

EFFECT OF FLUORIDE AND HEXAVALENT CHROMIUM
ON NITRIFICATION PROCESS

MASTER SCIENCE THESIS

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FLORÜR VE ALTI DEĞERLİKLİ KROMUN
NİTRİFİKASYON PROSESİNE ETKİSİ

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SUMMARY

In this study, the effect of fluoride and hexavalent chromium on nitrification process on Rotating Biological Contactor (RBC) was studied under shock loading condition. This condition is analogous to a practical situation in which -inadvertently or otherwise- a shock load of a toxicant enters an active biological waste treatment process.

In the first part of the report, sensitivity of biofilm reactors to the presence of toxic compounds are given.

In the second part of the report, a general literature survey about nitrification process are given. Within this survey, source of nitrogenous wastes, effect of nitrogen discharge on the environment, methods currently used for removal of ammonia from wastewaters, nitrification process, processes used for nitrification, RBC system, properties of biofilm, factors effecting nitrification are placed.

In the third part of the report, results of the experimental study are evaluated. It has been found that residual $\text{NH}_4\text{-N}$ concentration changes linearly with reaction time up to 5 to 10 mg/l $\text{NH}_4\text{-N}$ concentration. After this point, it changes exponentially. When the residual $\text{NH}_4\text{-N}$ concentration reaches 5-10 mg/l level, the $\text{NO}_2\text{-N}$ concentration in the bulk solution decreases rapidly whereas the $\text{NO}_3\text{-N}$ concentration increases rapidly.

Change in the average bulk solution temperature reflected as a change on $\text{NH}_4\text{-N}$ oxidation rate. It has been found that $\text{NH}_4\text{-N}$ oxidation rate increases linearly with the in average bulk solution temperature. The effect of fluoride and hexavalent chromium on $\text{NH}_4\text{-N}$ oxidation was found to be dependent on the initial $\text{NH}_4\text{-N}$ concentration in the system. Inhibition effect of fluoride and hexavalent chromium decreased as the initial $\text{NH}_4\text{-N}$ concentration were increased.

ÖZET

FLORÜR VE ALTI DEĞERLİKLİ KROMUN NİTRİFİKASYON PROSESİNE ETKİSİ

Azotlu materyaller su ortamlarına doğal veya insan sebepli kaynaklar olarak girmektedirler. Azotlu maddeler içeren doğal kaynaklar yağmur, toz, yüzey suları veya biyolojik filtrasyon olarak sıralanabilir. İnsan sebepli kaynaklar ise genellikle yüksek konsantrasyonlarda azotlu bileşikler içeren endüstriyel atıksulardır. Bu endüstrilere örnek olarak gübre endüstrisi, kimya endüstrisinin azotlu bileşikler üreten bölümleri, patlayıcı üreten endüstriler, soğutucu endüstrileri, petrol rafinerileri, et ve süt işleme endüstrileri, sentetik elyaf endüstrileri verilebilir.

Gübre endüstrilerinin proses atıksuları amonyak ve üre ile birlikte arsenik, florür ve kromun inorganik bileşiklerini ihtiva edebilmektedir. Literatürde bir gübre endüstrisinin normal işletme koşullarında atıksularında bulunması muhtemel florür, arsenik ve krom konsantrasyonları sırasıyla 0-200, 1-20 ve 0-10 mg/l olarak verilmektedir. Bu maddeler atıksu arıtma sistemine belirli bir kaynaktan sürekli olarak sabit konsantrasyonlarda gelebildikleri gibi, sızıntı veya kaçaklar dolayısıyla şok dozajlarda da gelebilmektedirler.

Atıksu arıtma sistemlerinden arıtılmadan deşarj edilen azotlu bileşiklerin zararlı etkileri olabilmektedir. Bu etkiler başlıca yüzey sularının canlandırılması, balıklar üzerinde toksik etkileri, klorun dezenfeksiyon etkisinin azalması, alıcı sularda çözülmüş oksijenin kullanımı, özellikle yeraltı sularına karışması durumunda insan sağlığı üzerine olumsuz etkileri, alıcı suların geri kullanımını zorlaştırması olarak sıralanabilirler. Amonyak azotunun atıksulardan arıtımı amacıyla kullanılan pek çok biyolojik, fiziksel ve kimyasal yöntemler bulunmaktadır. Bunlar başlıca biyolojik nitrifikasyon, iyon değiştirme, klorlama ve amonyak sıyırma olarak sıralanabilirler. Herhangi bir uygulamada hangi yöntemin kullanılacağına karar verebilmek için altı temel durum göz önünde bulundurulmalıdır. (1) Arıtma sistemi giriş atıksuyunda bulunan azotlu bileşiklerin şekli ve konsantrasyonu, (2) Arıtım sistemi çıkışında istenen atıksu kalitesi, (3) Kullanılan diğer arıtım prosesleri, (4) Maliyet, (5) Gerçekleştirilebilirlik, (6) Esneklik.

Azotun oksijenle kimyasal reaksiyonu sonucunda -III'den +V oksidasyon haline oksitlenmesi nitrifikasyon olarak adlandırılmaktadır. Biyolojik nitrifikasyon sonucunda ortamdan azot uzaklaştırılmış olmamaktadır. Nitrifikasyon arıtım

prosesinin başlıca etkisi amonyak azotunun nitrata dönüştürülmesidir. Eğer ortamdan nitratin da giderilmesi isteniyorsa nitrifikasyon sonrasında denitrifikasyon prosesi uygulanmaktadır.

Nitrifikasyon bakterileri çok özel organizmalardır. Büyüme ve hücre metabolizması için gerekli enerji ihtiyaçlarını bir inorganik azot substratının oksitlenmesi sonucunda açığa çıkan enerjiden sağlamaktadırlar. Büyüme için gerekli karbon kaynağı olarak ta karbon dioksit veya bikarbonatı kullanmaktadırlar. Nitrifikasyon bakterileri çevre şartlarına olduğu kadar toksik atıklar, ağır metaller, halojenli bileşikler, fenoller, merkaptanlar gibi büyümeyi engelleyici maddelere karşı da çok duyarlıdırlar.

Biyolojik sistemlerde substrat konsantrasyonuna bağlı olarak üç farklı inhibisyon mekanizması gözlenmektedir. Bu üç inhibisyon mekanizması noncompetitive, competitive ve anticompetitive inhibisyon olarak sınıflandırılmaktadır. Noncompetitive inhibisyonda inhibisyonun derecesi substrat konsantrasyonundan bağımsızdır. Competitive inhibisyonda inhibisyon derecesi ortamdaki substrat konsantrasyonuna bağlı olmaktadır. Genellikle substrat konsantrasyonu arttıkça inhibisyon derecesi azalmaktadır. Anticompetitive inhibisyonda ise substrat konsantrasyonu arttıkça inhibisyonun derecesi de artmaktadır.

Nitrifikasyon amacıyla kullanılan biyolojik prosesler havalı askıda büyüme, havalı tutunarak büyüme olarak sınıflandırılmaktadır. Daha ileri bir sınıflandırma ise nitrifikasyonun organik madde ihtiva eden atıksularla aynı reaktörde mi, ayrı bir reaktörde mi olduğu baz alınarak yapılmaktadır. Bunun için BOD_5/TKN oranı ölçü kabul edilmektedir. Eğer BOD_5/TKN oranı 1 ve 3 arasında ise ayrı kademe nitrifikasyon, 5'ten büyükse birleşik karbon oksidasyonu-nitrifikasyon prosesleri kullanılması daha uygundur.

Bu araştırmada nitrifikasyon biyofilm sistemlerinden biri olan Döner Biyolojik Disk (DBD) sisteminde ayrı kademe olarak çalışılmıştır.

Genelde DBD sistemi yatay bir şaft üzerine monte edilmiş bir seri plastik diskten oluşmaktadır. Bu diskler atıksu akış yönüne dik olarak dönmektedirler. Disk çapının yaklaşık %40'ı bir tanka batık durumdadır ve disk yüzey alanı aktif biyolojik kütle ile kaplıdır. Disklerin dönmesi disk yüzeyindeki biyokütlenin su ve gaz fazları ile ilişki kurmasını sağlamaktadır. Her bir diskin alt kısmı atıksu ile temas halinde iken üst kısmı atmosferle temas etmektedir. Böylelikle atıksuyun çözünmüş oksijen konsantrasyonu da ayarlanmaktadır. Yeni hücre oluşumu biyokütlenin sürekli büyümesine neden olmaktadır. Disk yüzeyindeki biyofilm belirli bir kalınlığa ulaştığında yerçekimi ve dönmeden kaynaklanan sürtünme kuvvetlerinin etkileriyle biyofilmin bir kısmı sıyrılmaktadır. Sıyrılan biyokütle tanktan atıksu çıkışı ile birlikte çöktürme tankına gelmektedir.

DBD sistemleri ařađıda verilen parametrelerden nemli lde etkilenmektedir. Bu parametreler giriř substrat konsantrasyonu, yzey hidrolik ykleme, disk dnme hızı, disk batma derinliđi, atıksu sıcaklıđı, hidrolik kalma zamanı, kademe sayısı ve debi olarak sıralanabilir.

Biyofilm katı bir yzeeye tutunan mikroorganizmaların bir tabaka řeklinde birleřmesi olarak adlandırılabilir. Biyofilm katı yzeyin geometrisi ve yzeyden geen akıřın oluřturduđu hidrodinamik srtnmenin bir fonksiyonudur ve sigmaoidal řekilde geliřmektedir. alıřmalar biyofilm oluřumunun ařađıda belirtilen tařınım ve biyolojik reaksiyon hızı proseslerinin net sonucu olduđunu gstermiřtir: (1) znmř substratların ıslak yzeyde adsorpsiyonu, (2) mikrobik partikllerin yzeeye tařınımı, (3) mikroorganizmaların yzeeye tutunması, (4) biyofilm retimi ve (5) biyofilm kopması.

znmř substratların biyofilm iinde arıtımı  temel olay sonucunda gerekleřmektedir. Substratın difzyonu, substrat reaksiyonları ve reaksiyon rnlerinin tařınımı.

Nitrifikasyon prosesi ařađıda belirtilen faktrlerden nemli lde etkilenmektedir; bakiye oksijen konsantrasyonu, iřletme sıcaklıđı, iřletme pH'ı, biyofilm kalınlıđı, hidrolik kalma zamanı ve toksik bileřikler.

Nitrifikasyonda amonyađın oksidasyonunun tamamlanabilmesi iin nitrifikasyon bakterileri molekler oksijene ok gereksinim duymaktadırlar. Amonyađın nitrite oksitlenebilmesi iin gerekli stokiometrik oksijen miktarı oksitlenen amonyak azotu bařına 3.43 kg oksijendir. Benzer řekilde nitritin nitrata evrimi iinde kg nitrit azotu bařına 1.14 kg oksijen gerekmektedir. Bu sebeple 1 kg amonyak azotunun nitrata oksidasyonu iin toplam 4.57 kg oksijen gerekmektedir. Eđer oksijenin amonyak azotuna oranı stokiometrik orana eřitse veya bykse, prosesin oksijenle sınırlı olmayacađı literatrde verilmektedir.

Biyolojik nitrifikasyon hızının sıcaklıđın kuvvetli bir fonksiyonu olduđu bilinmektedir. Sıcaklıktaki herhangi bir deđiřim oksidasyonu direk olarak deđiřtirmektedir. Sıcaklık aynı zamanda biyofilm sistemlerinin kinetiđinde substrat giderim hızı, oksijen doygunluk deđerı (aynı zamanda ktle transfer kuvvetleri) ve oksijen ve substratın difzyonu gibi pek ok mekanizmayı etkilemektedir. Bu sebeple mikrobik byme de sıcaklıktan etkilenmektedir.

Nitrifikasyon sırasında alkalinite kullanılmaktadır. 1 mg amonyak azotunun oksidasyonu sırasında oluřan hidrojen iyonlarının ntralizasyonu iin CaCO_3 olarak aıklanan 7.2 mg bikarbonat gerekmektedir. Evsel atıksuların alkalinitesi genellikle nitrifikasyon iin yeterli olmaktadır. Ancak problemler genellikle azot ieriđi zengin olan endstriyel atıksulardan kaynaklanmaktadır. Suyun alkalinitesi yeterli olmadıđı zaman, prosesteki pH deđerimi nitrifikasyon

hızının ve nitrifikasyon bakterilerinin büyüme hızlarının azalmasına neden olacaktır. Bu durumda yeterli miktarda alkalinite dışarıdan atıksuya ilave edilmelidir. Nitrifikasyon için optimum pH değerleri literatürde genellikle 7 ile 9 arasında verilmektedir.

Biyofilm reaktörlerinin performansı biyofilm kalınlığına bağlıdır. Eğer mikroorganizma kütlesi ve bu sebeple film kalınlığı artarsa sabit giriş şartlarında reaktörün performansı zamanla artmaktadır. Çünkü substrat giderimi direk olarak biyofilm kalınlığına bağlıdır. Amonyakın giderim verimi aynı zamanda hidrolik kalma zamanının bir fonksiyonudur. Bunun temel nedeni verilen bir zamanda ve mutlak bir temelde nitrifikasyon bakterilerinin konsantrasyonunun hidrolik kalma zamanına bağlı olmasıdır.

Diğer tüm biyolojik prosesler gibi, nitrifikasyon sistemlerinin de bazı ağır metaller ve organik bileşikler de içeren toksik bileşiklere karşı duyarlı oldukları bulunmuştur.

Bu çalışmada florür ve altı değerlikli kromun şok yükleme şartlarında nitrifikasyon prosesine etkisi araştırılmıştır. Şok yükleme şartı kaza ile veya başka bir sebeple bir toksik madde yükünün aktif şekilde çalışan bir biyolojik atık arıtma prosesine girmesi durumunda söz konusu olmaktadır. Ancak aynı toksik maddenin uzun bir zaman periyodunda bir biyolojik arıtım sistemine verilmesi durumundaki etkisinin şok yükleme şartındaki durumla aynı olmayabileceği göz önünde bulundurulmalıdır. Bunun sebebi biyolojik arıtım sistemlerinde mikroorganizmalar toksik maddeyi metabolize edebilecek heterotrof popülasyonunu geliştirerek bazı toksik bileşiklere karşı alışkın hale gelebilirler veya nitrifikasyon bakterilerini adapte edebilirler.

Bu çalışmada laboratuvar ölçekli bir DBD sistemi kullanılmıştır. Disk yatay bir shaft üzerine 2 cm aralıkla monte edilmiş 20 paralel pleksiglas dairesel diskten oluşmaktadır. Diskler 30 cm çapında ve 0.5 cm kalınlığında olup mikrobik büyüme için toplam 2.6 m² yüzey alanına sahip bulunmaktadır. Diskler 29.5 litrelik bir tank içinde çaplarının yaklaşık %33'üne kadar batık durumda bulunmaktadır. Sıyrılan biyokütle DBD ünitesine birleşik 7.25 l'lik çöktürme tankında ayrılmaktadır.

