2.5 days, all the biodegradable COD present in the influent can be accepted as utilized (44). Therefore, theoretically PAC addition to the CFSTR increases COD removal both by adsorbing nonbiodegradable COD only and also by increasing the activity of microorganisms by adsorbing toxic and inhibitory organics (see Section 2.4).

PAC addition to the CFSTR on the 19^{th} day showed its effect immediately (Fig.4.46) and TCOD concentration of the effluent decreased from the mean 161 mg/l to the mean 92 mg/l, and SCOD decreased from the mean 124 mg/l to the mean 41 mg/l. The TCOD and SCOD curves in Figure 4.46 were smoothed by using 3 period moving average (3 per. Mov. Avg.). The effect of PAC on COD removal continued in the first four days after addition, but after the 7^{th} day the COD values increased to concentrations before PAC addition (Fig. 4.46). This shows that the PAC became saturated and lost its effect after saturation.

Operation at an increased leachate ratio (13.3 % by volume) also showed that PAC became saturated and COD concentration tended to increase in the effluent. Hence, bioregeneration hypothesis was also not valid for the CFSTR operation in the scope of this study. To obtain a permanent improvement in COD removal, PAC should be added continuously to the reactor, because permanent COD removals were achieved in SCFB RUNS 3 and 4 in which PAC was daily added to the reactors.

The operation of CFSTR at increased leachate ratio (13.3 % by volume) resulted in better COD removal efficiencies compared to the AS reactor of SCFB RUN 4 which was fed with the same influent (Tables 4.7 and 4.9). This situation differed from the situation encountered in the operation of CFSTR with the leachate ratio of 6.7 % by volume in which steady-state effluent COD concentrations were similar to the COD concentrations in the SCFB reactors. As the ratio of leachate increases, the concentration of toxic and inhibitory compounds in the influent increases and during the once-a-day feeding of SCFB reactor, the activated sludge microorganisms are exposed to higher concentrations of toxic and inhibitory organics. Since in a CFSTR microorganisms are not exposed to high concentrations of toxic and inhibitory compounds, better COD removals are obtained.

PAC addition to the CFSTR fed at an increased leachate ratio (13.3 % by volume) also improved COD removal better than in the case of AS+PAC reactor of SCFB RUN 4. In the AS+PAC reactor of SCFB RUN 4 with daily PAC addition, TCOD concentrations were higher than 300 mg/l and SCOD concentrations were higher than 200 mg/l in the effluent, whereas those decreased to less than 200 mg/l for CFSTR after PAC addition (Fig. 4.48).

The OUR profiles of the continuous-flow reactor are illustrated in Figures 4.47 and 4.49. When they are compared with the COD profiles, it is obvious that COD and OUR profiles are parallel to each other both for feeds containing 6.7 per cent and 13.3 per cent leachate by volume. The reason for this is the dependency of the activity of microorganisms on the substrate concentration. OUR is higher when microorganisms are exposed to higher concentrations of biodegradable substrate in the reactor. Hence it can be deduced that OUR serves as a sensitive parameter to reflect the response of the system to substrate changes and PAC additions.

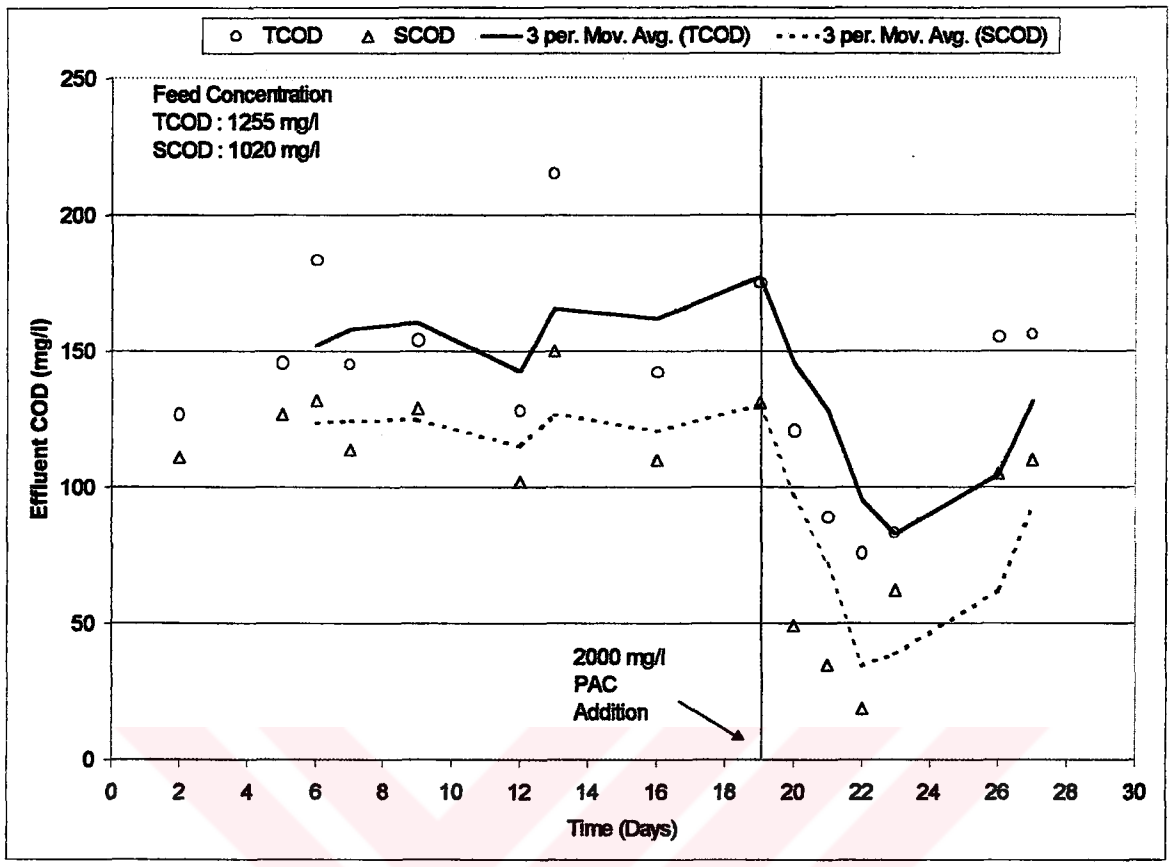


FIGURE 4.46. COD Profiles in CFSTR Operation (Leachate Ratio: 6.7% by volume).