Deneyisel çalışmalarda amonyum azotu kaynağı olarak (NH₄)₂SO₄, alkalinite kaynağı olarak NaHCO₃, fosfor kaynağı olarak Na₂HPO₄.12H₂O, florür kaynağı olarak NaF, altı değerlikli krom kaynağı olarak ise K₂Cr₂O₇ kullanılmıştır. Deneylerde her mg amonyum azotu için 10 mg alkalinite (CaCO₃ olarak) ve 0.25 mg fosfor besleme çözeltisine ilave edilmiştir.

Biyofilm oluşumu için öncelikle bir evsel atıksu arıtım sisteminden alınan aktif çamurla DBD sistemine aşılama yapılmıştır. Daha sonra sistem (NH₄)₂SO₄, NaHCO₃ ve Na₂HPO₄'ten oluşan bir çözelti ile 6 ay süre ile beslenmiştir. Disk

dönme hızı olarak 15 rpm seçilmiştir. 6 ay sonunda biyofilm oluşumu tamamlanmıştır. Bundan sonra deneysel çalışmalara geçilmiştir.

Deneysel çalışmalar üç aşamada gerçekleştirilmiştir. Yalnızca amonyum azotu ile gerçekleştirilen deneylerde reaktör boşaltıldıktan sonra çıkışı kapatılarak 60 mg/l amonyum azotu içeren bir çözelti reaktöre doldurulmaktadır. Daha sonra sistem kesikli reaktör esasına göre çalıştırılmaktadır. 7-7.5 saatlik periyot içinde reaktör altında bulunan numune alma musluklarından iki saatte bir örnek alınarak pH, çözünmüş oksijen, sıcaklık, amonyum azotu, nitrit, nitrat, fosfat, sülfat ve klorür parametrelerinin ölçüm ve analizleri yapılmaktadır. Deney süresi sonunda çıkışı açılarak reaktör boşaltılmakta, 10-15mg/l amonyum azotu içeren bir çözelti ile doldurulmaktadır. Daha sonra sistem sürekli olarak 1.25 l/saat debide 200 mg/l amonyum azotu ve uygun oranlarda NaHCO_3 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ilave edilerek hazırlanan bir çözelti ile beslenmeye başlanmaktadır.

Her gün veya günde bir sistem çıkışından numuneler alınarak amonyum azotu konsantrasyonu yaklaşık 5 mg/l seviyesine ulaşınca kadar (diğer bir deyişle % 97 verime) analiz edilmektedir. Daha sonra reaktörün beslemesi durdurulmakta ve reaktör boşaltılarak bir diğer deney için hazır hale getirilmektedir. Bu işlemler 80 ve 120 mg/l amonyum azotu konsantrasyonları için de tekrar edilmiştir.

Amonyum azotu ve florürle birlikte yapılan deneylerde florür konsantrasyonunun amonyum azotu oksidasyon hızına etkisinin belirlenebilmesi amacıyla 60, 80 ve 120 mg/l amonyum azotu konsantrasyonlarının her biri için 100-1000 mg/l aralığında değişen üç değişik florür konsantrasyonu kullanılmıştır. Deneysel çalışmalar yalnızca amonyum azotu ile yapılan deneylerle aynı prosedür izlenerek gerçekleştirilmiştir.

Amonyum azotu ve altı değerlikli krom ile gerçekleştirilen deneylerde altı değerlikli kromun amonyum azotu oksidasyon hızına etkisinin belirlenebilmesi amacıyla 60, 80 ve 120 mg/l amonyum azotu konsantrasyonlarının her biri için 0-130 mg/l aralığında değişen üç değişik altı değerlikli krom konsantrasyonu kullanılmıştır. Deneysel çalışmalar yalnızca amonyakla yapılan deneylerle aynı prosedür izlenerek gerçekleştirilmiştir.

DBD ünitesi laboratuvarında oda sıcaklığında çalıştırılmıştır. Oda sıcaklığındaki değişimler amonyum azotu oksidasyon hızını da değiştirmiştir. Bu deneysel çalışmalarda karşılaşılan büyük bir problem olmuştur. Deneysel sonuçlara göre amonyum azotu oksidasyon hızının bulk solusyon sıcaklığındaki artışla lineer olarak arttığı bulunmuştur. Florür ve altı değerlikli kromun amonyum azotu oksidasyon hızına etkisinin belirlenebilmesi amacıyla bulk solusyon sıcaklığı ile amonyum azotu oksidasyon hızı arasındaki bu ilişkiden yola çıkarak referans oksidasyon hızları bulunmuş ve deneysel amonyum azotu

oksidasyon hızları ile karşılaştırılmıştır.

Amonyum azotu ve florürle yapılan deneysel çalışmalarda, florürün inhibisyon etkisi başlangıç amonyum azotu konsantrasyonu ile yakın ilişkili bulunmuştur.

60 mg/l başlangıç amonyum azotu konsantrasyonu ile yapılan deneylerde florürün tüm denenen konsantrasyonlarında amonyum azotu oksidasyon hızı üzerine inhibisyon etkisi yaptığı bulunmuştur. Çünkü referans amonyum azotu oksidasyon hızları deneysel amonyum azotu oksidasyon hızlarının üzerinde bulunmuştur. 221, 421 ve 753 mg/l florür konsantrasyonlarında inhibisyon değerleri %9, %6 ve %14 olarak bulunmuştur.

Ancak 80 mg/l başlangıç amonyum azotu konsantrasyonu ile yapılan deneylerde florürün amonyum azotu oksidasyon hızına inhibisyon etkisinin azaldığı ve hatta yok olduğu bulunmuştur. 167 mg/l florür konsantrasyonunda, %8 inhibisyon olmuş, 513 mg/l florür konsantrasyonunda oksidasyon hızı %2.3 artmış, 783 mg/l florür konsantrasyonunda da yine %1 inhibisyon olmuştur.

120 mg/l başlangıç amonyum azotu konsantrasyonu ile yapılan deneylerde florürün etkisi pozitif yönde bulunmuştur. 175, 566 ve 990 mg/l florür konsantrasyonlarında amonyum azotu oksidasyon hızları sırasıyla %9, %11 ve %33.6 artmıştır. Buradan da florürün nitrifikasyon prosesine etkisinin başlangıç amonyum azotu arttıkça inhibisyon etkisinin azaldığı sonucuna varılmıştır.

Amonyum azotu ve altı değerlikli kromla gerçekleştirilen deneylerde de altı değerlikli kromun amonyum azotu oksidasyon hızına etkisinin sistemdeki başlangıç amonyum azotu konsantrasyonuna bağlı olduğu bulunmuştur. 60 ve 80 mg/l başlangıç amonyum azotu konsantrasyonlarında altı değerlikli kromun tüm denenen konsantrasyonlarında inhibisyon etkisi yaptığı bulunmuştur. 60 mg/l başlangıç amonyum azotu konsantrasyonunda ve 21, 54 ve 102 mg/l altı değerlikli krom konsantrasyonlarında inhibisyon sırasıyla %12, %27 ve %42 olmuştur.

Benzer şekilde 80 mg/l başlangıç amonyum azotu konsantrasyonunda ve 31, 66 ve 90 mg/l altı değerlikli krom konsantrasyonlarında inhibisyon sırasıyla %24, %28 ve %31 bulunmuştur.

120 mg/l başlangıç amonyum azotu konsantrasyonu ile yapılan deneylerde, altı değerlikli krom konsantrasyonu ve bulk solusyonun ortalama sıcaklığına bağlı olarak amonyum azotu oksidasyon hızının ya arttığı, ya etkilenmediği veya inhibisyona uğradığı bulunmuştur. 19 mg/l altı değerlikli krom konsantrasyonunda ve 12.8 °C ortalama bulk solusyon sıcaklığında amonyum azotu oksidasyon hızı referans hızın %24 üzerinde bulunmuştur. Ancak altı değerlikli krom konsantrasyonu 84 mg/l'ye artırıldığında ve 14°C ortalama bulk

solusyon sıcaklığında amonyum azotu oksidasyon hızı referans hıza göre %2.9 az bulunmuştur. Tekrar altı değerlikli krom konsantrasyonu 125 mg/l'ye artırıldığında ve ortalama bulk solusyon sıcaklığı 15°C iken, amonyum azotu oksidasyon hızının referans hıza göre %24 inhibisyona uğradığı bulunmuştur. Buradan da altı değerlikli kromun da nitrifikasyon prosesine etkisinin başlangıç amonyum azotu konsantrasyonuna bağlı olduğu ve başlangıç amonyum azotu konsantrasyonu arttıkça inhibisyon etkisinin azaldığı sonucuna varılmıştır.

Deneysel çalışmalarda elde edilen amonyum azotu, nitrit azotu ve nitrat azotu sonuçları incelendiğinde ise bulk solusyondaki bakiye amonyum azotu konsantrasyonu 5-10 mg>/l mertebesine ulaştığında nitrit azotu konsantrasyonunun hızla azaldığı, buna karşılık nitrit azotu konsantrasyonunun ise hızla arttığı bulunmuştur.



CHAPTER 1. INTRODUCTION

1.1. General

Fixed-film biological (biofilm) reactors are becoming more common in the treatment of municipal and industrial wastewaters. Recently, interest has grown in the application of fixed-film systems in the treatment of toxic and hazardous wastes. The high biomass concentration and mass transfer resistance from the bulk solution into the biofilm make fixed-film biological processes less sensitive to the presence of the toxic and inhibitory materials than dispersed growth systems. Biofilm systems are especially well suited for the treatment of slowly biodegradable compounds due to their high biomass concentration and, with the use of granular activated carbon as a support medium, their ability to immobilize compounds by adsorption for subsequent biodegradation and detoxification (Chang and Rittmann, 1988).

Fixed-film wastewater treatment processes are widely regarded as being more stable than their suspended growth counterparts. This is accredited to two factors. First, mass transfer limitations effectively shield the microorganisms from high concentrations of toxins or inhibitors during short term shock loads. Concentrations in biofilms change more slowly than those in the bulk solution, allowing for instance, a shock load of a refractory or recalcitrant toxic compound to pass out of the reactor before its impacts are fully realized. Second, since the microorganisms are physically retained in the reactor, washout is prevented if the organisms growth rate is reduced (Chang and Rittmann, 1988).

A considerable body of knowledge now exists about the effects of various environmental factors such as temperature, pH-alkalinity, and dissolved oxygen concentration on the kinetics of nitrification. Like all other biological processes, nitrification systems have been found to be critically sensitive to the presence of toxic compounds including some heavy metals and organic compounds (Beg et al, 1982; Huang and Skeikhdeslami, 1982; Ibrahim, 1988). However, little general information about the mechanism of their influence is available. Because of the presence of various toxic compounds, the waste may not be readily amenable to conventional biological processes that are commonly used for treatment of any of the industrial wastewaters.

The process effluents from fertilizer plants may contain inorganic compounds of arsenic, fluoride and chromium in addition to ammonia and urea which are usually present. For the normal operations of a fertilizer plant, the reported concentrations of fluoride, arsenic, and chromium in the plant effluents are in the range of 0 to 200, 0 to 20, and 0 to 10 mg/l respectively. It is likely that these compounds may also interfere with the biological process of nitrification. They may enter the system either continuously at fixed concentration from a permanent source or as shock dosages due to leakage or spills (Beg et al, 1980; Beg et al, 1982; Beg and Atiquillah, 1983; Beg and Hassan, 1987).

1.2. Scope of Study

In this study, the effect of fluoride and hexavalent chromium on biological nitrification in Rotating Biological Contactor (RBC) was studied under shock loading conditions. This condition is analogous to a practical situation in which -inadvertently or otherwise- a shock load of toxicant enters an active biological waste treatment process. However, it may be noted that the effect of the same toxicant over a long period of time in a biological waste treatment process may not be the same as shock-load conditions. This variation is

caused by the fact that the microorganisms in a biological waste treatment system may become acclimatized to some toxic compounds by developing a population of heterotrophs capable of metabolizing the agent, or by adapting the nitrifiers to the agent.



CHAPTER 2. LITERATURE REVIEW

2.1. Sources of Nitrogenous Wastes

Nitrogenous materials may enter the aquatic environment from either natural or man-caused sources. Further, the quantities from natural sources are often increased by man's activity. For example, while some nitrogen may be expected in rainfall, the combustion of fossil fuels or the application of liquid ammonia agricultural fertilizers with subsequent release to the air through volatilization can increase rainfall concentrations of nitrogen substantially. It has an appreciation of the quantities of nitrogen which may be expected from each.

Although the source of nitrogen causing a specific pollution problem is often obvious, difficulty may be encountered in determining which of several possible sources is most important. As an example, if a stream with excessive aquatic growths due to nitrogen receives effluent from a sewage treatment plant, drainage from fertilized cropland, and runoff from pastures and feedlots, the contribution of nitrogen from the treatment plant may be a small fraction of that from the other two sources. Thus in analyzing a nitrogen pollution problem, care must be taken to ensure that all possible sources are investigated and that the amount to be expected from each is accurately estimated. Once an estimate is made, nitrogen control measures can be oriented toward the more significant sources (EPA, 1975).

2.1.1. Natural Sources

Natural sources of nitrogenous substances include precipitation, dustfall, nonurban runoff, and biological fixation. Amounts from all may be increased in some way by man. It may be quite difficult to determine quantities which might be expected under completely natural conditions.

In order to find levels of nitrogenous substances include precipitation which are as close to natural as possible, it is necessary to take samples far from urban or agricultural areas. Even these values may be suspect, however. The quantities of nitrogen in nonurban runoff from non-fertilized land may be expected to vary greatly, depending on the erosive characteristic of the soil (EPA, 1975).

Nitrogenous pollution of waterways are also arises from natural and adventitious sources. An enormous amount of nitrogen from the air is converted to nitrogen compounds by natural means. This process is called as nitrogen fixation, and natural nitrogen fixation occurring is about double that carried out by the chemical industry. Most natural nitrogen fixation is effected by certain types of microorganisms, although about 15% of natural nitrogen fixation has been attributed to the action of lightning. A very wide variety of bacteria can fix nitrogen, and includes anaerobic as well as aerobic organisms, and certain photosynthetic blue green algae such as the species of Nostoc, Anabaena, Gleotrichia and Calothrix commonly occurring nitrogen fixers (Winkler, 1981; EPA, 1975).

2.1.2. Man-caused Sources

The activities of man may increase quantities of nitrogen added to the aquatic environment from three of the sources discussed above: precipitation, dustfall,

and nonurban runoff. These sources are increased principally by fertilization of agricultural land and the combustion of fossil fuels. Other man-related sources include runoff from urban areas and livestock feedlots, municipal wastewater effluents, and industrial wastewaters.

Nitrogen concentrations in raw municipal wastewaters are well documented. Values generally range from 15 to 50 mg/l, of which 60% is ammonia-nitrogen, 40% is organic nitrogen, and a negligible amount (one percent) is nitrite- and nitrate-nitrogen. Unless wastewater treatment facilities are designed to remove nitrogen specifically, most will pass through the treatment works to the receiving waters or land disposal sites.

Nitrogen discharged into individual septic tank systems can also create pollution problems. In a well-operating septic tank system, most of the nitrogen leaving the tank will be converted to nitrate in the leaching field. This may then percolate downward to a groundwater table. Problems from high nitrate concentrations occasionally occur when septic tank waste disposal is located near shallow wells used for water supply, particularly on the fringes of urban areas where the population density may be fairly high.