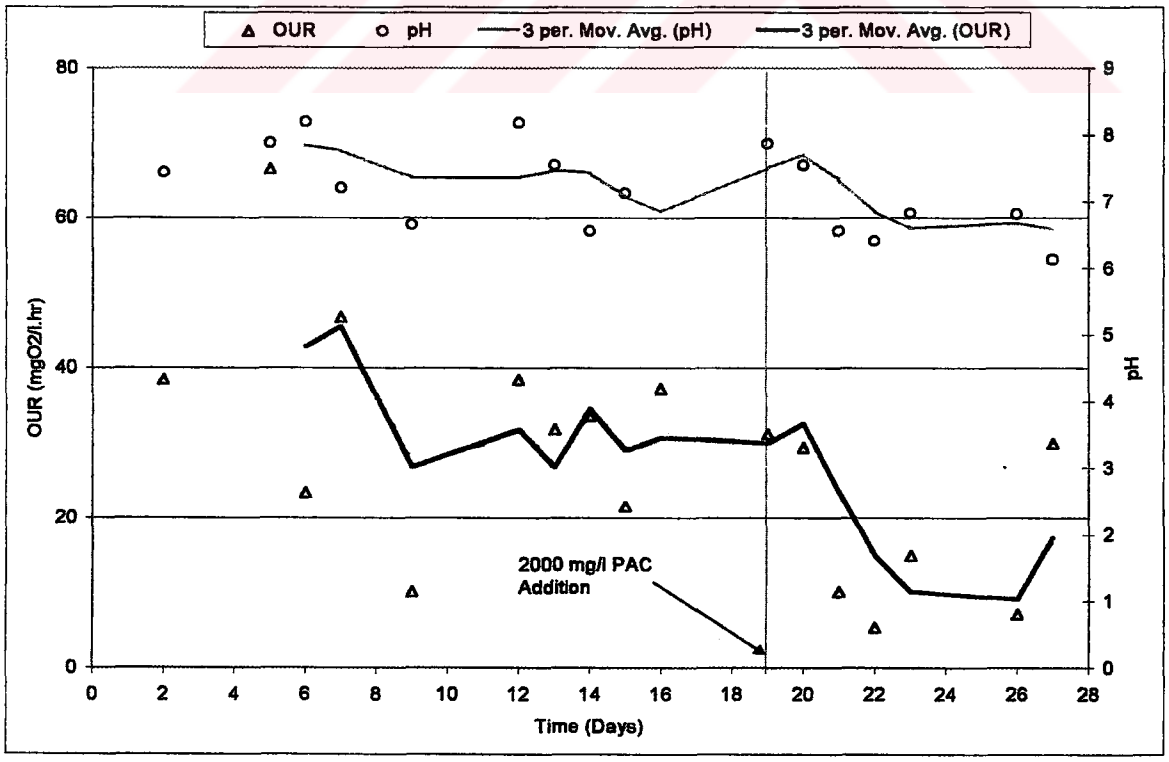


FIGURE 4.47. OUR and pH Profiles in CFSTR Operation (Leachate Ratio: 6.7% by volume).

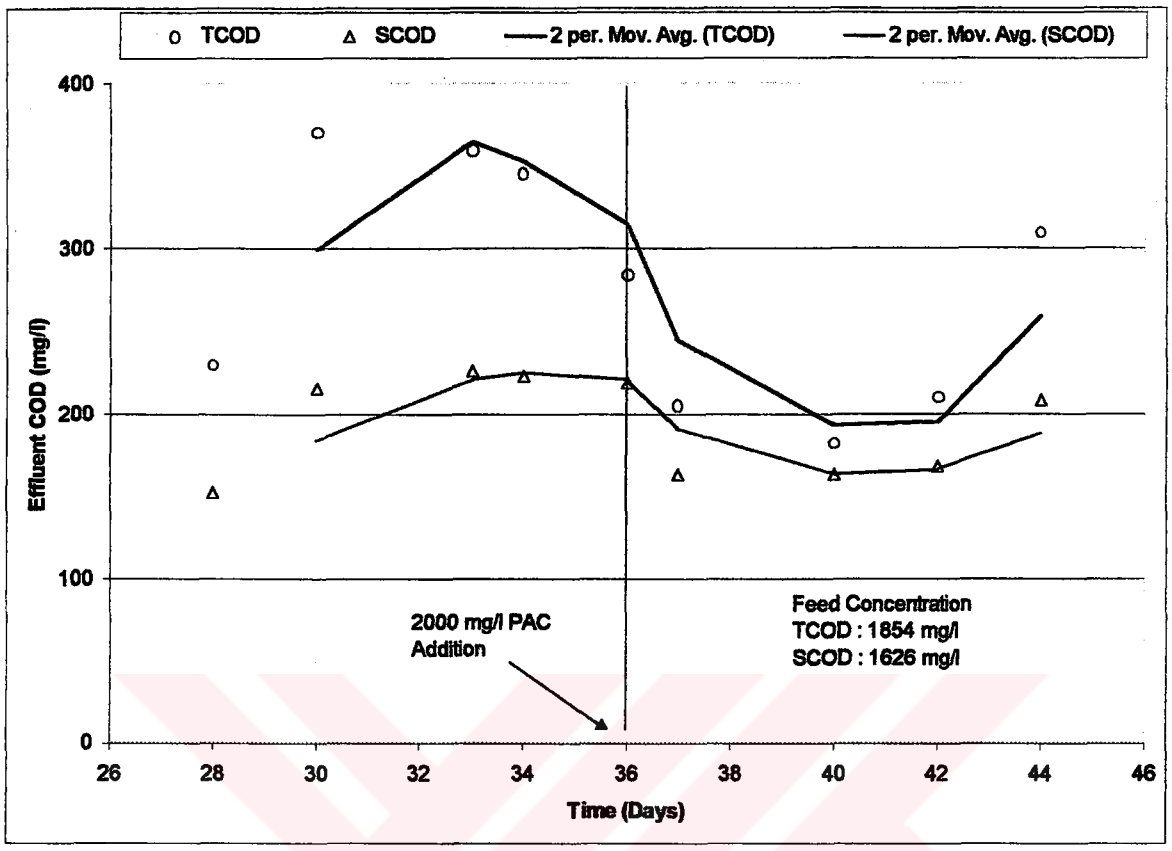


FIGURE 4.48. COD Profiles in CFSTR Operation (Leachate Ratio: 13.3% by volume).

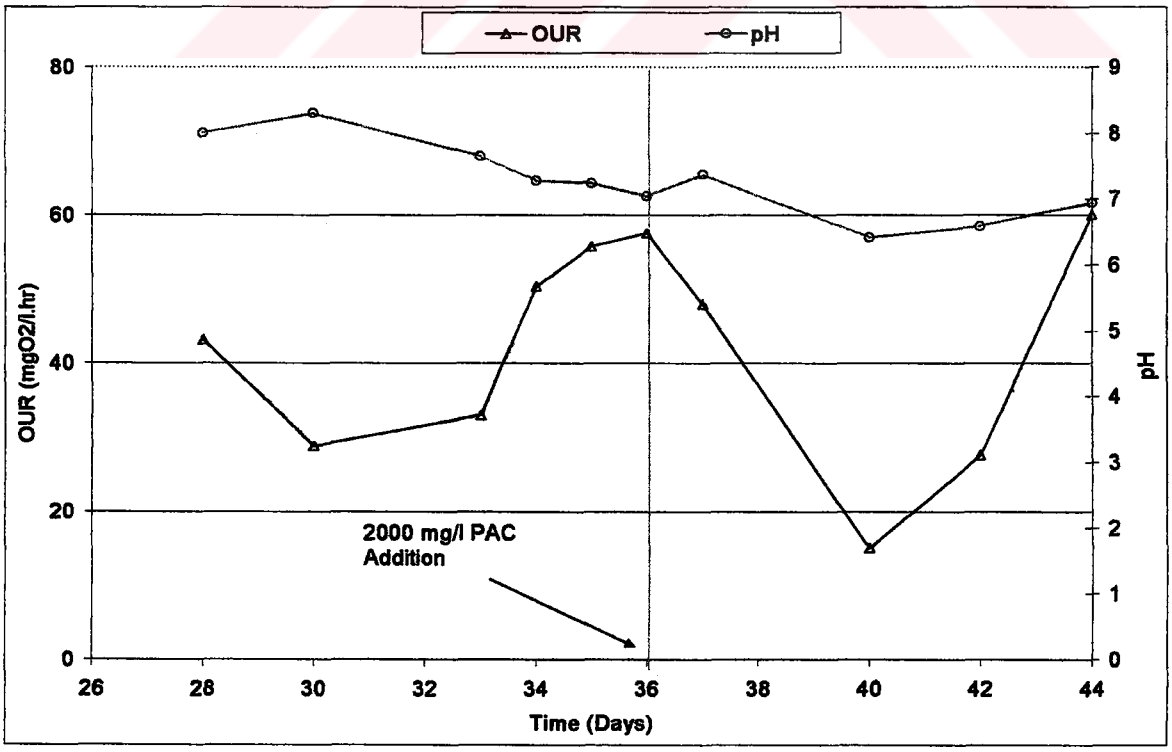


FIGURE 4.49. OUR and pH Profiles in CFSTR Operation (Leachate Ratio: 13.3% by volume).

TABLE 4.9. Evaluation of the CFSTR Operation in terms of COD removal efficiencies and COD utilization rates.