Feedlot runoff constitutes a source of nitrogen which has become significant as a result of the increased number of concentrated, centralized feedlots. Ammonium is a major constituents of feedlot waste as a result of urea hydrolysis. Ammonia-nitrogen concentrations may reach 300 mg/l, and organic nitrogen concentrations of up to 600 mg/l have been reported. While the majority of the animals are apparently still raised on small farms, the trend toward feedlot operations is continuing, and unless steps are taken to prevent drainage and runoff, serious localized problems can occur (EPA, 1975).

The principal sources of organic nitrogen are domestic wastes. Animal slurry from intensive farming operations and high protein wastes from certain food processing operations. Organic nitrogen is converted by heterotrophs to ammonia. Domestic wastewater is weak compared with wastewaters from biological industries as a result of dilution with bath water, lavatory flushes and so on (Winkler, 1981).

Urban runoff can contribute significant quantities of nitrogen to receiving waters during and after periods of precipitation. Sanitary or combined sewer overflows can also add to the nitrogen load (EPA, 1975).

The use of artificial fertilizers has increased the nitrogen concentrations which can be expected in nonurban runoff. Subsurface irrigation drainage from fertilizer cropland can contain high concentrations of nitrates.

In the same way that increased nitrogen concentrations in nonurban runoff and subsurface drainage have been caused by man's activities, increased nitrogen levels in precipitation and dustfall have also resulted. Most atmospheric nitrogen (other than nitrogen gas), however, is associated with soil picked up by the wind and can be returned to earth by gravitational settling (dry fallout) or in precipitation.

The most significant sources of nitrogenous wastes are those sections of the chemical industry manufacturing and using nitrogen compounds, and biological sources such as human, animal and food processing wastes (Winkler, 1981; Adams and Eckenfelder, 1977).

Ammonia and nitric acid are the key industrial chemicals, and the fertilizer industry in particular involves the manufacture of ammonia, nitric acid, ammonium nitrate, ammonium sulphate and urea. These are all likely to enter

wastewater streams as a result of spillages, vessel washout and scrubber blowdown.

The explosives industry also manufactures ammonium nitrate and uses nitric acid as a principal reagent for nitration of various metals such as cotton linters for nitrocellulose, toluene for TNT and glycerine for nitroglycerine and dynamite. Nitric acid is also used in the metal finishing industries for the metal pickling and de-scaling, and in the manufacture of the inorganic pesticide lead arsenate (Winkler, 1981)

Another significant source of ammonia is the coal carbonization process, in which coke is produced from coal. Coke is used in the manufacture of steel, and the carbonization process also yields ammonia and a number of valuable organic materials. With the increasing cost and eventual exhaustion of oil and natural gas supplies, it is likely that a significant proportion of the chemical industry will become or return to being, based on coal as a source of organic raw materials usually involves carbonization, an already large source of nitrogenous wastewater is likely to become even more significant in the future (Winkler, 1981).

The Solvay process for sodium carbonate manufacture is a key chemical process and uses ammonia as an intermediate reagent, thus giving rise to an ammonia containing wastewater stream.

Other sources of ammonia containing wastes are refrigeration plants and industries using ammonia in scouring and cleaning operations (Winkler, 1981).

Semiconductor manufacturing and other industries such as munitions, petroleum refining, meat and milk processing, and synthetic fiber production generate waste streams that contain high concentrations of nitrogenous

compounds (Collins et al, 1988).

2.2. Fertilizer Industry Wastewaters

Because of the expanding need for food production, the fertilizer industry is showing tremendous growth (Beg et al, 1982). Therefore, fertilizer industry presently ranks as one of the largest industries in the world (Beg et al, 1980).

A fertilizer industry produces mainly either the nitrogenous or the phosphatic fertilizers. Some produce both and also the complex fertilizers such as ammonium sulphate and the diammonium sulphate. It is difficult to define the volumes and the compositions of various wastewater streams from a fertilizer plant because of variations in the manufacturing process and the operational philosophies of different plants. In addition, a large fraction of the total wastewater discharges is due to the process spills, which are extremely irregular in frequency and size. An overview of the concentrations of the different nitrogen contaminants in the process waste streams from the nitrogenous fertilizer plants in the U.S. is shown in Table 2.1 (Beg et al, 1980). Further, the wastes produced are related to the type of fertilizer being manufactured. Table 2.2 shows the characteristics of process effluents from various sections of a typical complex fertilizer plant (Beg et al, 1980).

The process effluents from fertilizer plants may contain inorganic compounds of arsenic, fluoride and chromium in addition to ammonia and urea which are usually present. For the normal operations of a fertilizer plant, the reported concentrations of fluoride, arsenic, and chromium in the plant effluents are in the range of 0 to 200, 0 to 20, and 0 to 10 mg/l respectively. It is likely that these compounds may also interfere with the biological process of nitrification. They may enter the system either continuously at fixed concentration from a permanent source or as shock dosages due to leakage or spills (Beg et al,

1980; Beg et al, 1982; Beg and Atiqullah, 1983; Beg and Hassan, 1987).

Table 2.1. Nitrogen Compounds in Process Waste Streams and Wastewater Volume from Nitrogen Fertilizer Plants in the U.S.(Beg et al, 1980).

Contaminant	NH ₃ Plant	NH ₄ NO ₃ Plant	(NH ₄) ₂ SO ₄ Plant	Urea Plant
NH ₃ (mg/l)	20-100	200-2000	10-10000	200-4000
NO ₃ ⁻ (mg/l)	-	50-1000	-	-
Urea (mg/l)	-	-	-	50-1000
Volume (l/ton of product)	400-4000	200-4500	400-40000	800-15000

2.3. Effects of Nitrogen Discharge

Nitrogenous compounds discharged from wastewater treatment facilities can have deleterious effects. These effects include biostimulation of surface waters, toxicity to fish life, reduction of chlorine disinfection efficiency, an increase in the dissolved oxygen depletion in receiving waters, adverse public health effects- principally in groundwater, and a reduction in the suitability for reuse.

2.3.1. Biostimulation of Surface Waters:

A major problem in the field of water pollution is eutrophication, excessive plant growth and/or algae blooms resulting from over fertilization of rivers, lakes and eustuaries. Results of eutrophication include deterioration in the

Table 2.2. Characteristics of Process Effluents from Various Sections of a Typical Complex Fertilizer Plant (Beg et al, 1980).

Characteristics	Ammonia Plant				Urea Plant	Ammonium Sulphate Plant	Phosphoric Acid Plant	Diammonium Phosphate Plant
	Reboiler Vetro-Coke	Reboiler MEA	Compressor House	Ammonia Rectification Unit				
pH	8.5	8.0	7.3	9.3	8.3	8.4	4.9	7.4
Free Ammonia (mg/l)	-	-	-	12	524	31	-	12
Fixed Ammonia (mg/l)	-	-	-	385	1785	144	-	26
Total Ammonia Nitrogen (mg/l)	-	-	-	397	2309	175	-	38
Phosphate (PO ₄)(mg/l)	-	-	-	-	-	-	1800	-
Fluoride (F)(mg/l)	-	-	-	-	-	-	200	-
Arsenic (As ₂ O ₇)(mg/l)	20	2.5	-	-	-	-	-	-
Oil (mg/l)	-	-	1040	-	-	-	-	-

appearance of previously clear waters, odor problems from decomposing algae, and a lower dissolved oxygen level which can adversely affect fish life.

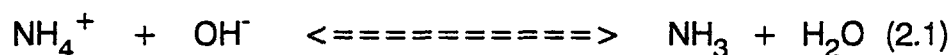
Four basic factors are required for algal growth: nitrogen, phosphorus, carbon dioxide, and light energy. The absence of any one will limit growth. In special cases, trace micronutrients such as cobalt, iron, molybdenum and manganese may be limiting factors under natural conditions (EPA, 1975). Nitrogen in the fixed forms of ammonium and nitrate ions is considered to be one of the major nutrients supporting blooms of green and non-nitrogen fixing blue-green algae (Wild et al,1971; McHarness et al, 1975; Tsai et al, 1981).

Eutrophication is of most concern in lakes because nutrients which enter tend to be recycled within the lake and build up over a period of time. A river, by contrast, is a flowing system. Nutrients are always entering or leaving any given section. Accumulations tend to occur in sediment or in slack water, and the effects of these accumulations are normally moderated by periodic flushing of floods (EPA,1975).

In estuaries and oceans, nitrogen compounds are often present in very low concentrations and may limit the total biomass and the types of species it contains. Thus upwelling, which brings nutrient rich waters to the surface, may result in periodic blooms of algae or other aquatic life. While in some eustuaries discharges from wastewater treatment plants may increase nitrogen concentrations to the level where blooms occur, the high dilution provided by a direct ocean discharge probably eliminates the danger of algae blooms caused by such discharges (EPA, 1975).

2.3.2. Toxicity:

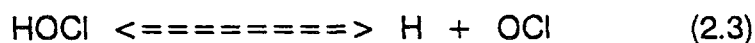
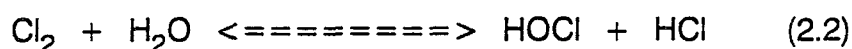
The principal toxicity problem is from ammonia in the molecular form (NH_3) which can adversely affect fish life in receiving waters. A slight increase in pH may cause a great increase in toxicity as the ammonium ion (NH_4) is transformed to ammonia in accordance with the following equation.



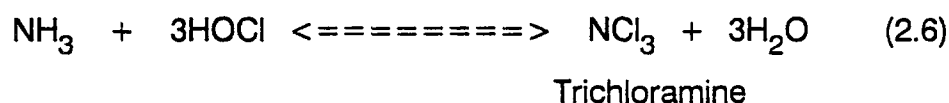
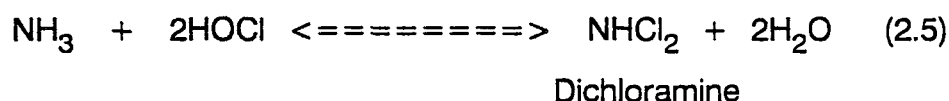
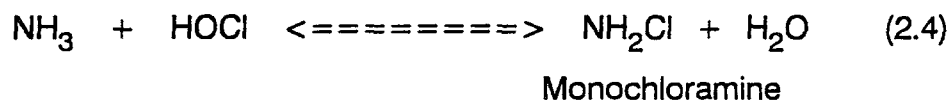
Factors which may increase ammonia toxicity at a given pH are: greater concentrations of dissolved oxygen and carbon dioxide; elevated temperatures; and bicarbonate alkalinity. Reported levels at which acute toxicity is detectable have ranged from 0.01 mg/l to over 2 mg/l of molecular ammonia-nitrogen (EPA, 1975). Sawyer and McCarty (1978) concluded that NH_3 toxicity would not be a problem in receiving waters with pH below 8 and NH_3 -N concentrations less than 1 mg/l.

2.3.3. Effect on Disinfection Efficiency:

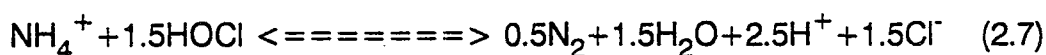
Ammonia reduces the effectiveness of chlorination, which is widely used as a final stage of water treatment to remove traces of organic material, including microorganism. The disinfective activity in chlorination results from the unionized hypochlorous acid, HClO , formed by the reaction of chlorine with water, and to a much lesser extent from the hypochlorite ions, OCl ;



Hypochlorous acid reacts with ammonia to form chloramines, which are much less effective as disinfectants. For example, to produce the same kill rate of the bacterium *Escherichia Coli*; about forty times as much monochloramine is required as is free chlorine.



Ammonia can thus be said to exert a chlorine demand on a chlorination process, which for complete removal of ammonia-nitrogen can be seen from equation below to be stoichiometrically 1.5 to 1 on a molar basis, chlorine to ammonia, or 7.6 to 1 on a molar basis, chlorine to ammonia nitrogen. This demand has to be overcome before residual free chlorine as hypochlorous acid becomes available for disinfection.



In addition, while the main breakdown product is nitrogen gas, undesirable byproducts can be formed, such as nitrogen trichloride (trichloramine) at low pH levels, or nitrate at high pH levels and when the chlorine dose required is high, production of trihalomethanes and organochlorine compounds is significant (Metcalf and Eddy, 1982; Winkler, 1981).

2.3.4. Dissolved Oxygen Depletion in Receiving Waters:

Ammonium can be biologically oxidized to nitrite and to nitrate in receiving waters and thereby add to the oxygen demand imparted by carbonaceous materials. If either conventional biological treatment or physical-chemical treatment is utilized to provide 90% BOD₅ removal, an effluent will be discharged which still contains over 100 mg/l of oxygen demand. This high level of oxygen demand may cause significant oxygen depletion in the receiving water if insufficient dilution is available. Nitrification (or ammonia nitrogen removal) will reduce the total oxygen demand of the effluent to less than 40 mg/l (EPA, 1975).

2.3.5. Public Health:

The public health hazard from nitrogen is associated with the nitrate form and is limited principally to groundwater where high concentrations can occur. Nitrate in drinking water was first associated in 1945 with methemoglobinemia, a sometimes fatal blood disorder which affects infants less than three months old. When water high in nitrate is used for preparing infant formulas, nitrate is reduced to nitrite in the stomach after ingestion. The nitrites react with hemoglobin in the blood to form methemoglobin, which is incapable of carrying oxygen. The result is suffocation accompanied by a bluish tinge to the skin, which accounts for the use of the term blue babies in conjunction with methemoglobinemia. In suspect areas water should be analyzed for both nitrite and nitrate since either form will cause methemoglobinemia (EPA, 1975). Additionally, it has been stated that high nitrate concentrations in drinking water causes cardiac problems in adults (Shin and Polprasert, 1988). Therefore, the removal of nitrogen compounds from wastewater prior to discharging into water courses is important.

2.3.6. Water Reuse:

While direct wastewater reuse for domestic water supply is not a reality because of public health considerations, plans for industrial reuse are being carried out in several areas. When reclaiming wastewater for industrial purposes, ammonia may need to be removed in order to prevent corrosion. Further, nitrogen compounds can cause biostimulation in cooling towers and distribution structures (EPA, 1975).

2.4. Methods Currently Used for Removal of Ammonia from Wastewaters

Several biological and physical-chemical methods are currently available for removal of ammonia nitrogen from wastewaters. Most feasible among them are biological nitrification, selective ion exchange, break-point chlorination and ammonia stripping. (Tsai et al, 1981).

In determining which method is most suitable for a particular application, consideration must be given to six principal aspects:

1. form and concentration of nitrogen compounds in the process influent,
2. required effluent quality,
3. other treatment processes to be employed,
4. cost,
5. reliability, and
6. flexibility.

Great care must be taken in developing and evaluating alternatives.

Presented below are the brief descriptions of the processes employed in wastewater treatment facilities which, to varying degrees, remove ammonia-nitrogen from the waste stream. Process characteristics, compound

selectivity, and normal range of efficiency are presented (EPA, 1975).

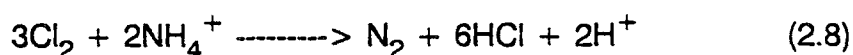
2.4.1. Biological Nitrification

Biological nitrification does not increase the removal of nitrogen from the waste stream over that achieved by conventional biological treatment. The principal effect of nitrification treatment process is to transform ammonia-nitrogen to nitrate. The nitrified effluent can be denitrified biologically. Overall removal efficiency in a nitrification- denitrification plant can range from 70 to 95 %.

Nitrification is also used without subsequent biological denitrification when treatment requirements call for oxidation of ammonia nitrogen. Oxidation of ammonium can be as high as 98%. Overall transformation to nitrate depends on the extent to which organic nitrogen is transformed to ammonia-nitrogen in the secondary stage or is removed by another process. Nitrification can be carried out in conjunction with secondary treatment or in a tertiary stage; in both cases, either suspended growth reactors (activated sludge) or attached growth reactors (such as trickling filters) can be used (EPA, 1975).

2.4.2. Breakpoint Chlorination

Breakpoint chlorination (or superchlorination) is accomplished by the addition of chlorine to the waste stream in an amount sufficient to oxidize ammonia-nitrogen to nitrogen gas. After sufficient chlorine is added to oxidize the organic matter and readily oxidizable substances present, a stepwise reaction of chlorine with ammonium takes place. The overall theoretical reaction is as follows:



In practice, approximately 10 mg/l of chlorine is required for every 1 mg/l of ammonia-nitrogen. In addition, acidity produced by the reaction must be neutralized by the addition of caustic soda or lime. These chemicals add greatly to the total dissolved solids and result in a substantial operating expense. Often dechlorination is utilized following breakpoint chlorination in order to reduce the toxicity of the chlorine residual in the effluent.

An important advantage of this method is that ammonia-nitrogen concentrations can be reduced to near zero in the effluent. Nitrite and nitrate are not removed by this method (EPA,1975).

2.4.3. Selective Ion Exchange:

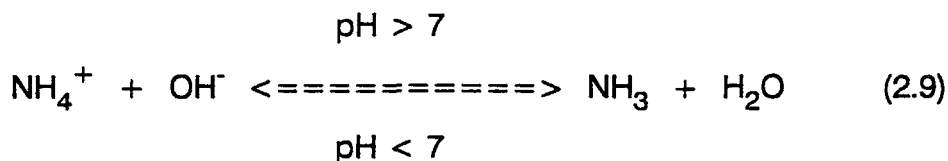
Selective ion exchange for removal of ammonium from wastewater can be accomplished by passing the wastewater through a column of clinoptilolite, a naturally occurring zeolite which has a high selectivity. Regeneration of the clinoptilolite is undertaken when all the exchange sites are utilized and breakthrough occurs.

Filtration prior to ion exchange is usually required to prevent fouling of the zeolite. Ammonium removals of 90-95% can be expected. Nitrite, nitrate, and organic nitrogen are not affected by this process (EPA, 1975).

2.4.4. Ammonia Stripping Process:

For high strength ammonia wastes, with ammonia nitrogen concentrations greater than 1000 mg/l, ammonia stripping is a viable process because of its high removal efficiency and competitive cost (Tsai et al, 1981).

In the ammonia stripping process, caustic soda or lime is added to the wastewater to raise its pH to above 7. This alkaline pH favors the conversion of ammonium ions to free ammonia according to the following equation:



At a pH of 11 and a temperature of 20°C, approximately 95% of ammonia nitrogen will be in the form of free ammonia. The free ammonia produced may then be stripped by allowing wastewater droplets to contact with large volumes of air or steam either by circulation through a packed tower or by agitation in a holding pond. Under temperate wheather conditions in an air stripping process, removal approaching 90% may be achieved using packed towers. If a high degree of phosphorus removal is also required, this process offers the advantage of combining the removal of two nutrients (i.e., nitrogen and phosphorus) into one system with lower space requirements operating costs than required for separate removal of each. This is because the lime addition will precipitate phosphorus in the wastewater at approximately the same optimum pH for ammonia stripping.

However, the air ammonia stripping process is not without shortcomings. Removal efficiencies decrease to about 75% when ambient temperatures fall to 10°C, and complete shut down of stripping towers is forced when temperatures drop below freezing. In addition, the sludge produced from caustic or lime addition presents a serious disposal problem, and calcium carbonate scale must be periodically cleaned from the tower packing material. Because of these problems associated with air ammonia stripping, the steam stripping process is considered to be a more feasible approach for the handling of high strength ammonia wastes such as those from fertilizer

manufacturing plants, coal-conversion plants and chemical plants. The low temperature problem can be eliminated if steam is available at the industrial plant for ammonia stripping uses (Tsai et al, 1981).

2.5. Nitrification

The oxidation of nitrogen from the -III to the +V oxidation state through chemical combination with oxygen is termed nitrification. Under the physicochemical conditions commonly found in well-aerated natural and domestic-wastewaters, nitrification occurs at a detectable rate only in the presence of certain chemoautotrophic and heterotrophic bacteria. The bulk of oxidation is carried out by nitrifying chemoautotrophs belonging to two separate groups: the first oxidizing N(-III) to N(+III); the second oxidizing N(+III) to N(+V). The species *Nitrosomonas Europea*, oxidizing ammonia-nitrogen(-III) to nitrite-nitrogen(+III), dominates the first group; whereas, *Nitrobacter Winogradski*, oxidizing nitrite-nitrogen(III) to nitrate-nitrogen(+V), dominates the second (Quinlan, 1984).

The oxidation step mediated by *Nitrosomonas Europea* is thought to be the rate limiting step for nitrification. If so, then the conditions required to optimize the overall rate of nitrification may be assumed equivalent to those required to maximize the rate of ammonia-nitrogen oxidation by *N. Europea*. However such optimization of the first step of nitrification may cause the second step, nitrite-nitrogen oxidation by *Nitrobacter*, to become rate limiting. This situation could arise if the optimum pH of the second step were substantially different from that of the first. In this case optimizing the first step would not optimize the rate of nitrification (Quinlan, 1984).

Oxidation of ammonia to nitrates simply converts dissolved oxygen to a form in which it is still available to prevent development of anaerobic conditions

(Wild et al, 1970).

2.5.1. Main Properties of Nitrifiers:

It has been reported that there are seven genera of autotrophic nitrifiers. Organisms belonging to genera of *Nitrosomonas* and *Nitrobacter* are common in soil and aquatic ecosystems, and undoubtedly are the nitrifiers of importance. The other genera are rarely reported and the validity of some is debatable (Bhargava, 1989).

Nitrifiers are very special organisms, the population of which is minimal in surface waters (Wild et al, 1971). They derive energy requirements of growth and cellular metabolism from the energy released by the oxidation of an inorganic nitrogen substrate. The source of carbon used for growth is obtained from carbon dioxide or bicarbonate (Sutton et al, 1979; Bhattacharyya and Middleton, 1980).

The generation time of nitrifying organisms is approximately 30 h which is much longer than that of the heterotrophs (Bhargava, 1989).

Nitrifiers are very sensitive to environmental conditions as well as growth inhibitors, such as toxic wastes and heavy metals, halogenated compounds, phenols, mercaptans, guanidines and thiourea (Adams and Eckenfelder, 1977). Nitrification is inhibited by 2-chloro-6-(trichloromethyl)-pyridine (TCMP) in the BOD test (Washington et al, 1983). Growth rates and thus nitrification rates, are profoundly influenced by such environmental factors as pH, temperature, and dissolved oxygen (D.O.) concentrations. Since nitrifiers are autotrophic, inorganic carbon sources, such as carbon dioxide, carbonates, and bicarbonate, and subsequently alkalinity have a large influence on microbial growth rates. The mineral requirements of the autotrophic nitrifiers

include calcium, magnesium, phosphorus, copper and iron (Adams and Eckenfelder, 1977).

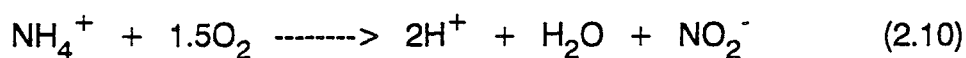
Nitrifying organisms are extremely sensitive to certain organic and inorganic constituents which may be present in industrial waste streams, thereby requiring much longer detention times (or sludge ages) with one waste as compared to another to attain the same degree of nitrification (Adams and Eckenfelder, 1977).

The soluble biodegradable carbon in the raw wastewater tends to suppress the simultaneous oxidation of ammonia. This means that nitrification must be performed under conditions where the amount of easily degradable soluble carbon is small (Henze, 1984; Parker and Richards, 1986).

On a biochemical level, the nitrification process is more complex than simply the sequential oxidation of ammonia to nitrite by *Nitrosomonas* and the subsequent oxidation of nitrite to nitrate by *Nitrobacter*. Various reaction intermediates and enzymes are involved. More important than an understanding of these pathways is knowledge of the response of nitrification organisms to environmental conditions.

2.5.2. Energy and Synthesis Relationships:

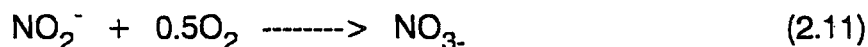
The stoichiometric reaction for oxidation of ammonium to nitrite by *Nitrosomonas* is:



The loss of energy by this reaction at physiological concentrations of the reactants has been estimated to be between 58 and 84 kcal per mole of

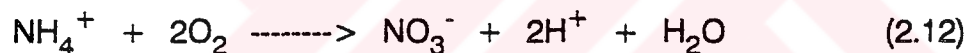
ammonia.

The reaction for oxidation of nitrite to nitrate by Nitrobacter is:

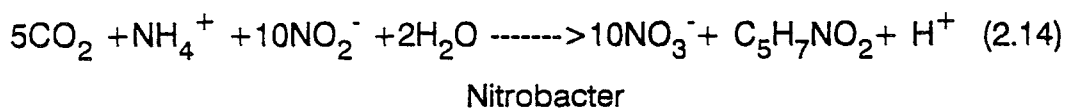
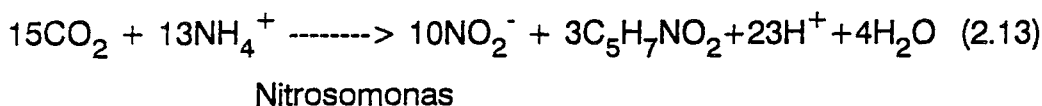


This reaction has been estimated to release between 15.4 to 20.9 kcal per mole of nitrite. Thus, Nitrosomonas obtains more energy per mole of nitrogen oxidized than Nitrobacter. If it is assumed that the cell synthesis per unit of energy produced is equal, there should be greater mass of Nitrosomonas formed than Nitrobacter per mole of nitrogen oxidized. As will be seen, this is in fact the case.

The overall oxidation of ammonium by both groups is obtained by adding Equations 2.10 and 2.11:



As previously mentioned, these reactions furnish the energy required for growth of the nitrifying organisms. Assuming that the empirical formulation of bacterial cells is $\text{C}_5\text{H}_7\text{NO}_2$, the equations for the growth of Nitrosomonas and Nitrobacter are shown in Equations 2.13 and 2.14, respectively:



Equations 2.10, 2.13 and 2.14 have terms showing the production of free acid (H^+) and the consumption of gaseous carbon dioxide (CO_2). In actual fact, these reactions take place in aqueous systems in the context of the carbonic acid system. These reactions usually take place at pH levels less than 8.3. Under this circumstance, the production of acid results in immediate reaction with bicarbonate ion (HCO_3^-) with the production of carbonic acid (H_2CO_3). The consumption of carbon dioxide by the organisms results in some depletion of the dissolved form of carbon dioxide, carbonic acid (H_2CO_3). Table 2.3 presents the modified forms of Equations 2.10 to 2.14 to reflect the changes in the carbonic acid system. As will be later described, the variations occurring in pH resulting from changes in the carbonic acid system can significantly affect nitrification process performance.

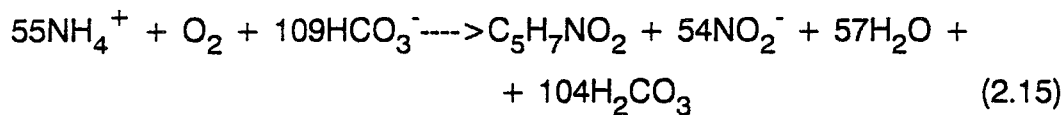
The equations for energy yielding reactions (Equations 2.10 and 2.11) can be combined with the equations for organism synthesis (Equations 2.13 and 2.14) to form overall synthesis-oxidation relations by knowledge of the yield coefficients for the nitrifying organisms. Experimental yield values for *Nitrosomonas* range from 0.04 to 0.13 g VSS grown per g ammonia nitrogen oxidized. Experimental yields for *Nitrobacter* are in the range from 0.02 to 0.07 g VSS grown per g of nitrite nitrogen oxidized. Values based on thermodynamic theory are 0.29 and 0.084 for *Nitrosomonas* and *Nitrobacter*, respectively. The experimentally based yield may be lower than theoretical values due to the diversion of a portion of the free energy released by oxidation to microorganism maintenance functions.

Table 2.3. Relationship for oxidation and growth in nitrification reactions in relationship to the carbonic acid system (EPA, 1975).

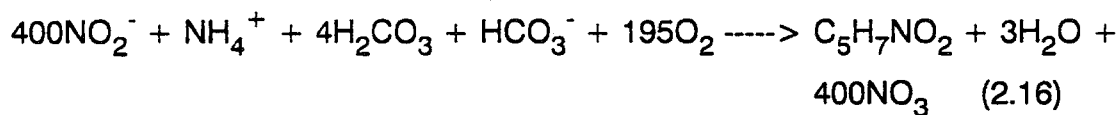
Reaction	Equation	Eq.No:
Oxidation- Nitrosomonas	$\text{NH}_4^+ + 1.5\text{O}_2 + 2\text{HCO}_3^- \text{-----} > \text{NO}_2^- + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$	2.10A
Oxidation- Nitrobacter	$\text{NO}_2^- + 0.5\text{O}_2 \text{-----} > \text{NO}_3^-$	2.11
Oxidation- Overall	$\text{NH}_4^+ + 2\text{O}_2 + 2\text{HCO}_3^- \text{-----} > \text{NO}_3^- + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$	2.12A
Synthesis- Nitrosomonas	$13\text{NH}_4^+ + 23\text{HCO}_3^- \text{-----} > 8\text{H}_2\text{CO}_3 + 10\text{NO}_2^- + 3\text{C}_5\text{H}_7\text{NO}_2 + 19\text{H}_2\text{O}$	2.13A
Synthesis- Nitrobacter	$\text{NH}_4^+ \text{NO}_2^- + 4\text{H}_2\text{CO}_3 + \text{HCO}_3^- \text{---} > 10\text{NO}_3^- + 3\text{H}_2\text{O} + \text{C}_5\text{H}_7\text{NO}_2$	2.14A

Equations for synthesis- oxidation using representative measurements of yields and oxygen consumption for Nitrosomonas and Nitrobacter are as follows:

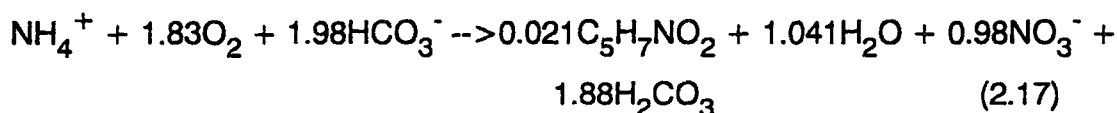
Nitrosomonas



Nitrobacter



Using Equations 15 and 16, the overall synthesis and oxidation reaction is:



In these equations yields for *Nitrosomonas* and *Nitrobacter* are 0.15 mg cells/mg NH_4^+ -N and 0.02 mg cells/mg NO_2^- -N, respectively. On this basis, the removal of twenty mg/l of ammonia nitrogen would yield only 1.8 mg/l of nitrifying organisms. Oxygen consumption ratios in the equations are 3.22 mg O_2 /mg NH_4^+ -N oxidized and 1.11 mg O_2 /mg NO_2^- -N oxidized, which is in agreement with measured values (EPA, 1975).