Reactor Operation	Leachate Ratio (Vol. %)	X' (mgMLVSS/l)	PAC Conc. (mg/l)	θ (hr)	Basis	So (mgCOD/l)	S* (mgCOD/l)	COD Removal (%)	F/M (mg/mg.h)	q (mg/mg.h)	$-r_{su}$ (mgCOD/l.h)
AS	6.7	2018	-	34.1±3.9	TCOD	1255	161±28	87	0.0182	0.0159	32.03
					SCOD	1020	124±15	88	0.0148	0.0130	26.23
AS+PAC	6.7	1080[a]	2000	30.6±2.5	TCOD	1255	92±20	93	0.0379	0.0352	38.01
					SCOD	1020	41±18	96	0.0309	0.0296	31.99
AS+PAC	13.3	1065[a]	2000	33.3±3.9	TCOD	1854	340±39	82	0.0522	0.0427	45.51
					SCOD	1626	221±5	86	0.0459	0.0397	42.23
AS+PAC	13.3	1200[a]	4000	29.3±0.5	TCOD	1854	198±15	89	0.0527	0.0471	56.52
					SCOD	1626	165±3	90	0.0462	0.0416	49.86

a: Superscript a denotes the biomass MLVSS in AS+PAC reactor determined according to the procedure of Arbuckle et al. (1982).
* Steady-state effluent values.

TABLE 4.10. Evaluation of CSTR Operation in terms of NH_4-N removal efficiencies and NH_4-N utilization rates.

Reactor Operation	Leachate Ratio (Vol.%)	X' (mgMLVSS/l)	PAC Conc. (mg/l)	θ (hr)	So ($mgNH_4$/l)	S* ($mgNH_4$/l)	TKN Removal (%)	NH_4-N Removal (%)	NH_4-N Removal due to NOx-N Production (%)	$-r_{su}$ ($mgNH_4$-N/l.h)
AS	6.7	2018	-	34.1±3.9	205	67±13	57	67	46	4.05
AS+PAC	6.7	1080[a]	2000	30.6±2.5	205	48±4	67	77	60	5.13
AS+PAC	13.3	1065[a]	2000	33.3±3.9	345	106±15	68	69	58	7.18
AS+PAC	13.3	1200[a]	4000	29.3±0.5	345	80	79	77	64	9.04

a: Superscript a denotes the biomass MLVSS in AS+PAC reactor determined according to the procedure of Arbuckle et al. (1982).
* Steady-state effluent values.

4.4.2. Nitrification in CFSTR

Until the 19th day of CFSTR operation, no significant difference between NO_x and NO_2 concentrations were observed (Fig. 4.50) indicating that nitratification (conversion of nitrite to nitrate) was inhibited in this period just as in the SCFB RUNS 1 and 2. The NH_4-N removal efficiencies were also similar in the CFSTR and SCFB operations at 6.7 per cent leachate feeding (Tables 4.8 and 4.10). However nitrification percentage was a little greater in the CFSTR. This may be due to higher probability of nitrification inhibition in SCFB Runs for the same reasons as in heterotrophs inhibition as explained in Section 4.4.1.

In spite of the difference in nitrification, the reason for the same ammonia removals in CFSTR and SCFB Runs may be the higher heterotrophic growth rates in the SCFB reactors. In the first hours of feeding in SCFB and Batch Runs, the microorganisms are at or very close to their maximum growth rates due to the high substrate concentrations, whereas the microorganisms in the CFSTR are never exposed to such high concentrations. Hence more cell growth might have occurred in the SCFB reactor resulting in higher NH_4-N removal due to utilization for cell synthesis.

After the PAC addition on the 19th day, NH_4-N removal efficiency increased by 10 per cent and also ammonia removal rate and nitrification rate increased apparently (Table 4.10). No improvement in nitrification had been observed due to PAC addition in the SCFB RUNS 1 and 2 as for COD removal. The reason is that the PAC became saturated with the biodegradable and noninhibitory organic matter and did not stimulate microbial activity in these SCFB Runs. Figure 4.50 shows that NO_x production increases after PAC addition whereas NO_2 concentration does not change apparently. This shows that after PAC addition, the inhibition of *Nitrobacter* species is prevented to some extent. This was not observed in any of the Batch and SCFB Runs. The effect of PAC on nitrification was slower than for COD removal. PAC improves nitrification only by stimulating the activity of nitrifiers, whereas it improves COD removal both by adsorbing nonbiodegradable COD and also stimulating the activity of heterotrophs.

NO_x and NO_2 concentrations did not change significantly in the first 5-6 days after the increase of leachate ratio to 13.3 per cent on the 27th day (Fig. 4.51). But on the 34th day a

sudden improvement in nitrification was observed. This period can be regarded as the time required for the reactor to reach steady-state under the conditions of the new feeding and the acclimation of nitrifiers to the new feeding regime. After the addition of PAC on the 36th day, NO_x-N increased and NH_4-N decreased as it had happened after the first PAC addition at the 27th day (Fig. 4.51). NH_4-N removal efficiency increased by 8 per cent after PAC addition. But the most striking effect of PAC addition in this period was the complete nitrification so that most of the NO_x-N in the effluent consisted of NO_3-N indicating that the inhibition of *Nitrobacter* had almost completely been prevented. NO_2-N concentrations decreased from above 100 mg/l to about 10 mg/l in this period.

Owing to the high alkalinity consumption in nitrification, pH decreased very significantly in the reactor. In the CFSTR, after PAC additions, the amount of nitrification in the reactor increased. Figures 4.47 and 4.49 show that pH decreased apparently when nitrification took place.

Throughout the continuous operation, FNA concentrations were calculated to be below 0.2 mg/l so that no nitrification inhibition occurred in the CFSTR due to FNA. FA concentration were calculated to be below 6 mg/l. FA concentrations between 1 and 6 mg/l might have contributed to the *Nitrobacter* inhibition, but *Nitrobacter* inhibition was also observed in periods when FA was below 1 mg/l that would not be inhibitory (see Section 2.3.3.2). Hence the main mechanism of nitrification inhibition was due to the inhibitory organics and metals in the leachate.

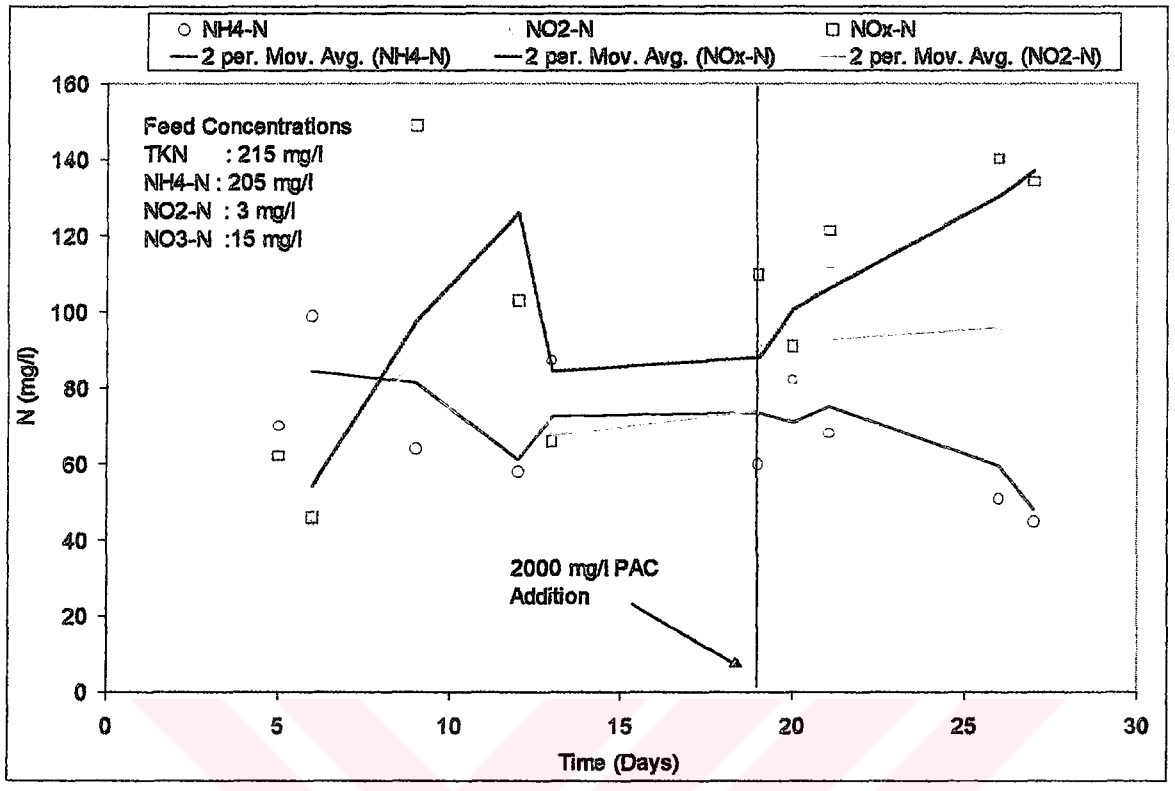


FIGURE 4.50. Nitrogen Profiles in CFSTR Operation (Leachate ratio: 6.7% by volume).

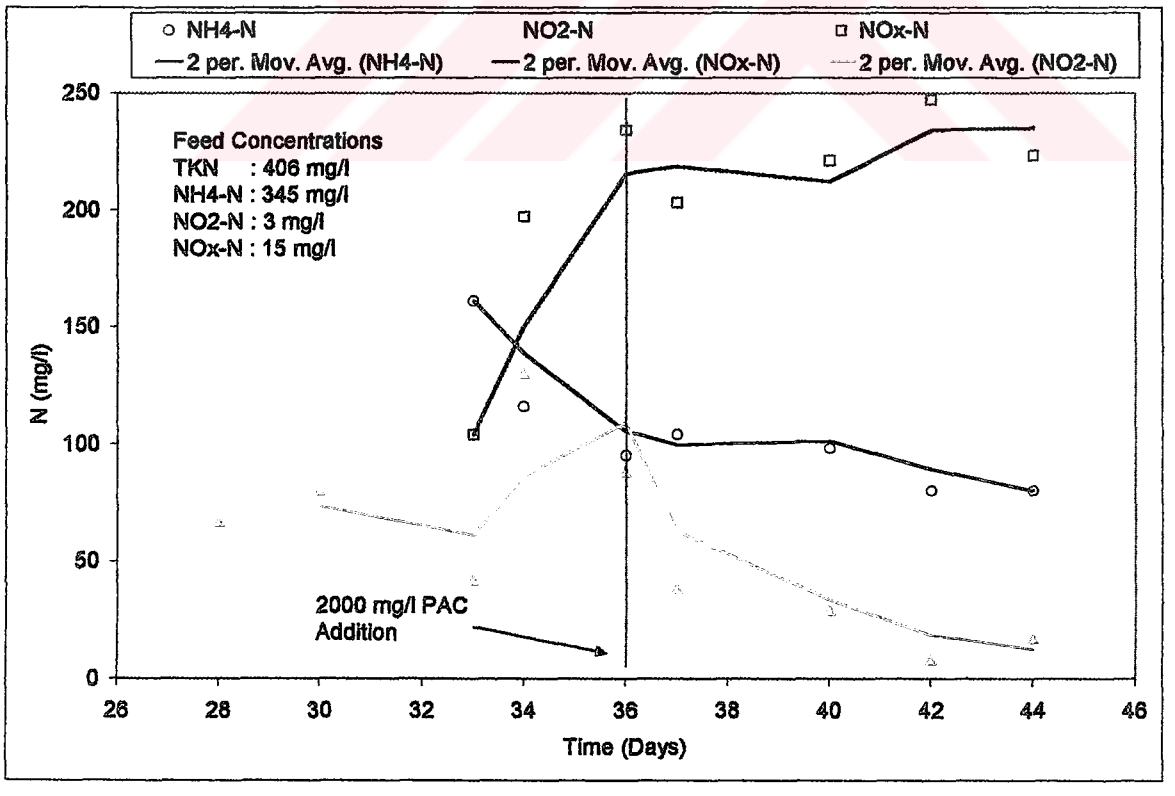


FIGURE 4.51. Nitrogen Profiles in CFSTR Operation (Leachate ratio: 13.3% by volume).

5. CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to evaluate the treatment of leachate in combination with synthetic domestic wastewater in PAC added activated sludge systems. The experiments were first conducted in lab-scale batch and Semi-Continuously Fed Batch (SCFB) reactors and then in a lab-scale Continuous-Flow Stirred Tank Reactor (CFSTR). In batch and SCFB operations, both the conventional activated sludge reactors and PAC added activated sludge reactors were used simultaneously for comparison purposes.

Experiments in batch reactors were performed to investigate the biological treatability of leachate when combined with synthetic domestic wastewater and the effect of PAC addition to activated sludge. Kinetic rate constants were calculated from the results obtained in batch runs. The results obtained from batch runs helped to gain an understanding for the CFSTR operation. The PAC concentration to be applied, the required biomass concentration, and the achievable organics and ammonia removal efficiencies were all estimated during these experiments. SCFB runs were performed for practical purposes to be able to provide simultaneously the same conditions for activated sludge and PAC added activated sludge reactors, considering that SCFB reactors can be successfully used to simulate a CFSTR.

The leachate used in this study was a unique sample taken from the landfill. Its characteristics represents the leachate produced in the landfill during the period of sampling. Therefore, the results obtained in this study only demonstrate the treatability of the unique sample. Considering the variable characteristics of the leachate quality, various samples taken in different periods would give a more comprehensive conclusion about the applicability of PAC added activated sludge systems for the treatment of leachate. However, the results of this study give a clear idea about the treatment of leachate from a young landfill in PAC added activated sludge systems.

In batch runs, it was seen that more than 85 percent COD removal occurred in activated sludge reactors. This showed that leachate used in this study was highly biodegradable

when combined with synthetic domestic wastewater at a volumetric ratio of 5 percent. Hence it can be concluded that biological treatment of leachate was an applicable option when leachate is combined with domestic wastewater in a proper ratio. PAC addition to activated sludge increased COD removal efficiencies to more than 90 percent. PAC addition also increased oxygen uptake rates (OUR) in the reactors.

The results obtained from the batch runs also showed that more than 90 % ammonia removal was achievable. Although some nitrification occurred, the main mechanisms of ammonia removal were through utilization for heterotrophic growth and ammonia stripping. PAC addition increased nitrification. But in all of the batch and SCFB reactors, NO_2-N accumulation took place indicating that the second step of nitrification is inhibited due to the inhibitory compounds in leachate.

The COD removals obtained in the SCFB runs and CFSTR Operation operated at the same conditions showed that, a SCFB reactor could be successfully used to simulate a CFSTR for COD removal under the conditions of this study. However, in case of PAC addition to both SCFB and CFSTR reactors, a simulation of CFSTR by a SCFB reactor may be misleading. The results obtained for ammonia removal and nitrification also showed that a simulation of CFSTR by a SCFB reactor may be misleading if nitrification is the major concern, since the nitrifiers are more severely inhibited in a SCFB reactor than in a CFSTR reactor.

As the leachate ratio in the wastewater was increased in the batch runs, SCFB runs and CFSTR operation, both COD and ammonia removal efficiencies decreased. Hence it can be concluded that the biological treatability of leachate in combination with domestic wastewater was very dependent on the volumetric ratio of leachate in this mixture. As the leachate ratio was increased, the positive effect of PAC became more apparent both in terms of COD removal and nitrification. This showed that PAC removes the nonbiodegradable organic matter and nitrification inhibitors in the leachate. However, in the SCFB reactor at a high leachate ratio (20 % by volume), no nitrification enhancement was observed when PAC was added. Therefore it is recommended that the leachate ratio should be optimized for both organic matter removal and nitrification purposes.

The results obtained in this study showed that the bioregeneration hypothesis of activated carbon was not valid for the conditions encountered in this study. If the activated carbon had been regenerated by the action of microorganisms, in the CFSTR Operation the COD concentrations in the effluent would not increase up to the initial high concentrations after the exhaustion of PAC adsorption capacity.