2.5.3. Alkalinity and pH Relationships:

Equation 2.12A (Table 2.3) shows that alkalinity is destroyed by the oxidation of ammonia and carbon dioxide (H_2CO_3 in the aqueous phase) is produced. When synthesis is neglected, it can be concluded that 7.14 mg of alkalinity as CaCO_3 is destroyed per mg of ammonia nitrogen oxidized. The effect of synthesis is relatively small; in Equation 2.17, the ratio is 7.07 mg of alkalinity per mg of ammonia nitrogen oxidized.

These changes may have a depressing effect on pH in the nitrification system, as the relationship for pH in the system is:

$$\text{pH} = \text{p}K_1 - \frac{(\text{H}_2\text{CO}_3)}{(\text{HCO}_3^-)} \quad (2.18)$$

Since nitrification reduces the HCO_3^- level and increases the H_2CO_3 level, it is obvious that the pH would tend to be reduced. The effect is mediated by stripping of carbon dioxide from the liquid by the process of aeration and the

pH is elevated upwards. If the carbon dioxide is not stripped from the liquid, such as in enclosed high purity oxygen systems, the pH can be depressed as low as 6.0. It has been calculated that to maintain the pH greater than 6.0 in an enclosed system, the alkalinity of the wastewater must be 10 times greater than the amount of ammonia nitrified.

Even in open systems where the carbon dioxide is continually stripped from the liquid, severe pH depression can occur when the alkalinity in the wastewater approaches depletion by the acid produced in the nitrification process. For example, if in a wastewater 20 mg/l of ammonia nitrogen is nitrified, 143 mg/l of alkalinity as CaCO_3 will be destroyed. In many wastewaters there is insufficient alkalinity initially present to leave a sufficient residual for buffering the wastewater during the nitrification process. The significance of pH depression in the process is that nitrification rates are rapidly depressed as the pH is reduced below 7.0 (EPA, 1975).

2.5.4. Oxygen Requirements:

The theoretical oxygen requirement for nitrification, neglecting synthesis, is 4.57 mg O_2 /mg NH_4^+ -N (Equation 2.12). Synthesis has an effect on oxygen requirements; the oxygen requirement is calculated to be, from Equation 17, 4.19 mg O_2 /mg NH_4^+ -N. An oxygen requirement sufficiently accurate to be used in engineering calculations for aeration requirements is 4.6 mg/mg NH_4 -N (EPA, 1975).

2.5.5. Kinetics:

Different rate expressions have been proposed and experimentally determined for biological nitrification process which include zero-order, first-order and Michaelis-Menten kinetics. A comprehensive review has been presented.

For zero-order kinetics, the reaction rate is independent of substrate concentration and is given as:

$$-\frac{dS}{dt} = K_0 \quad (2.19)$$

where (dS/dt) is the rate of depletion of substrate due to oxidation and K_0 is the zero-order rate constant. With initial condition $S=S_0$ at $t=0$, the solution of equation (2.19) gives:

$$S = S_0 - K_0 t \quad (2.20)$$

For first-order kinetics, the reaction rate is proportional to the first power of reactant concentration,

$$-\frac{dS}{dt} = K_1 S \quad (2.21)$$

where K_1 is first order rate constant. For $S=S_0$ at $t = 0$, the solution of equation (2.21) given as:

$$S = S_0 \exp(-K_1 t) . \quad (2.22)$$

The Michaelis-Menten model model is one of the most widely used expressions in the wastewater treatment processes, which may be expressed as:

$$\alpha_o = -\frac{dS}{dt} = V_{\max} \left(\frac{S}{K_s + S} \right) \quad (2.23)$$

where $V_{\max}$ is the maximum ammonia oxidation rate constant and K_s is the Michaelis constant. It follows from the above equation that for low concentration of substrate or when $S \ll K_s$, equation (2.22) reduces to first order expression. However, for higher substrate concentration or when $S \gg K_s$, it becomes a zero order expression.

Equation (2.23) may be rearranged as:

$$\frac{1}{a_o} = \frac{1}{V_{\max}} + \frac{K_s}{V_{\max}S} \quad (2.24)$$

Therefore, according to equation (2.24), a plot of $(1/a_o)$ vs $(1/S)$ gives a straight line relationship from which the kinetic parameters $V_{\max}$ and K_s can be evaluated (Beg and Hassan, 1987).

The saturation coefficient K_s for nitrification has been reported in the range of 0.2 to 0.4 mg/l, an amount that is much less than the concentration of ammonium usually encountered in the nitrification process. Further, it has been shown that the nitrifiers work at a maximum efficiency at all times independent of residual substrate concentration of ammonium nitrogen (Beg et al, 1982).

2.5.6. Classical Inhibition Mechanisms

The degree of inhibition is related to the velocities of the inhibited reaction and uninhibited reaction by

$$i = 1 - \frac{\alpha_i}{\alpha_o} \quad (2.25)$$

where

i = degree of inhibition

α_o = velocity of the uninhibited reaction

α_i = velocity of the inhibited reaction

In biological systems, three different kinds of inhibition mechanisms with respect to substrate concentration have been observed. These three mechanisms of inhibition are categorized as noncompetitive, competitive, and anticompetitive inhibition (Beg et al, 1982; Oslislo and Lewandowski, 1985;

(Greenfield and Neufeld, 1981).

Noncompetitive inhibition. The degree of inhibition is unaffected by the concentration of substrate. This model leads to the rate equation of the following form:

$$\alpha_i = \frac{V_{\max} S}{(K_s + S) \left[1 + \left(\frac{I}{K_i} \right) \right]} \quad (2.26)$$

where K_i = inhibitor coefficient and gives the indication of the strength of the inhibitor.

Competitive inhibition. The degree of inhibition depends upon the concentration of the substrate present. Usually, the degree of inhibition is reduced as the substrate concentration is increased. This model leads to the rate equation of the following form:

$$\alpha_i = \frac{V_{\max} S}{K_s \left[1 + \left(\frac{I}{K_i} \right) \right] + S} \quad (2.27)$$

Anticompetitive inhibition. The degree of inhibition is increased as the substrate concentration is increased. The rate equation for this model is given as

$$\alpha_i = \frac{V_{\max} S}{K_s + \left[1 + \left(\frac{I}{K_i} \right) \right] S} \quad (2.28)$$

(Beg et al, 1982; Beg and Hassan, 1987).

Knowledge of the type of inhibition which a metal exerts on the nitrification process is important to design engineers. A classical competitive inhibitor is

one that has a larger effect at low substrate/inhibitor ratios because it can then compete more effectively with the substrate for a place on the active site of the enzyme. An inhibitor of this type would cause less inhibition in wastewaters containing high concentrations of ammonia; thus, nitrification could still be possible in those wastewaters. On the other hand, with a classical noncompetitive inhibitor, the extent of inhibition is independent of the substrate concentration-that is, independent of ammonia concentration in the wastewaters (Huang and Skeikhdeslami, 1982).

The above expressions may be modified by introducing degree of inhibition i , which is defined as the ratio of the reduction in velocities brought about by an inhibitor to the velocity of inhibited reaction. The corresponding expressions for the degree of inhibition are;

Non-competitive inhibition

$$i = 1 - \frac{1}{K_i + I} \quad (2.29)$$

or

$$\frac{1}{i} = \left(1 + \frac{K_i}{I}\right) \quad (2.30)$$

Competitive inhibition

$$i = \frac{\frac{K_s I}{K_i}}{K_s \left[\left(1 + \frac{I}{K_i}\right) \right] + S} \quad (2.31)$$

or

$$\frac{1}{i} = 1 + \frac{(K_s + S)}{\left(\frac{K_s}{K_i}\right) I} \quad (2.32)$$

Anti-competitive inhibition

$$i = \frac{\frac{S_s I}{K_s}}{K_s + \left[1 + \left(\frac{I}{K_i}\right) S\right]} \quad (2.33)$$

or

$$\frac{1}{i} = \frac{K_s}{K_i} + \frac{(K_s + S)}{\left(\frac{S}{K_s}\right) I} \quad (2.34)$$

The effect of the dimensionless substrate inhibition constant K_i is to decrease the conversion as its value is increased (Hassan and Beg, 1987).

2.6. Nitrification Processes

The biological processes used for nitrification were identified as aerobic suspended growth and aerobic attached growth. A further distinction was made based on whether nitrification is accomplished in the same reactor used for the removal of carbonaceous BOD or in a separate reactor. The BOD_5/TKN ratio can be used as a measure. For BOD_5/TKN ratios between 1 and 3, separate stage nitrification, for BOD_5/TKN ratios greater than 5, combined carbon oxidation-nitrification processes can be used (Metcalf and Eddy, 1982).

2.6.1. Process Selection:

In many cases, the selection of either a separate stage nitrification process or a combined carbon oxidation-nitrification process is governed by the preference of the design engineer. However, each process has certain advantages and disadvantages that should be considered before a selection is made. The use of a combined process is suggested, because sludge production is minimized in this system. This is true, yet the separate stage nitrification process may be desirable in many situations because of the following reasons:

1. This type of the system offers the capability of separate control and optimization of each process.
2. To maximize the nitrogen removal efficiency, a tank geometry conducive to plug flow can be used in the second stage construction without fear of producing a high oxygen demand at the head of the tank.
3. Nitrifying bacteria comprise a much larger fraction of the biomass in the second stage as a result the process is less temperature sensitive.
4. Biodegradable organic materials which may be toxic to nitrifying bacteria are removed in the carbon oxidation stage.
5. A lower residual D.O. concentration may be used in either of the two stages than would be required for the combined processes to ensure that D.O. did not affect maximum specific growth rate of nitrifiers.
6. Operating experience seems to indicate that separate stage nitrification has a greater reliability.
7. When the overall design is controlled by BOD removal kinetics, separate stage nitrification process will require less total aeration tank volume and total oxygen (Benefield and Randall, 1980).

2.6.2. Combined Carbon Oxidation-Nitrification Processes

Nitrification can be accomplished in any of the suspended growth activated sludge processes. All that is required is the maintenance of the conditions suitable for the growth of nitrifying organisms. The two attached growth processes that can be used for combined carbon oxidation nitrification processes are the trickling filter and the rotating biological contactor (Metcalf and Eddy, 1982).

2.6.3. Separate Stage Nitrification Processes

In most details, separate stage suspended growth nitrification processes are similar in design to the activated sludge process. Both continuous flow stirred tank staged flow reactors and plug flow reactors are favored. Three different types of attached growth processes have been used for separate stage nitrification. They are the trickling filter processes, the rotating biological contactor, and the packed bed reactor (Metcalf and Eddy, 1982).

In this research, separate stage nitrification was studied in a Rotating Biological Contactor (RBC) system which is one of the applications of the fixed film biological processes (Figure 3.1 and 3.2).

2.7. Rotating Biological Contactor (RBC) System

The increasing demand for the removal of organic and inorganic pollutants from both domestic and industrial discharges has resulted in a general acceptance of biological wastewater treatment processes, which are both effective and economical. The Rotating Biological Contactor (RBC), a fixed film biological reactor system, has been widely employed as a secondary treatment process, such as activated sludge and trickling filter, for

pretreatment and/or polishing purposes (Wu et al, 1980; Torpey et al, 1971). The possibility of utilizing RBC's was directed to other paths, such as operation in anaerobic conditions where high carbon concentrations were introduced, or as an upgrading plant of the final effluents (Sagy and Kott, 1990).

Although the RBC system is similar to the trickling filter process, the operational parameters, biological growth environment, and substrate utilization taking place on the disc media are different.

In general, RBC system consists of a series of circular plastic discs mounted on a horizontal shaft and rotated perpendicular to the direction of the waste flow. Approximately, 40% of the disc diameter is submerged in a tank and the total disc surface area is almost entirely covered with active biological mass. The rotating movement of the discs causes an intensive contact between the biomass on the discs, the water and the gas phase. The lower portion of each disc extends into the wastewater while the upper portion of the discs rotates in the atmosphere. Thus, a unit area of biological slime is alternately submerged to absorb the nutrients from the wastewater and raised out of the liquid to oxidize the absorbed nutrients as well as maintain dissolved oxygen in the wastewater stream. The formation of new cell mass causes a continuous growth of the biomass. When a certain thickness of the layer on the disc is reached, part of the mass is pushed off due to gravity and the forces caused by rotation. This mass is kept in suspension in the trough and carried along with the effluent in a settling basin (Lehman et al, 1983; Zeevalkink et al, 1979; Bintanja et al, 1976; Wu et al, 1980; Clark et al, 1978; Paolini et al, 1979).

It has been observed that although the exact composition of the microbial population on a disc depends upon the type of wastewater being treated and

the relative position of the disc in the reactor, in general the population tends to consist more of filamentous rather than fewer slime forming organisms. Consequently, the sloughed biosolids tend to be relatively dense with good settling characteristics (Borghi et al, 1985).

Oxygen can be transferred to the water of an RBC in two ways. First, the oxygen can be transferred from the air directly to the water in the basin. The mass transfer constant for direct transfer to the liquid is dependent upon the turbulence at the air water interface. Second, oxygen can be transferred to the thin film of liquid that adheres to the disc when the disc surface rotates out of the water. When the water in the film returns to the basin, it contains more oxygen than when it was removed from the basin (assuming no reactions on the disc) and a net oxygen transfer to the liquid occurs. For an RBC, turbulent liquid-layer transport can possibly describe oxygen transfer directly from the air to the bulk liquid in the tank, from the air to the water adhering to the discs, or from the water adhering to the submerged discs to the bulk liquid (Rittmann et al, 1983).

Analysis of the oxygen transfer mechanisms lead to the prediction that larger units will have a lower oxygen transfer rate than a smaller unit having the same tip speed and specific surface area (Rittmann et al, 1983).

The efficiency of the rotating biological contactor is based on how well the growth of microorganisms, which affect the oxidation of a given waste, become established on the discs. The operation of an activated sludge system, on the other hand, depends on the ability of the microorganisms to settle and concentrate in a secondary clarifier (Lue-Hing et al, 1976).

It is well known that multistage plants attain higher abatement efficiency than the single stage plants working with the same surface area and operating

conditions. This is probably due to the possibility that growth of different types of organisms each one able to remove a restricted substrate concentration, can be achieved in the various stages (Borghi et al, 1985).

A change in the disc rotational speed does not result in a big change in its treating capacity but, to a greater extent, affects the power economy. Since at low rotational speeds, power economy of RBC is several times higher than that of the activated sludge process, the lowest peripheral speed of the disc should be selected. Thus to obtain a high power economy, the RBC should be operated with a peripheral speed close to its minimum (Fujie et al, 1983).