The results obtained from both PAC-added activated sludge systems and adsorption isotherm studies with PAC showed that COD removal was a simple combination of adsorption and biodegradation in the PAC added activated sludge systems used in this study. No enhancement of heterotrophic biological activity seemed to occur due to PAC addition.

However, PAC addition significantly enhanced the activity of nitrifiers. In the CFSTR operation, the enhancement of nitrification due to PAC addition was more apparent. Complete nitrification was achieved in the CFSTR which had never been observed in batch and SCFB runs. Hence it can be deduced that PAC addition could prevent nitrification inhibition completely and NO_2-N accumulation could be overcome. The effect of PAC on COD removals was immediately observed after its addition. However, the effect of PAC on nitrification was detected much later in SCFB runs and CFSTR operation. Since the inhibition of nitrifiers was more long lasting, the positive effect of PAC on nitrification was observed with delay.

The results show that PAC dosage is a very important factor in PAC added activated sludge systems. If a permanent improvement in treatment efficiency is required, a continuous addition of PAC is necessary. The CFSTR operation showed that the effect of PAC persisted for a few days after the shock addition of PAC. Hence, instead of continuous addition, PAC can be added to a CFSTR periodically to compensate for the peak loadings that may frequently occur due to the variations in leachate quality. This application may lower operating costs of a PAC added activated sludge system.

In this study, also an improvement in the settling characteristics of activated sludge was observed when PAC was added. It is recommended to examine the effect of PAC on settling characteristics in a further study.

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APPENDIX A

TABLE A1.Determination of the equilibrium time for adsorption on activated carbon.

	PAC= 1000 mg/l		PAC= 5000 mg/l		PAC= 15000 mg/l	
Time (h)	SCOD (mg/l)	pH	SCOD (mg/l)	pH	SCOD (mg/l)	pH
0	575	8.46	575	8.46	575	8.46
1	442	-	455	-	415	-
2	429	-	402	-	368	-
3	415	-	429	-	335	-
24	275	8.11	222	8.03	156	9.29
48	269	7.71	136	7.57	49	7.90
72	122	7.47	69	7.49	16	7.72
96	122	-	95	-	16	-

TABLE A2. Determination of the adsorption isotherm (at 23°C) for diluted leachate (5%) with high PAC concentrations.

	t=0 hrs		t=24 hrs		t=72 hrs	
PAC Conc. (mg/l)	SCOD (mg/l)	pH	SCOD (mg/l)	pH	SCOD (mg/l)	pH
0	509	8.65	455	8.27	255	7.85
1000	509	8.65	276	8.02	82	7.74
2500	509	8.65	255	8.07	69	7.70
5000	509	8.65	229	8.30	42	7.84
10000	509	8.65	216	8.43	16	7.82
15000	509	8.65	202	8.55	8	7.91

TABLE A3. Determination of the adsorption isotherm (at 23°C) for diluted leachate (5%) with low PAC concentrations.

	t=0 hrs		t=72 hrs	
PAC Conc. (mg/l)	SCOD (mg/l)	pH	SCOD (mg/l)	pH
0	501	8.51	442	8.27
100	501	8.51	362	8.02
250	501	8.51	349	8.07
500	501	8.51	290	8.30
1000	501	8.51	282	8.43
2500	501	8.51	216	8.55

TABLE A4. Determination of the adsorption isotherm (at 22.4°C) for combined leachate (5% by volume) and synthetic domestic wastewater .

	t=0 hrs		t=72 hrs	
PAC Conc. (mg/l)	SCOD (mg/l)	pH	SCOD (mg/l)	pH
0	905	7,90	655	7,40
100	905	7,90	636	7,44
500	905	7,90	591	7,44
1000	905	7,90	562	7,45
2500	905	7,90	503	7,63
5000	905	7,90	487	7,76

APPENDIX B

TABLE B1. Results of the Batch Runs performed with synthetic domestic wastewater.

RUN	t(h)	TCOD (mg/l)	pH	MLSS(mg/l)	MLVSS(mg/l)
1	0	1055	7.82	2795	2255
	24	272	8.26	-	-
	48	106	7.98	-	-
2	0	1038	8.13	-	
	48	322	-	2435	2045
3	0	1505	7.52	-	-
	72	429	3.69	-	-
4	0	1605	-	3400	2625
	48	322	4.12	-	-
5	0	1771	6.45	-	-
	72	349	4.22	-	-
6	0	1271	5.90	3125	2580
	24	405	6.35	-	-
	48	402	-	-	-
7	0	1571	7.31	-	-
	48	349	4.22	-	-
8	0	1405	6.38	3230	2720
	24	295	5.41	-	-
	48	280	4.47	-	-
9	0	1338	6.54	-	-
	48	349	5.25	-	-
10	0	1071	7.03	3485	3045
	24	335	6.48	-	-
	48	322	6.47	-	-
11	0	1505	6.60	3925	3280
	72	381	6.50	-	-
12	0	1072	6.66	4430	3705
	1	725	7.15	-	-
	2	452	7.61	-	-
	24	144	6.38	-	-
	48	282	6.38	-	-
13	0	514	6.98	-	-
	24	162	7.36	-	-

TABLE B2. Results of the Batch Runs performed with the leachate combined with the synthetic domestic wastewater.

RUN	Reactor	Time (h)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO_2/l/h)	Leachate Ratio	
												Volume Per cent	COD Per cent
1	AS	0	1005	659	-	425	328				140	5	62.6
		1	872	672	8.06	-	-				-		
		2	-	-	-	-	-				100		
		3	619	559	-	-	-				-		
		24	189	176	8.27	-	-				24		
		48	189	172	8.13	-	-				30		
		72	192	184	7.38	975	755				40		
		144	109	96	6.80	675	605				5		
1	AS+PAC(100 mg/l)	0	952	752	-	525	428				140	5	62.6
		1		722	8.09						-		
		2		-	-						80		
		3		499	-						-		
		24		141	8.38						24		
		48		141	8.04						36		
		72		160	7.32	1380	1280				29		
		144		61	6.89	780	760				4		
1	PAC(100 mg/l)	0	1058	739	-							5	62.6
		1		872	8.23								
		2		-	-								
		3		819	-								
		24		142	8.44								
		48		129	8.54								
		72		168	8.37								
		144		149	7.42								

TABLE B2. Continued.

RUN	Reactor	Time (h)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_3-N (mgN/l)	OUR (mgO_2/l/hr)	Leachate Ratio	
												Volume Per cent	COD Per cent
2	AS	0	1058	639	-	375	355	-			120	5	54.3
		1	972	639	-	-	-	-			-		
		3	772	639	8.42	-	-	0			75		
		24	198	129	8.83	570	450	11			14		
		48	134	82	8.66	-	-	25			25		
		72	104	100	8.39	-	-	34			23		
		144	109	101	8.37	-	-	19			5		
		168	106	81	8.30	-	-	14			1		
		192	113	85	-	645	595	8			2		
		216	79	66	8.35	-	-	10			-		
2	AS+PAC(100 mg/l)	0		705	-	535	450	-			120	5	54.3
		1		765	-	-	-	-			-		
		3		699	8.41	-	-	0			75		
		24		120	8.74	640	495	15			17		
		48		87	8.66	-	-	25			25		
		72		97	8.31	-	-	40			27		
		144		90	8.19	-	-	15			5		
		168		69	8.13	-	-	12			3		
		192		73	-	710	650	8			3		
		216		58	8.20	-	-	10			-		
2	PAC(100 mg/l)	0		945	-	135	130	-			4	5	54.3
		1		732	-			-			-		
		3		805	8.47			-			-		
		24		157	8.82			-			10		
		48		157	8.83			10			16		
		72		124	8.90			12			4		
		144		149	8.89			12			2		
		168		107	8.82			14			1		

TABLE B2. Continued.