A higher RBC power economy will be achieved if the unit is designed and operated for a daily average effluent substrate concentration (Fujie et al, 1983).

The operation of the RBC systems is closely affected by the following important parameters:

- influent substrate conditions;
- surface hydraulic loading;
- disc rotational speed;
- submerged disk depth;
- wastewater temperature;
- liquid retention time;
- stage number;
- flow rate (Borghi et al, 1985).

Major advantages offered by a RBC system are as follows:

1. Short contact periods are required because of the large active surface (Generally less than 1 hr).
2. It is capable of handling wide range of flows (less than 1 MGD to over 100 MGD).
3. The recycling of solids is not required in the RBC process because of the high concentration of microorganisms on the discs surface (10-25 g/l).
4. The high density of the sludge solids generated by the process indicates significant potential savings in overall treatment plant construction and operating costs. Because sloughed biomass generally has good settling characteristics.
5. Operating costs are low because little skill is required in plant operation.
6. Its performance can be predicted.
7. It has a better shock load and or transient state response than slurry reactor systems in that, because of the short residence time, the shock does not kill the whole biomass and the recovery is fairly rapid.
8. Head loss during the operation is low.
9. Waste distribution problems are minimum.
10. Sludge production is low.
11. Maintenance requirements are low.
12. Nuisance problems are less.
13. The film thickness and the rate of oxygen transfer can be controlled although in a narrow range, by adjusting the rotational speed of the discs.
14. It has high efficiency in carbon and nitrogen removal.
15. It has exhibited stable operation under conditions of fluctuating hydraulic and organic loading and wastewater temperature.

16. It has a low power requirement because the only power required for rotation is needed in overcoming the drag friction of discs in the liquid. Its minimal power requirement gives the RBC a big advantage over other wastewater treatment facilities like the activated sludge process, as energy conservation has become the object of recent attention.

(Anthonie et al, 1974; Borghi et al, 1985; Benefield and Randall, 1980; Weng and Molof, 1973; Wu et al, 1980; Poon et al, 1979; Fujie et al, 1983; Friedman et al, 1976).

The major disadvantages associated with RBC are;

1. Lack of reserve capacity and the absence of operational controls. Once the biomass is built, little can be done to alter its performance.
2. The rate of oxygen transfer from rotation of the discs places limitation on how heavily they may be loaded.
3. With high strength wastewaters, it may be impossible to supply sufficient oxygen from rotation alone in order to keep the reactors fully aerobic.
4. Sludge production appears to be same as that from activated sludge with a short mean cell residence time (MCRT). This means that the sludge disposal cost may be greater than that in the case of activated sludge with a longer MCRT.
5. The construction cost of RBC is generally higher than that of the activated sludge process.
6. RBC is not well suited for use in large scale wastewater treatment operations, but rather only for small scale treatment operations where the floor area of the RBC is not an important factor to reckon with in the plant. (Borghi et al, 1985; Fujie et al, 1983).

The rotating disc process requires an enclosure to protect the biomass from freezing temperatures. There are no special requirements for the enclosure, except that it be constructed of the suitable corrosion-resistant materials and have windows covered structures in the sides for ventilation. Forced ventilation is not necessary. Heating of the enclosure is also not necessary, because the temperature of the air within the enclosure will be approximately that of the wastewater. However, in the wintertime, this will result in considerable amounts of condensation within the enclosure. To minimize the corrosion caused by condensation and to improve operator comfort, it is recommended that a small amount of heat be added to the enclosure during winter operation. If the temperature of the air within the enclosure is kept several degrees above the temperature of the wastewater, condensation is significantly reduced (Anthonie et al, 1974).

2.8. Properties of Biofilm

A biofilm is a layer-like aggregation of microorganisms attached to a solid surface. (La Motta, 1976; Rittmann and McCarty, 1980; Rittmann and McCarty, 1978). Microorganisms, primarily bacteria, adhere to surfaces ranging from the human tooth and intestine to the metal surface of condenser tubes exposed to turbulent flow of water. The microorganisms "stick" by means of extracellular polymer fibers, fabricated and oriented by the cell, that extend from the cell surface to form a tangled matrix termed as "glycocalyx". The fibers may conserve and concentrate extracellular enzymes necessary for preparing substrate molecules for ingestion, especially high molecular weight or particulate substrate frequently found in natural waters. The biofilm surface is highly adsorptive, partially due to its polyelectrolyte nature, and can collect significant quantities of silt, clay, and other detritus in natural waters (Characklis, 1981).

Biofilm are emerging as a most critical factor affecting natural aquatic systems, water distribution systems, wastewater treatment systems, heat exchangers, fuel consumption by ships, and even human disease. More attention must be directed to their behavior (Characklis, 1981).

Biofilm is a function of the geometry of the support material and of the hydrodynamic shear exerted on the biofilm by the flow past the interface (Benefield and Molz, 1985; Harremoës, 1981).

In many natural aquatic systems especially those having a high specific surface area and low nutrient concentrations, biofilms constitute 90 to 99.9% of the bacteria. Biofilms are found in or on stream beds, groundwater aquifers, lake benthos, water pipes, ship hulls, piers and aquatic plants and animals. Engineered processes that utilize films of bacteria include trickling filters, rotating biological contactors, biological activated carbon beds, submerged filters, and land treatment systems (Rittmann and McCarty, 1980; Rittmann and McCarty, 1978; Kissel et al, 1984).

Biofilm develops in a sigmoidal fashion (Figure 2.1). Evidence suggests that biofilm development is the net result of the following transport and biological reaction rate processes:

1. Adsorption of dissolved organics at the wetted surface: Investigations report that materials of diverse surface properties are conditioned by an adsorbed organic layer within minutes of exposure to natural water.
2. Transport of microbial particles to the surface: Particles suspended in a turbulent flow stream can be transported to the surface by either molecular diffusion, turbulent eddy transport, sedimentation, and thermophoresis.

3. Microorganism adhesion to the surface: It has been suggested that bacterial cell adhesion to a solid is a two-stage process: reversible adhesion followed by irreversible adhesion. Adhesion studies have generally been

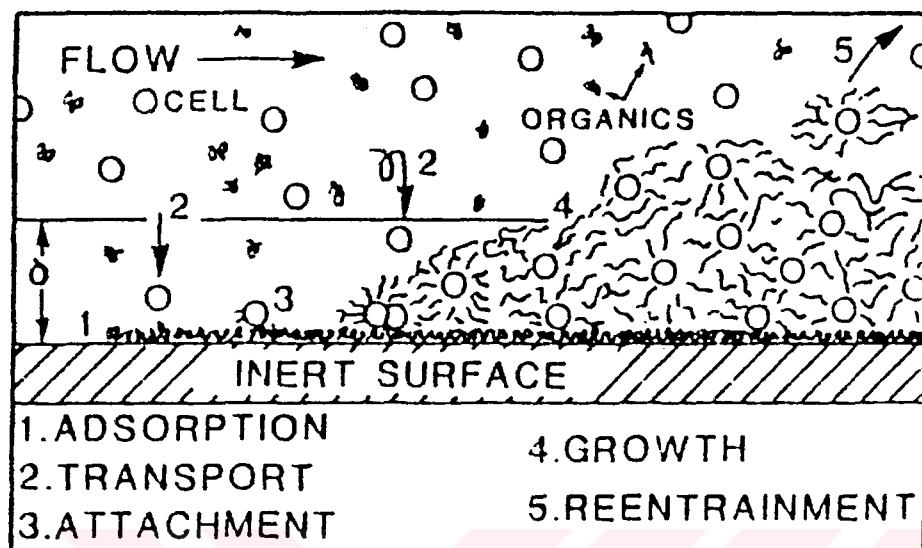


Figure 2.1. Processes contributing to biofilm accumulation; sigma represents the viscous sublayer thickness. No scale is intended. (From Bryers and Characklis (1982))

conducted at very low fluid shear rates. Biofilm accumulation rates in these studies may have been mass transfer rate limited and, therefore, the data are not necessarily applicable to turbulent flow conditions.

The presence of multivalent cations (especially Ca^{+2} , Mg^{+2} , and Fe^{+3}) also influences the attachment process, possibly by altering surface characteristics or by bridging cellular anionic polyelectrolytes to anionic polyelectrolytes adsorbed on the wetted surface.

4. Biofilm production: If the discussion is restricted to chemosynthetic organisms, the attached microbial cells assimilate reduced organic or

inorganic compounds, nutrients, and oxygen or some other electron acceptor. The process yields energy with which cells reproduce, maintain their internal structure, and form extracellular products. Therefore, growth, maintenance, and product formation are fundamental processes carried out by microbial cells in the presence of sufficient nutrients. If nutrients are depleted, or toxic substances are present, death and lysis may occur.

5. Biofilm detachment: As the biofilm grows thicker, the fluid shear stress at the biofilm interface generally increases. Also, as biofilms grow thicker, the potential for substrate, oxygen, or nutrient limitation in the deeper portions is great. These limitations may weaken the biofilm matrix and cause detachment.

At high substrate loadings, increasing fluid velocity increases biofilm detachment rate which minimizes the plateau biofilm thickness. However, at low substrate loadings, fluid velocity seems to have no measurable effect on the plateau thickness. It has been demonstrated that plateau biofilm mass exhibits a maximum when fluid velocity is increased. At low fluid velocities, mass transfer limits the rate of biofilm production. Therefore, increasing fluid velocity increases substrate flux into the biofilm and net biofilm development rate increases. As fluid velocity continues to increase, biofilm detachment rate becomes the dominant process and net biofilm development begins to decrease.

In summary, biofilm formation is the net result of several processes occurring simultaneously. Naturally, certain processes can predominate over others at specific times during biofilm development (Characklis, 1981; Bryers and Characklis, 1982).

Suspended biofilm deposition is a prerequisite to biofilm formation but the

relative contribution of biomass deposition to biofilm net accumulation decreases with biofilm development.

Suspended biomass deposition rate is directly proportional to suspended biomass concentration which suggests deposition in these experiments is controlled by particle transport to surface rather than cellular adhesion.

For the thin biofilms, endogenous decay rates are considered a negligible influence on net biofilm accumulation. This may not be true in much thicker biofilms when transport of essential nutrients is reduced and microbial population densities are higher.

Biofilm production, due to microbial cell reproduction and extracellular polymer production, is the major positive contribution to biofilm net accumulation.

Biofilm removal rate is the only process that significantly offsets the biological production of biofilm, thus detracting from biofilm net accumulation.

Biofilm removal due to shear forces, occurs continually throughout biofilm development and increases dramatically if the biofilm exceeds the existing viscous sublayer (Bryers and Characklis, 1982).

Biofilm growth is proportionate to substrate utilization in the film, while two mechanisms contribute to biofilm loss: decay and shear stresses. Biofilm decay and shear loss are modeled with a rate expression that is first order with respect to attached biomass. When the average shear stress is constant, it seems highly that shear loss rate depends on the supporting medium surface structure (Chang and Rittmann, 1988).

Physical, chemical, and biological properties of biofilm are dependent on the environment to which the attachment surface is exposed. The physical and chemical microenvironment combine to select the prevalent microorganisms which, in turn, modify the microenvironment of the surface. As colonization proceeds and a biofilm develops, gradients develop within the biofilm and average biofilm properties change. Changes in biofilm properties that occur during biofilm development must be considered when attempting to predict the effect of biofilms on fluid and heat transport in turbulent flow systems.

Physical Properties:

Relevant thermodynamic properties of biofilm are its volume (thickness) and mass. In turbulent flow systems, wet biofilm thickness seldom exceeds 1000 micrometer. The biofilm dry mass density can be determined from the wet biofilm thickness if the biofilm mass is known. The biofilm dry mass density reflects attached dry mass per unit wet biofilm volume and measured values in turbulent flow systems range from 10 to 50 mg/cm³. The biofilm dry mass density increases with increasing turbulence and increasing substrate loading. This may be caused by one of the following phenomena:

1. Selective attachment of only certain microbial species from the available population;
2. Microbial metabolic response to environmental stress;
3. Fluid pressure forces "squeeze" loosely bound water from the biofilm.

The transport properties of biofilm are of critical importance in quantifying effects of biofilms on mass, heat, and momentum transfer. Diffusion coefficients for various compounds through microbial aggregates have been reported in the literature, mostly for floc particles. In biofilms, the diffusion coefficient is most probably related to biofilm density (Characklis, 1981).

Chemical Properties:

Inorganic composition of biofilms undoubtedly varies with the chemical composition of the bulk water and probably affects the physical and biological structure of the film. Calcium, magnesium and iron affect intermolecular bonding of biofilm polymers which are primarily responsible for the structural integrity of the deposit. The organic composition of the biofilm is strongly related to the energy and carbon sources available for metabolism (Characklis, 1981).

Biological Properties:

The organisms which colonize the attachment surface will strongly influence biofilm development rate and biofilm chemical and physical properties. However, organism-organism and organism-environment interactions undoubtedly shift population distributions during biofilm accumulation.

The first visible signs of microbial activity on a surface are usually small "colonies" of cells distributed randomly on the surface. As biofilm development continues, the colonies grow together forming a relatively uniform biofilm. The viable cell numbers are relatively low in relation to the biofilm volume (10^4 - 10^8 /cm³ biofilm) occupying only 1-10 % of the biofilm in dilute nutrient solutions.

In many cases filamentous forms emerge as the biofilm develops further. Hyphomicrobium, Sphaerotilus, and Beggiatoa are frequently identified. The filamentous forms may gain an ecological advantage as the biofilm develops since their cells can extend into the flow to obtain needed nutrients or oxygen which may be depleted in the deeper portions (Characklis, 1981).

Under two environmentally significant conditions, the fundamental assumption of the steady state biofilm model -biomass growth just balances biomass losses- is not applicable. One condition occurs when environmental conditions, such as substrate concentration and flow rate, change frequently and prevent the establishment of a true steady state. The second conditions apply when the substrate of interest is not growth rate limited. In the second case, the biofilm thickness is not directly proportional to the substrate flux, because the substrate utilization does not control the growth of the biofilm (Namkung et al, 1983).

Substrate Removal in Biofilms:

Removal of soluble substrates inside biofilms includes three basic phenomena; transportation (diffusion) of substrates, substrate reactions and transportation of the reaction products.

The transportation of the substrates inside the film is a prerequisite for the bacterial reactions. However, the transport in biofilms (diffusion) is dependent on the biofilm thickness and the structure of the film made by the bacteria.

Substrate removal causes formation of reaction products. The outtransportation of these products is important. The products form part of the micro-environment for the bacteria, and build up of reaction products inside the biofilm may create environmental conditions detrimental to the bacteria. Such conditions may be unrecognizable outside the film. Furthermore build up of reaction products inside the biofilm may have a strong influence on the transportation of substrates in the film (Christensen et al, 1989).

In fixed-film reactors, the specific substrate utilization rate is expressed in term of the mass of substrate removed per unit surface area per unit time. The surface area represents the active mass of the biofilm microorganisms (attached biomass). The removal of substrate by suspended biomass is assumed to be negligible in comparison to the substrate consumption by attached biomass because of the relatively small quantity of suspended biomass and short hydraulic retention time as the reactor operates at high flowrates with no cell recycle (Hamoda, 1989).