RUN	Reactor	Time (h)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_3-N (mgN/l)	OUR (mgO_2/l/hr)	Leachate Ratio	
												Volume Per cent	COD Per cent
		192		-	-	290	285	13			1		
		216		85	8.75			22			-		
3	AS	0	963	798	-	365	180	8	128	14	50	5	59.2
		1	-	-	-	-	-	-			42		
		2	-	-	-			-			37		
		3	-	-	-	-	-	-			36		
		4	770	646	-			8			-		
		5	-	-	-						28		
		24	240	143	8.83	-	-	9.4			20		
		48	192	112	-	550	470	9	-	-	13		
		72	-	-	8.67	-	-	-	23	23	14		
		168	139	85	8.43	430	240	26.6	-	-	4		
		240	150	67	8.58	410	-	16.6	-	-	2		
		312	-	-	-	-	-	-	6	35	-		
3	AS+PAC(250 mg/l)	0		753	-	645	465	8	122	12	40	5	59.2
		1			-	-	-				38		
		2									34		
		3			-	-	-				33		
		4		670				8			-		
		5		-							28		
		24		118	8.94	-	-	7			21		
		48		101	-	795	690	7			18		
		72		-	8.73	-	-		29	17	20		
		168		50	8.68	680	500	32.1			4		
		240		46	8.67	450	-	23.8			3		
		312		-	-	-	-	-	6	46	-		

TABLE B2. Continued.

RUN	Reactor	Time (h)	MLCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO_2/l/hr)	Leachate Ratio	
												Volume per cent	COD per cent
3	Aerated feed	0		779	-	195	90	8	122	14	4	5	59.2
		1		-	-						2		
		2		-							2		
		3		-	-						2		
		4		839				8			-		
		5		-							-		
		24		180	8.96			5			20		
		48		149	-	370	320	6.5			9		
		72		-	9.02	-	-	-	46	12	10		
		168		106	8.98	135	70	2.7			4		
		240		76	8.96	115	-	8.2			2		
		312		-	-	-	-	-	6	12	-		
4	AS	0	920	712	-			4.6	145	12	10.2	5	54.5
		1	-	-	-			-	-	-	11.4		
		2	-	-	8.47			-	-	-	11.4		
		3	-	-	-			-	-	-	11.4		
		4	-	-	-			-	-	-	12		
		24	679	114	-			7.1	-	-	4.2		
		48	576	75	-			5.7	70	12	4.2		
		72	-	-	8.69			-	-	-	1.8		
		144	406	81	-			21	12	33	1.2		
		216	573	80	8.08			26.2	3.4	30.8	1.2		
		312	486	86	-			21	2.8	30.8	0		
	(New Feeding)	360	1028	775	-			-	-	-	7.8		
		384	868	242	-			-	-	-	4.8		
		408	784	130	-			-	-	-	1.8		

TABLE B2. Continued.

RUN	Reactor	Time (h)	MLCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO_2/l/hr)	Leachate Ratio	
												Volume per cent	COD per cent
4	AS+PAC(500 mg/l)	0		695	-			5.3	139	12	13.2	5	54.5
		1		-	-			-	-	-	13.8		
		2		-	8.55			-	-	-	13.8		
		3		-	-			-	-	-	13.8		
		4		-	-			-	-	-	13.8		
		24		97	-			6.5	-	-	4.8		
		48		68	-			13.1	70	12	5.4		
		72		-	8.67			-	-	-	4.2		
		144		68	-			13	29	23	3.6		
		216		60	8.32			20.2	10.1	28	1.8		
		312		54	-			25.8	2.8	30.8	0		
	New feeding	360		754	-			-	-	-	27		
		384		130	-			-	-	-	5.4		
		408		101	-			-	-	-	3.6		
4	AS+PAC(2500 mg/l)	0		636	-			5.3	139	14	13.2	5	54.5
		1		-	-			-	-	-	15		
		2		-	8.56			-	-	-	15.6		
		3		-	-			-	-	-	14.4		
		4		-	-			-	-	-	15		
		24		167	-			8.3	-	-	39.6		
		48		52	-			3.5	93	23	6.6		
		72		-	8.74			-	-		6.0		
		144		36	-			5.9	35	17.5	3.0		
		216		25	8.66			3.5	21.3	16.2	1.2		
		312		33	-			7.7	15.1	15.6	1.2		
	(New Feeding)	360		748	-			-	-	-	19.8		
		384		90	-			-	-	-	7.2		
		408		90	-			-	-	-	6.6		

TABLE B2. Continued.

RUN	Reactor	Time (h)	MLCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO_2/l/hr)	Leachate Ratio	
												Volume Per cent	COD Per cent
5	AS	0	1108	658	6.71	205	180	8.7	135	18	6.6	5	52,1
		1	-	-	-	-	-	-	-	-	9.6		
		3	-	-	-	-	-	-	-	-	12.6		
		4	1010	637	7.88	-		4.6	-	-	16.2		
		5	-	-	-	-		-	-	-	18		
		24	639	106	-	-	-	3	-	-	4.2		
		48	-	71	8.79	-	-	2.3	78	14	1.2		
		72	-	-	-	-	-	-	-	-	1.2		
		144	516	95	8.38	-	-	10.1	39	21	1.8		
		168	-	-	-	-	-	-	-	-	1.2		
		216	481	78	6.58	350	320	33	20	37	1.2		
5	AS+PAC(1000 mg/l)	0		659	6.85	1100	1075	8.2	134	19	6.6	5	52.1
		1		-	-			-	-	-	9.6		
		3		-	-			-	-	-	12.6		
		4		636	8.46			5.8	-	-	15.6		
		5		-	-			-	-	-	16.8		
		24		59	-			4.9	-	-	4.8		
		48		50	8.82			5.8	68	21	2.4		
		72		-	-			-	-	-	2.4		
		144		61	8.29			17.7	31	26	1.8		
		168		-	-			-	-	-	3.0		
		216		26	5.73			46.8	10	52	0.6		
5	AS+PAC(3500 mg/l)	0		658	7.1	3415	3300	8.7	141	19	9	5	52.1
		1		-	-			-	-	-	10.8		
		3		-	-			-	-	-	12.6		
		4		636	8.42			5.8	-	-	14.4		
		5		-	-			-	-	-	18		
		24		23	-			5.3	-	-	7.2		

TABLE B2. Continued.

RUN	Reactor	Time (h)	MLCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO2/l/hr)	Leachate Ratio	
												Volume Per cent	COD Per cent
		48		25	8.85			3.7	81	18	6		
		72		-	-			-	-	-	4.8		
		144		45	8.56			7.6	41	18	3.6		
		168		-	-			-	-	-	3.6		
		216		22	8.22			10.5	28	21	3		
6	AS	0	4421	934	6.64	-	-	49	233	88	35	5	49.4
		3	3168	521		2680	2160	37	-	-	n.s.v		
		4	-	-	7.71	-		-	-	-	46		
		5	-	-	-	-		-	-	-	41		
		24	2234	159	8.23	-	-	39	-	-	9.6		
		48	2415	120	8.13	2360	1800	38	151	70	4.8		
		96	2049	94	7.72	-	-	50	131	87	4.2		
		168	2082	100	7.24	-	-	56	-	-	-		
6	AS+PAC(500 mg/l)	0		861	6.86	-	-	48	241	93	36	5	49.4
		3		324	-			46	-	-	n.s.v.		
		4		-	7.91			-	-	-	47		
		5		-	-			-	-	-	51		
		24		115	8.03			55	-	-	9.6		
		48		99	7.83			57	151	93	6.6		
		96		103	6.40			103	116	128	8.4		
		168		48	5.36			128	-	-	-		
6	AS+PAC(1000 mg/l)	0		882	6.98			36	237	97	36	5	49.4
		3		228	-			49	-	-	n.s.v.		
		4		-	7.91			-	-	-	40		
		5		-	-			-	-	-	37		
		24		88	7.83			73	-	-	9		

TABLE B2. Continued.