2.9. Factors Effecting Nitrification Proceess

2.9.1. Residual Oxygen Concentration

A major factor with regard to nitrification is the large requirement of molecular oxygen demand needed by nitrifiers to complete the oxidation of ammonia. The stoichiometric requirement to oxidize ammonia to nitrite is 3.43 kg of oxygen per kg of ammonia nitrogen oxidized. Similarly, the conversion of nitrite to nitrate requires 1.14 kg of oxygen per kg of oxygen per kg of nitrite nitrogen oxidized. The total oxygen requirement is therefore 4.57 kg of oxygen required for the total oxidation of 1 kg of ammonia nitrogen (Williamson and McCarty, 1976a; Adams and Eckenfelder, 1877). It has been observed that if oxygen to ammonia ratio is equal or greater than the stoichiometric ratio, then the overall process will not be oxygen limited (Tanaka and Dunn, 1982).

It has been found that the nitrification rate depends on the bulk oxygen concentrations. At low concentrations, the reaction rate is first order due to liquid film diffusion, but it approaches to a half order reaction at 10 mg O₂/l and would be expected to increase to a zero order reaction at full penetration. At high ammonia concentrations, reaction rate becomes a half order reaction

in the oxygen concentrations (Harremoes et al, 1981).

It has been stated that rotating disk act as a pump replacing water from the trough by water saturated with oxygen and oxygen transfer can be controlled in a narrow range, by adjusting the rotational speed of the discs (Borghi et al, 1985).

It has been observed that, fixed film reactors are oxygen rate limited and ammonia reduction by nitrifying bacteria is a zero order reaction for most of the applications. Because the Monod saturation constant is low in many cases (Watanabe et al, 1980; Jansen and Harremoes, 1984; Kristensen and Harremoes, 1976; Gönenç and Harremoes, 1985; Harremoes et al, 1981; La Motta, 1976; Rittmann and McCarty, 1978). It has been stated that this is a fact that has been ignored in practical design and given rise to a number of design failures for rotating discs (Harremoes et al, 1981).

It has been assumed that the transfer of oxygen and organics into the biofilm is controlled by molecular diffusion and the diffusivity of each is constant throughout the biofilm structure (Benefield and Molz, 1985). At low oxygen concentrations or at low carbonaceous substrate concentrations, the rate of uptake was strongly effected by internal diffusion.

In aerobic biological oxidation processes the efficiency of oxygen transfer, which takes place via the boundary layer water/gas phase, mainly depends on the oxygen deficiency in the water phase (saturation concentration of oxygen minus actual oxygen concentration) (Bintanja et al, 1976). The increase in oxygen saturation cause the increase in removal rate for RBC systems. The oxygen concentration at the disc slime interface will be zero for the limiting case (Scroeder, 1977).

The critical values of the concentration of dissolved oxygen below which the oxygen uptake by microorganisms involved in the biological oxidation processes drastically declines; these critical values are approximately 0.3-0.5 mg/l. In practice conventional activated sludge processes are operated with much higher dissolved oxygen values (at least 2 mg/l), besides, these values are required to achieve a distinct nitrification. The saturation concentration of oxygen in water is limited to approximately 9 mg/l when air is used as a gas phase at NTP and thus the maximum value of the oxygen deficiency amounts to approximately 7 mg/l (Bintanja et al, 1976).

It has been reported that, in most aerobic biofilm systems, oxygen does not fully penetrate into the whole biofilm. Penetration thickness of oxygen within the biofilm is proportional to the square root of the partial pressure of oxygen in the gaseous phase (Watanabe et al, 1980). The rate of oxygen transfer from rotation of discs places how heavily they may be loaded. Within high strength wastewaters, it may be impossible to supply sufficient oxygen from rotation alone in order to keep the reactors fully aerobic (Borghi et al, 1985).

It has been suggested that for practical conditions, the transitions to ammonia rate limitation requires the ammonia concentration to be less than 2 mg/l for 5 mg/l D.O. It confirms that nitrification in rotating disc is oxygen rate limited for all practical purposes- a fact that has been ignored in practical design and given rise to a number of design failures in rotating disc practice (Gönenç and Harremoes, 1985).

It has been observed that bulk-liquid dissolved oxygen is critical to nitrifying biofilter performance when oxygen flux limitation conditions exist. When the percent of dissolved oxygen saturation drops below 60 to 65%, nitrification performance will be diminished. When the percent of dissolved oxygen saturation drops below 45 to 50%, nitrification may be totally eliminated

(Gullicks and Cleasby, 1990).

A considerable increase in dissolved oxygen can be obtained by raising the partial pressure of oxygen in the gas phase by partial or total replacement of air by oxygen (Bintanja et al, 1976; Gönenç and Harremoes, 1985). Oxygen limitation has been suppressed by operating the proses in a closed vessel under an oxygen atmosphere. In this case, organic matter was more likely to represent the rate limiting substrate (Bintanja et al, 1976).

It has been found that when using oxygen instead of air in the biodisc process, substrate concentration determines the rate of conversion. In the experiments with air, on the contrary at higher loads, the rate of conversion becomes dependent on the actual oxygen concentration (Bintanja et al; 1976).

Advantages of the application of oxygen in a biodisc installation are mainly; a higher efficiency of the substrate conversion, a lower sludge production and better settleability of the sludge. Moreover the self-cleaning capacity of the receiving water is enlarged as a consequence of the relatively high concentration of the dissolved oxygen in the effluent (Bintanja et al, 1976).

In actual practice the application of oxygen might be of importance particularly in case of strongly polluted waste water, in order to remove as much as possible of the organic compounds present in one step; eventually a consecutive bio-oxidation step in air might follow to complete the process (Bintanja et al, 1976).

Another way of increasing the oxygen concentration in the bulk liquid is the diffused air aeration. In an investigation, it has been found that diffused air aeration below the rotating discs increases the removal rate and increasing the size of the discs does not increase the oxygenation capacity per unit

metre square of disc, it decreases with increasing size (Harremoes et al, 1981).

It has been stated that the oxygen concentration at the surface of the biofilm will be less than the concentration in the bulk liquid and will be greatly influenced by the degree of turbulence in the aeration tank (Benefield and Randall, 1980).

It has been found that the critical oxygen concentration depends on biofilm thickness (Atkinson and Daoud, 1980), and the local oxygen concentration depends on biofilm will be largely influenced by the bulk oxygen concentrations (Tanaka and Dunn, 1982).

It has been reported that there was no inhibition to nitrification at dissolved oxygen levels greater than 1 mg/l, and increasing dissolved oxygen concentration above 1 mg/l would increase the oxidation rate (Benefield and Randall, 1980; Wild et al, 1971).

It has been observed that low D.O. (0.5mg/l) did not affect ammonia oxidation as a whole in the pure nitrification system. The growth yield of ammonia oxidizers was doubled at low D.O. compensated the reduced ammonia oxidation rate per unit mass of cell. Nitrite oxidation was strongly inhibited by low D.O (Hanaki et al, 1990).

It has been reported that the nitrifying rate is largely influenced by dissolved oxygen. When D.O. is below 0.2 mg/l, the nitrifying reaction occurs very slowly, but when D.O. is more than 2.0 mg/l, it proceeds rapidly (Terashima and Ishikawa, 1984).

It has been stated that nitrification consumes significantly more oxygen than

heterotrophic growth per unit mass of substrate. Penetration depth of oxygen is at maximum in the heterotrophic films which may be explained by the fact that autotrophic microorganisms have a much higher oxygen consumption per unit mass than heterotrophic organisms (Wanner and Gujer, 1984). Effect of dissolved oxygen concentration on the specific growth rate of *Nitrosomonas* should be considered when combined carbon oxidation- nitrification processes are used (Benefield and Randall, 1980). In these processes, autotrophic microorganisms are located in the depth of the biofilms and consume any oxygen which is not required by the heterotrophs (Wanner and Gujer, 1984).

In the combined carbon oxidation- nitrification process, the nitrifying bacteria compose only a very small percentage of the total biomass (approximately 5%). Under such a circumstance it is easy to visualize that a large fraction of the nitrifying organisms would lie some depth below the surface of the activated sludge floc. Thus, an increase in the dissolved oxygen concentration would increase the depth of penetration as well as the dissolved oxygen concentration within the sludge floc. This would increase the fraction of nitrifiers in the aerobic zone which are exposed to a dissolved oxygen level above critical. Hence, it is logical that increasing the dissolved oxygen concentration in a combined process will increase the rate of nitrification.

In the separate-stage nitrification process the biomass has a larger nitrifying fraction, which would suggest that increasing the dissolved oxygen level above 1.0 mg/l, an upper limit that is generally accepted for critical oxygen concentration, would not result in an increase in the ammonium oxidation rate. It can, therefore be argued that effects of dissolved oxygen concentration on the specific growth rate of *Nitrosomonas* should be considered when combined carbon oxidation-nitrification processes are used but can be

neglected in separate-stage nitrification since the process is always designed to maintain dissolved oxygen levels greater than 1 mg/l. Furthermore, dissolved oxygen effects in the combined process can probably be neglected if the aeration system is designed to maintain a minimum dissolved oxygen level of 2.0 mg/l, which would always be the case (Benefield and Randall, 1980).

The concentration of dissolved oxygen in a fixed film reactor has only a minor effect on the cell yield coefficient. Although the observed data showed a slight increase of the cell yield with an increasing D.O., the trend of such a correlation is not quite definite (Huang et al, 1985).

The oxygen mass transfer coefficient under constant temperature conditions is considered to be a function of the surface area of the tank, the volume of the liquid bulk, the diameter of the contact media (or contact media cage) which acts as a stirrer, the viscosity of the wastewater, and diffusivity of oxygen in the wastewater (Ouano, 1978).

It has been observed that when the estimated autotroph population is low then nitrification is likely to be lost if the dissolved oxygen is partially inhibiting activity. In this situation substantial increases in aeration can alleviate loss of nitrification. A further observation was that increasing the concentration of autotrophs by reducing sludge wastage does not significantly affect nitrification if the dissolved oxygen is limiting. A decrease in sludge wasting combined with a small increase in aeration can effectively maintain the required effluent ammonia concentration (Lumbers et al, 1989).

It has been observed that the dynamics of the nitrification process are such that large input variations will always be reflected in the effluent quality regardless of the autotroph population and the dissolved oxygen

concentration (Lumbers et al, 1989).

It has been stated that, in the absence of biomass, aeration through the liquid film is the dominant mechanism for physical oxygen transfer only when bench-scale RBC units are operated at high disc rotational speeds. At low velocities, the contribution of reactor liquid turbulence is significant to total physical oxygen transfer. The biomass enhances the oxygen transfer rate with respect to the rate in clean water. This enhancement is particularly significant at low rotational speeds and probably results from enhancement of oxygen diffusion through the liquid film as a consequence of the oxygen consumption by the biofilm and increased surface area for transfer. Aeration through the liquid film thus seems to be the dominant mechanism for biochemical oxygen transfer at all rotational speeds investigated (3-25rpm). Therefore, physical transfer tests misleading information on the oxygen transfer mechanisms and transfer capabilities of RBC systems, when the discs are rotated at low velocities (Paolini, 1986).

As a summary, residual oxygen concentration is an important factor affecting nitrification. If oxygen to ammonia ratio is equal to or greater than the stoichiometric ratio, then the overall process will not be oxygen limited.

As it is known, oxygen in Rotating Biological Contactor is supplied by rotation of discs. But this amount might not be enough in wastewaters containing high concentrations of $\text{NH}_4\text{-N}$. In order to increase bulk oxygen concentration in Rotating Biological Contactors, various applications are present. One of them is in a narrow range by adjusting the rotational speed of the discs. Another way is the diffused air aeration of the bulk liquid. Further, oxygen limitation can be suppressed by operating the process in a closed vessel under an oxygen atmosphere.

2.9.2. Operating Temperature:

All the process of growth are dependent on chemical reactions and the rates of these reactions are influenced by temperature. Thus the rate of microbial growth as well as the total amount of growth can be effected by temperature (Benefield and Randall, 1980).

Temperature effects several of the mechanisms involved in the kinetics of the fixed film processes, including substrate removal rates, oxygen saturation values (also mass transfer driving forces), and the diffusivities of oxygen and substrate (Lehman et al, 1983).

The rate of biological nitrification has been known to be a strong function of temperature. Any change in temperature tends to change oxidation directly (Metcalf and Eddy, 1982; Wong-Chong and Loehr, 1978). For many reactions, the dependence of the rate of reaction on temperature can be expressed empirically by the Van't Hoff. Arrhenius Law. This law may be represented as follows:

$$K = K^* e^{-\frac{E}{R(\frac{1}{T} - \frac{1}{T_o})}} \quad (2.35)$$

where:

$$K^* = Ae^{-E/RT_o}$$

K = reaction rate constant (h^{-1}),

A = frequency factor,

E = activation energy (cal/g-mole),

R = universal gas constant (cal/g-mole, $^{\circ}K$),

T = temperature ($^{\circ}K$), and

T_o = median of the temperature range investigated ($^{\circ}K$).

(Sutton et al, 1979; Wild et al, 1971; Murphy et al, 1977; Borghi et al, 1985).

Several observations on the effect of temperature on removal rate have been reported and some of them are given as follows:

1. At temperatures less than 13 °C, changes in hydraulic loading result in significant changes in removal rate. As the hydraulic loading rate increases with temperature, the effect of wastewater temperature becomes more significant. As a result, rate of substrate utilization increases with temperature (Lehman et al, 1983).
2. Increasing the liquid temperature from 20.7 to 29.3 °C, increased the nitrification efficiency (Weng and Molof, 1974).
3. The difference in removal rate between 15 and 20 °C is smaller than 0.5% (Anthonie et al, 1974).
4. The rate of nitrification increased through the range of 5 to 30 °C, in reasonable agreement with the van't Hoff-Arrhenius law (Wild et al, 1971).
5. The process of nitrification is a function of temperature within the range of approximately 4 to 45 °C. The optimum temperature for *Nitrosomonas* is about 35 °C, and for *Nitrobacter*, 35 to 42 °C (Sutton et al, 1979).
6. The temperature range of 25 °C to 30 °C was found to be favourable for nitrification, during aerobic digestion of activated sludges, and a temperature of around 30 °C was optimum in yielding a maximum rate of nitrification (Bhargava, 1989).
7. Low winter temperatures adversely effect biological growth but provide higher dissolved oxygen saturation concentration in wastewater. Therefore although reduced removal is expected during winter operation, because of suppression of the kinetic removal rate, the increased oxygen driving force appears to provide effective compensation (Lehman et al, 1983).
8. In cold climates, wastewater cooling as a result of heat transfer between the RBC disc surfaces and the atmosphere could significantly reduce

biological activity and may cause icing problems. To minimize this problem, covers should be installed on all units or they should be housed in a building (Murphy et al, 1977).