RUN	Reactor	Time (h)	MLCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO2/l/hr)	Leachate Ratio	
												Volume Per cent	COD Per cent
		48		68	7.33			85	151	122	7.2		
		72		15	6.04			134	110	160	6		
		168		55	4.93			129	-	-	-		
7	AS	0	3568	840	-	1810	1525	2	139	12	n.s.v.	5	49,3
		1		-	7.34	-	-	-	-	-	n.s.v.		
		3		-	-	-	-	-	-	-	60.6		
		4		-	-	-	-	-	-	-	25.2		
		5		-	*	-	-	-	-	-	20.4		
		24		139	7.62	-	-	34	-	-	14.4		
7	AS+PAC(1000 mg/l)	0		840	-			2	139	12	n.s.v.	5	49.3
		1		-	7.47			-	-	-	n.s.v.		
		3		-	-			-	-	-	75.6		
		4		-	-			-	-	-	63.6		
		5		-	-			-	-	-	31.2		
		24		66	8.01			27	-	-	39.6		
8	AS	0	3407	826	6.96	1620	1390	2	148	10	n.s.v.	5	50.2
		3	-	-	-	-	-	-	-	-	21.6		
		5	-	-	-	-	-	-	-	-	18.6		
		24	2631	130	8.08	-	-	42	-	-	16.8		
8	AS+PAC(1000 mg/l)	0		826	6.70			2	148	10	n.s.v.	5	50.2
		3		-	-			-	-	-	70.8		
		5		-	-			-	-	-	43.2		
		24		77	7.97			25	-	-	28.2		

TABLE B2. Continued.

RUN	Reactor	Time (h)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	NH_4-N (TKN) (mgN/l)	NO_x-N (mgN/l)	OUR (mgO2/l/hr)	Leachate Ratio	
												Volume Per cent	COD Per cent
9	AS	0	1513	1255	7.62	1630	1225	4	356 (406)	9	n.s.v.	15	72
		3	520	365	-	-	-	4	-	-	34.2		
		24	537	320	9.07	-	-	8	165 (186)	15	10.8		
9	AS+PAC(2000 mg/l)	0	-	1216	7.62			4	370 (426)	9	n.s.v.	15	72
		3	-	339	-			4	-	-	38.4		
		24	-	215	8.58			14	165 (190)	17	22.8		
10	AS	0	1490	1225	7.46	2045	1750	4	°246	12	66	10	58.7
		1	-	-	8.31	-	-	-	-	-	48		
		3	516	501	-	-	-	8	-	-	156		
		4	-	-	-	-	-	-	-	-	66		
		5	-	-	-	-	-	-	-	-	28.8		
		6	-	-	-	-	-	-	-	-	26.4		
		24	355	231	9.16	2265	1770	16	144	21	12		
10	AS+PAC(2000 mg/l)	0	1490	1225	7.46			4	246	12	114	10	58.7
		1	-	-	8.30			-	-	-	72		
		3	608	479	-			5	-	-	120		
		4	-	-	-			-	-	-	84		
		5	-	-	-			-	-	-	70.2		
		6	-	-	-			-	-	-	26.4		
		24	362	152	8.95			29	124	35	9.6		

n.s.v. : no static value

TABLE B3. The results of the Batch Run in which one of the reactors was inhibited by $HgSO_4$.

Reactor	Time(days)	MLCOD (mg/l)	SCOD(mg/l)	pH	OUR ($mgO_2/l/hr$)	Leachate Ratio	
						Volume Per cent	COD Per cent
Feed Only	0	908	828	8.38	1.8	5	48.7
	1	522	189	-	7.5		
	2	309	221	-	2.4		
	5	216	141	9.01	1.2		
Feed+Inhibitor($HgSO_4$)	0	908	828	8.38	0	5	48.7
	1	882	775	-	0		
	2	402	269	-	29.4		
	5	216	149	8.97	4.2		
Feed +PAC(250 mg/l)	0		802	8.70	-	5	48.7
	1		269	-	6.6		
	2		184	-	4.8		
	5		130	9.37	1.2		

TABLE B4. Results of the Semi-Continuously Fed Batch (SCFB) Runs.

RUN	Reactor	Time (day)	MLCOD (mg/l)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	TKN (mg/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR (mgO_2/l/h)	Leachate Ratio (Volume %)
1	**AS**	**Feed**		**1338**	**1035**	**7.17**			**2**	**265**	**197**	**15**		**6.7**
		1	3568		139	7.62	1810	1525	34	-	-	-	14.4	
		2	-		142	7.97	-	-	43	-	-	-	19.8	
		3	-		150	7.44	-	-	60	-	98	58	25.8	
		4	-		118	6.73	-	-	89	-	-	-	21	
		5	3783		116	6.42	2825	2480	84	84	72	91	12.6	
1	**AS+PAC (1000 mg/l)**	**Feed**		**1338**	**1035**	**7.17**			**2**	**265**	**197**	**15**		**6.7**
		1			66	8.01			27	-	-	-	39.6	
		2			118	8.50			11	-	-	-	65.4	
		3			134	8.14			25	-	114	34	61.8	
		4			129	7.83			30	-	-	-	36	
		5			110	6.56			84	79	70	89	33.6	
2	**AS**	**Feed**		**1338**	**1035**	**7.17**			**2**	**265**	**197**	**15**		**6.7**
		1	2631		130	8.08	1620	1390	42	-	-	-	16.8	
		2	-		150	8.03	-	-	24	-	-	-	33	
		3	-		130	7.85	-	-	54	-	84	52	20.4	
		4	-		127	7.44	-	-	81	-	-	-	24	
		5	2918		124	7.03	-	-	84	-	70	81	24	
		6	2957		115	6.86	2150	1775	96	-	57	89	14.4	
		7	-		116	6.44	-	-	88	-	55	82	8.4	
		8	-		141	6.58	-	-	97	-	55	91	7.2	
		11	3036		122	6.47	-	-	61	-	52	60	13.8	
		12	-		99	6.19	-	-	78	-	56	73	6.6	
		13	-		124	6.35	-	-	78	-	55	75	9.6	
		15	2979		153	6.20	-	-	76	-	62	72	9	

TABLE B4. Continued.

RUN	Reactor	Time (day)	MLCOD (mg/l)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	TKN (mg/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR ($mgO_2/l/h$)	Leachate Ratio (Volume %)
		16	-		176	7.59	-	-	19	-	73	33	20.4	
		17	-		111	6.78	-	-	93	-	57	93	5.4	
		18	3212		146	5.44	-	-	83	-	55	82	9	
		22	2859		171	6.70	-	-	76	-	74	80	7.8	
	[pH Adjust.]	23	-		-	6.88	-	-	-	-	-	-	12.6	
		26	-		119	7.24	-	-	136	-	46	116	23.4	
		27	4197		124	7.20	-	-	132	-	28	115	17.4	
		31	5091		185	6.84	3570	3080	120	48	32	136	9.6	
		35	-		163	6.56	-	-	96	37	16	114	-	
2	**AS+PAC (1000 mg/l)**	**Feed**		**1338**	**1035**	**7.17**			**2**	**265**	**197**	**15**		**6.7**
		1			77	7.97			25	-	-	-	28.2	
		2			133	7.93			51	-	-	-	22.8	
		3			137	8.28			35	-	116	46	46.8	
		4			163	6.98			96	-	-	-	30	
		5			108	5.77			98	-	70	104	18	
		6			107	5.86			90	-	53	85	12	
		7			119	5.38			93	-	57	82	10.8	
		8			139	5.34			94	-	57	91	10.8	
		11			105	5.24			76	-	58	72	10.2	
		12			120	4.81			82	-	58	78	7.2	
		13			156	4.81			78	-	57	73	8.4	
	[PAC Addition (1000 mg/l)]	15			156	4.99			78	-	48	81	10.2	
		16			90	5.05			90	-	58	89	9	
		17			144	6.87			65	-	63	67	24	
		18			135	5.91			90	-	61	95	16.8	
		22			174	5.46			74	-	73	80	13.2	

TABLE B4. Continued.

RUN	Reactor	Time (day)	MLCOD (mg/l)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	TKN (mg/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR ($mgO_2/l/h$)	Leachate Ratio (Volume %)
	[PH Adjust.]	23			-	5.71			-	-	-	-	13.2	
		26			169	6.96			139	-	41	138	18.6	
		27			140	6.85			129	-	30	116	17.4	
		31			153	6.34			129	44	23	132	10.8	
		35			132	5.73			119	40	19	127	,	
3	**AS**	**Feed**		**2277**	**2153**	**7.62**			**4**	**542**	**484**	**12**		**20**
		1	2636	537	320	9.07	1630	1225	8	186	165	15	10.8	
		2	2860	616	371	9.12	-	-	9	-	-	-	10.8	
		3	3960	735	399	9.08	-	-	6	-	202	14	12.6	
		5	3661	591	462	9.07	2795	2130	8	-	-	-	16.8	
		6	3806	620	426	8.89	-	-	5	-	207	10	19.2	
		7	3901	663	483	9.02	-	-	1	-	209	12	79.2	
		8	3708	593	425	8.87	-	-	2	-	196	12	74.4	
		11	-	-	-	8.96	-	-	-	-	-	-	33	
		12	3580	662	456	8.82	2820	1860	2	323	262	22	25.8	
		13	-	685	440	8.84	-	-	5	-	238	41	34.2	
		16	3580	510	355	9.22	-	-	0.5	-	218	14	34.2	
		17	-	600	381	9.15	-	-	0.5	-	226	12	22.8	
		18	-	639	406	8.91	-	-	1	-	-	-	25.8	
3	**AS+PAC (2000 mg/l)**	**Feed**		**2277**	**2153**	**7.62**			**4**	**542**	**484**	**12**		**20**
		1		-	215	8.58			14	190	165	17	22.8	
		2		-	283	8.92			12	-	-	-	14.4	
		3		-	420	8.93			11	-	218	20	27.6	

TABLE B4. Continued.

RUN	Reactor	Time (day)	MLCOD (mg/l)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	TKN (mg/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR ($mgO_2/l/h$)	Leachate Ratio (Volume %)
		5		-	349	8.98			5	-	-	-	39	
		6		-	406	9.03			5	-	208	28	27.6	
		7		-	439	8.62			5	-	226	20	26.4	
		8		533	425	9.01			2	-	245	17	43.2	
		11		-	-	9.00			-	-	-	-	45.6	
		12		607	452	8.99			5	319	277	12	42.6	
		13		503	370	8.99			5	-	259	12	42.42	
	[PAC Addition (2000 mg/l)]	16		431	354	9.08			13	-	268	22	34.2	
		17		403	302	9.02			20	-	270	26	47.4	
		18		450	313	9.00			26	-	-	-		
4	**AS**	**Feed**		**1854**	**1626**	**7.46**			**3**	**406**	**345**	**15**		**13.3**
		1	3278	355	231	9.16	2265	1770	16	-	144	21	12	
		3	-	-	-	9.21	-	-	-	-	-	-	6	
		4	3025	393	257	9.39	-	-	12	-	-	-	11.4	
		5	3188	395	220	9.29	-	-	5	-	159	12	32.4	
		9	3826	420	299	9.34	-	-	11	-	127	15	13.2	
		10	4216	424	303	9.03	3450	2730	7	-	-	-	18	
		11	4282	407	291	8.96	-	-	7	156	145	16	12	
4	**AS+PAC (2000 mg/l)**	**Feed**		**1854**	**1626**	**7.46**			**3**	**406**	**345**	**15**		**13.3**
		1		362	152	8.95			29	-	124	35	9.6	
		3		-	-	8.97			-	-	-	-	24.6	
		4		348	232	8.70			30	-	-	-	27.6	
		5		345	229	8.83			9	-	197	17	46.8	

TABLE B4. Continued.

RUN	Reactor	Time (day)	MLCOD (mg/l)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	TKN (mg/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR ($mgO_2/l/h$)	Leachate Ratio (Volume %)
	[PAC Addition (2000 mg/l)]	9		282	184	8.38			151	-	139	221	36	
		10		89	27	7.33			239	-	-	-	40.2	
		11		105	76	7.15			239	69	61	214	22.2	

TABLE B5. Results of the Continuous-Flow Stirred Tank Reactor (CFSTR) Operation.

Reactor Operation	Time (day)	MLCOD (mg/l)	TCOD (mg/l)	SCOD (mg/l)	pH	MLSS (mg/l)	MLVSS (mg/l)	NO_2-N (mgN/l)	TKN (mg/l)	NH_4-N (mgN/l)	NO_x-N (mgN/l)	OUR ($mgO_2/l/h$)	Leachate Ratio (Volume %)
AS Only	**Feed**		**1255**	**1020**	**7.38**			**2**	**215**	**205**	**15**		**6.7**
	2	-	127	111	7.44	-	-	48	-	-	-	38.4	
	5	3838	146	127	7.88	3410	2825	48	-	70	62	66.6	
	6	2500	183	132	8.20	-	-	44	-	99	46	23.4	
	7	3068	145	114	7.21	-	-	114	-	-	-	46.8	
	9	3496	154	129	6.66	-	-	135	-	64	149	10.2	
	12	2824	128	102	8.18	2690	2050	78	-	58	103	38.4	
	13	2936	215	150	7.55	-	-	57	93	87	66	31.8	
	14	-	-	-	6.56	-	-	-	-	-	-	33.6	
	15	-	-	-	7.13	-	-	-	-	-	-	21.6	
	16	-	142	110	-	-	-	124	-	-	-	37.2	
PAC Addition (2000 mg/l)	19	2384	175	131	7.87	1430	1180	91	-	60	110	31.2	
	20		121	49	7.55	-	-	72	-	82	91	29.4	
	21		89	35	6.56	-	-	113	-	68	121	10.2	
	22		76	19	6.41	-	-	129	-	-	-	5.4	
	23		83	62	6.82	-	1080[a]	102	-	-	-	15	
	26		155	105	6.81	-	-	79	-	51	140	7.2	
	27		156	110	6.13	-	-	68	70	45	134	30	
New Feeding	**Feed**		**1854**	**1626**	**7.46**			**3**	**406**	**345**	**15**		**13.3**
	28		229	152	8.00	-	1020[a]	67	-	-	-	43.2	
	30		370	215	8.30	-	-	80	-	-	-	28.8	
	33		360	226	7.65	-	-	42	-	161	104	33	
	34		346	223	7.28	-	1110[a]	130	128	116	197	50.4	
	35		-	-	7.24	-	-	-	-	-	-	55.8	
PAC Addition (2000 mg/l)	36		284	219	7.04	-	-	88	-	95	234	57.6	
	37		205	163	7.37	-	-	38	-	104	203	48	
	40		181	163	6.41	-	-	29	-	98	221	15	
	42		209	168	6.58	-	-	8	-	80	247	27.6	
	44		309	208	6.94	-	1200[a]	17	85	80	223	60	

a: Superscript a is used to denote the biomass MLVSS in the PACT sludge determined according to the procedure of Arbuckle et al., 1982.

APPENDIX C

Table C1. Classes of Organic Compounds Adsorbed on Activated Carbon (4).

Organic Chemical Class	Examples of Chemical Class
Aromatic Hydrocarbons	Benzene, Toluene, Xylene
Polynuclear Aromatics	Naphtalene, anthracenes, biphenyls
Chlorinated Aromatics	Chlorobenzene, polychlorinated biphenyls, aldrin, endrin, toxaphene, DDT
Phenolics	Phenol, Cresol, resorcenol, polyphenyls
Chlorinated phenolics	Trichlorophenol, pentachlorophenol
High molecular weight aliphatic and branch-chain hydrocarbons [a]	Gasoline, kerosene
Chlorinated aliphatic hydrocarbons	1,1,1 Trichloroethane, trichloroethylene, carbon tetrachloride, perchloroethylene
HMW aliphatic acids and aromatic acids[a]	Tar acids, benzoic acids
HMW aliphatic amines and aromatic amines[a]	Aniline, toluene, diamine
HMW ketones, esters, ethers and alcohols[a]	Hydroquinone, polyethylene glycol
Surfactants	Alkyl benzene sulfonates
Soluble organic dyes	methylene blue, indigo carmine

(a) HMW includes compounds in the range of 4-20 carbon atoms.

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