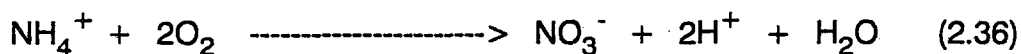
9. Lue-Hing et al (1976) indicated a significant increase in ammonia removal with increasing temperature for a high strength ammonia wastewater (average concentration of 780 mg $\text{NH}_4\text{-N/l}$). The ammonia nitrogen removal rate almost doubled by increasing the temperature from 9° to 20°C. During the winter operation, the effluent was clarified and flow was recycled in an attempt to improve effluent quality and it has been found that the effects of recycling flow were minimal.
10. Nitrification in the RBC exhibits a relatively low temperature sensitivity which is comparable to the temperature sensitivity of combined activated sludge nitrification systems with high SRT's (Murphy et al, 1977).
11. It has been found that the nitrifying growth must be established on the discs before the onset of colder temperatures; otherwise, there would be little or no response in the removal of $\text{NH}_4\text{-N}$ for a considerable period of time (Lue-Hing et al, 1976).

It has been suggested that the lower nitrification performance at colder wastewater temperatures is the result of the following factors:

- Lower diffusivities of reactants in the bulk liquid and in the biofilm,
- Low bulk liquid dissolved oxygen concentrations compared with saturation dissolved oxygen (that is, actual concentrations comparable to or only slightly higher than summer values),
- Higher carbonaceous oxygen demand,
- Greater sloughing and partial plugging associated with winter operation, and
- Possibly the lower metabolism rate of the microorganisms, although this effect would be small in flux limited processes (Gullicks and Cleasby, 1990).

2.9.3. Operating pH:

The nitrification reaction consumes alkalinity. From the following:



It is seen that 2 meqv of alkalinity is consumed per mmole of ammonia oxidized (Henze, 1984). In other words, 7.2 mg of bicarbonate expressed as CaCO_3 are required to neutralize the hydrogen ions produced during the oxidation of 1 mg of ammonia nitrogen (Sutton et al, 1979). Usually the wastewater alkalinity is sufficient to buffer the pH during nitrification of domestic wastewater (Lewandowski, 1985). But the problems may arise usually in nitrogen rich industrial wastewaters. Therefore, discharge of untreated nitrogen rich industrial wastewaters might give problems for softwater areas (Henze, 1984).

When the alkalinity of water is not sufficient, the pH change during the process causes the lowering of the nitrification rate and the nitrifiers growth rate (Lewandowski, 1985). In the fixed-film nitrification processes, acidity is produced inside the biofilm and this acidity has to diffuse out of the biofilm. This is carried out by a balance between the diffusion of the species of the carbonate system (In the acidic range, CO_2 and HCO_3^-) (Harremoes et al, 1980).

Various pH optima have been reported for nitrification. There is a general agreement that as the pH decreases into the acidic range, the rate of nitrification also decreases. Some of them are given as follows:

1. Optimum pH for nitrification ranges between 8 and 9 (Sutton et al, 1979).
2. Even though nitrifying bacteria initially prefer a pH near 8, they are capable

of acclimating to lower environmental pH's where in they will reestablish their maximum growth rate (Scroeder, 1977).

3. Nitrifiers favour a mildly alkaline environment, with an optimum pH at about 8.5. Thus, below that optimal pH, nitrification rates decrease with decreasing pH and nitrification is completely stopped at pH levels below about 5 (Winkler, 1981).
4. Maximum rate of nitrification occurs between pH values of about 7.2 and 9.0 (Metcalf and Eddy, 1982).
5. Optimum pH for nitrification has been found to be 8.4. 90% of the maximum nitrification rate occurs in the range of 7.8 to 8.9 and that outside the ranges of 7 to 9.8, less than 50% of the optimum rate occurs (Wild et al, 1971).
6. Nitrification has been found to be most efficient in the range of 7.8 to 8.3 and pilot results have indicated that inefficient nitrification system can be improved by adjusting the influent pH level so that the aeration basin contents within the optimum range (Adams and Eckenfelder, 1977).
7. Optimum pH values have been summarized between 7.1 and 9.0 for various fixed film studies (Collins et al, 1988).
8. A pH value in the range of 6.0 to 8.0 was found to be essential for the occurrence and progress of nitrification (Bhargava, 1989).

Anthonisen et al (1976) provided a fundamental discussion of the influence of pH in terms of nitrification inhibition by free ammonia (high pH) and free nitrous acid (low pH). The range of free ammonia concentrations that begin to inhibit the nitrifying organisms are: free ammonia inhibition to nitrosomonas, 10 to 150 mg/l and free ammonia inhibition to nitrobacters, 0.1 to 1.0 mg/l. The inhibition of nitrifying organisms was initiated at concentrations of free nitrous acid between 0.22 and 2.8 mg/l.

The optimum pH has been shown to decrease almost linearly with the logarithm of total ammonia nitrogen concentration over the concentration range found in natural and domestic wastewaters. Although the shift is small (about 0.8 pH units between 1 ppm and 50 ppm total ammonia nitrogen), the optimum pH shift has important consequences for nitrification control (Quinlan, 1984).

Sodium hydroxide has been recommended for pH adjustment since lime may precipitate as calcium carbonate and limit the system from the standpoint of inorganic carbon, particularly with high ammonia wastes. Lime may be satisfactory for low strength ammonia wastewaters (Adams and Eckenfelder, 1977).

It has been found that gradients in pH did not influence biofilm nitrification kinetics (Tanaka and Dunn, 1982), and the degree of inhibition because of a pH change has been found to be independent of the substrate concentration (Benefield and Randall, 1980).

It has been observed in a study that the activated sludge with suspended marble particles is able to nitrify without chemical addition for pH and alkalinity control. It does not show the limitations caused by pH value and alkalinity. Nitrification proceeds with full efficiency down to a pH value of 5.5 and alkalinity close to zero. The natural limitations of the nitrification process efficiency is determined by the washed out velocity of the marble particles (Lewandowski, 1985).

2.9.4. Biofilm Thickness:

Mixing in natural environments, such as lakes, ponds, soils, seawater, and sediments, is rarely adequate to maintain complete dispersion, however; as

a result, bacterial growth generally occurs on available surfaces. Bacteria as charged micron sized particles become adsorbed and attached at solid-liquid interfaces, and, after multiplying over several generations, a biofilm of closely packed bacteria is formed (Williamson and McCarty, 1976).

In a fixed film system, accumulation of biomass on the support media is a complicated matter, which depends on many factors such as oxygen availability, substrate nature and concentrations, hydraulic shearing and microbial species (Huang et al, 1985).

Generally, the maximum biofilm thickness under an atmospheric operating condition was found to vary from a few hundred microns to several millimeters, depending on the substrate concentration and hydraulic shearing stress. However, for a thicker biofilm, an aerobic condition can not be maintained throughout its depth under atmospheric environment. It has been further observed that aerobic biofilms were more effective in oxidizing organic matters and had a better settleability than the anaerobic counterpart (Huang et al, 1985).

It has been suggested that the film thickness is a function of the velocity profile on the disc (Zeevalkink et al, 1978).

To maximize the biological metabolism of a soluble pollutant, the electron donor or the electron acceptor associated with the pollutant should be supplied in sufficient quantity in order that the pollutant concentration limits the pollutant utilization rate. In dispersed bacterial reactors, this condition is usually easily obtained; for example, the dissolved oxygen concentration in activated sludge treatment needs to be only several milligrams per liter for oxygen not to be limiting.

In contrast to the dispersed bacterial case, biofilms may be flux limited by the associated electron donor or electron acceptor concentrations in many cases. The concentration needed to prevent this limitation depends on the stoichiometric requirements and the diffusion coefficients within the biofilm (Williamson and McCarty, 1976).

Performance of a biofilm reactor is dependent upon the thickness of the microbial film. This subject has been studied by many investigators and found that:

1. If the mass of organisms and therefore the film thickness is allowed to increase, the performance of reactor improves with time for constant input conditions (Atkinson and Daoud, 1980).
2. The removal rate is proportional to the concentration of nitrifiers per unit volume of biofilm at the surface of the biofilm and increases exponentially with the thickness of the aerobic biofilm and the growth rate. Faster growth of biofilm decreases the removal rate (Gönenç and Harremoës, 1985).
3. Due to varying production of polysaccharides which make up the slimy matrix of the film, then thickness of the biofilm may in periods increase rapidly without increase in the number of bacteria. This leads to a decrease of the calculated removal rate based on the total biofilm volume (Jansen and Harremoës, 1984).
4. Substrate removal is directly proportional to film thickness. When thickness is less than a critical value, and once this value is exceeded, removal no longer depends on film thickness (La Motta, 1976).
5. Biological process performances depend on the biomass amount in the reactor. This is especially true for biofilm processes, in which high volumetric loading rates or low effluent concentrations are associated with the ability to accumulate a large biofilm mass in the reactor. The biofilm mass accumulating on a supporting medium depends on substrate

utilization, biofilm growth and decay, and shear loss. Of the factors affecting biofilm accumulation, shear loss is the least understood and the main biofilm loss mechanism. Shear loss results from hydrodynamic stress caused by liquid flowing over the biofilm. Actually, practical attachment media are quite different from the smooth, regular surface of an annular reactor. Sand, gravel, rock, pumice, clay, plastic-clumped media, plastic modular media, coal, activated carbon, and resin beads are practical attachment media that are not regular and do not sustain uniform shear stress. Crevices, pores, and other surface irregularities provide some attachment sites, which are protected from shearing, while other sites are exposed to increased shearing (Chang and Rittmann, 1988). Therefore, biofilm loss due to the fluid shear seems to be a complex function of a variety of hydrodynamic and biological factors, such as biofilm thickness, surface characteristics of the attaching medium, biofilm growth rate, and shear stress of the flow (Chang and Rittmann, 1987).

6. The loss of biomass from fixed film reactors as a result of shearing forces may be an important design and operating consideration, especially at low substrate concentrations. Data collected under a rapidly changing biodegradation rate indicated that biofilm shearing was much more closely related to the microbial growth rate than to the amount of attached biomass, as had been previously proposed (Speitel and DiGiano, 1987).
7. Growth of bacteria inside a biofilm is expected to follow an exponential growth pattern like cultures in suspension under conditions where substrates are provided in excess. In a study, it has been observed experimentally that the increase in biofilm thickness does not follow the exponential increase found for the removal rate. Where the removal rate is tenfolded the biofilm thickness has only doubled. The observed difference in rate of increase is explained by a dramatic increase in bacteria density in the biofilm. Change of bacteria density of the biofilm has a marked effect on the substrate removal since it may change the

significance of the extension of the film. In a biofilm with low density the distances of transportation of substrates to the bacteria can be the dominating phenomenon. In the case of a high density of bacteria, the reaction takes place in the outer thin layer of the film and can be taken as a surface phenomenon independent of the biofilm thickness (Christensen et al, 1989).

8. It has been reported that the rate of substrate stabilization increases with the biofilm thickness, but the maximum rate is reached by a film thickness of generally less than 0.2mm. Beyond that thickness, no significant improvement of the stabilization rate would take place (Huang et al, 1985).

2.9.5. Hydraulic Detention Time:

The ammonia removal efficiency is found to be a function of hydraulic detention time and that it increases with the increase of detention time. The basic reason is that the concentration of nitrifiers in the system at a given time on an absolute basis depends on detention time. The fact, that detention time is a tool to achieve the desired concentration of nitrifiers and, therefore, is particularly important for reactor start up (Beg, S.A. and Hassan, M.M, 1985).

2.9.6. Toxic Compounds

A considerable body of knowledge now exists about the effects of various environmental factors such as temperature, pH-alkalinity, and dissolved oxygen concentration on the kinetics of nitrification. Like all other biological processes, nitrification systems have been found to be critically sensitive to the presence of toxic compounds including some heavy metals and organic compounds (Beg et al, 1980; Beg et al, 1982; Beg and Atiqullah, 1983; Beg and Atiqullah, 1983a; Beg ve Hassan, 1987; Hockenbury and Grady, 1977;

Hooper and Terry, 1973; Huang and Skeikhdeslami, 1982; Neufeld et al, 1986; Oslislo and Lewandowski, 1985; Stafford. 1974; Stensel, 1976; Ibrahim, 1988).

It has been found that the inorganic compounds of Cr, As and F inhibit the ammonia oxidation rates; and the inhibited reaction follows a zero order reaction (Beg et al, 1982). For the reported concentrations of F^- , As and Cr^{+6} , in the range of 0-200 mg/l, 0-20 mg/l and 0-10 mg/l, in fertilizer industry wastewater, the corresponding inhibitory effect at upper limit of these ranges would be 14, 7, and 17% respectively (Beg et al, 1980).

It has been found that toxic inhibition to biological nitrification in the order of free cyanide, tar acid phenolics, phenol, 2,3,6-trimethylphenol, 2-ethylpyridine, 2,4,6-trimethylphenol, complexed cyanide and thiocyanate. The concentrations up to which there is no effect on NH_4-N are 1.2 mg/l for the tar acid phenolics, 1.4 mg/l for reagent phenol, 4.9 mg/l for 2,3,6-trimethylphenol, 10 mg/l for 2-ethylpyridine, 30 mg/l for complexed cyanide and 236 mg/l for thiocyanate. Complexed cyanide, a common constituent of coke plant wastewaters, appears virtually noninhibitory to biological nitrification at effluent concentrations of about 80 mg/l. At an effluent concentration of 100 mg/l, the NH_4-N oxidation rate would equal 80% of the maximum value obtainable in the absence of complexed cyanide. Thiocyanate, a major constituent of coke plant and synfuels wastewaters, is known to exist in the range of 600-700 mg/l. At an effluent thiocyanate concentration of 600 mg/l, the NH_4-N oxidation rate would equal 58% of the maximum value obtainable in the absence of thiocyanate (Neufeld et al, 1986).

In an investigation, effect of the presence of four organic compounds on nitrification process under shock loading conditions were studied. The K_i value which in fact is the concentration of inhibitor which causes the 50% reduction in substrate conversion rate has been determined for methanol as

equal to 116 mg/l. K_i value has been determined as 61.5 mg/l for formalin and 804.2 mg/l for acetone. Glucose in applied concentration up to 11.3 mg/l had no effect on the nitrification process (Neufeld et al, 1986).

The effect of chromium, nickel and zinc on the ammonia and nitrite oxidations of acclimated nitrifying microorganisms was investigated by Huang and Skeikhdeslami (1982) and of the three metals investigated, nickel was found to be the most toxic to both ammonia oxidation and nitrite formation, followed by zinc and chromium. Of these two steps of nitrification, the former step was found to be more susceptible to inhibition, thus representing the weak link in the nitrification chain.



CHAPTER 3. MATERIALS AND METHODS

3.1. Experimental System

3.1.1. Experimental Set-up

Nitrification was studied in a laboratory scale RBC unit which consists of 20 parallel circular discs mounted 2 cm apart on a horizontal shaft and rotated perpendicular to the direction of the wastewater (Figure 3.1). The discs are 30 cm in diameter and 0.5 cm thick giving a total surface area of 2.6 m^2 for microbial growth. They are submerged in a 29.5 l tank to about 33% of the disc diameter. Sloughed biomass is separated in a 7.25 l settling tank combined to the RBC unit. There are six sampling ports below the trough. A photograph of the RBC unit are given on Figure 3.2.

3.1.2. Chemicals Used in the Experiments

In the experimental study, as a source of $\text{NH}_4\text{-N}$, technical grade $(\text{NH}_4)_2\text{SO}_4$ (Yarpet); as a source of alkalinity, technical grade NaHCO_3 ; as a source of phosphorus, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (Horasan Kimya); as a source of fluoride, NaF (Merck) and as a source of hexavalent chromium, $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck) were used.

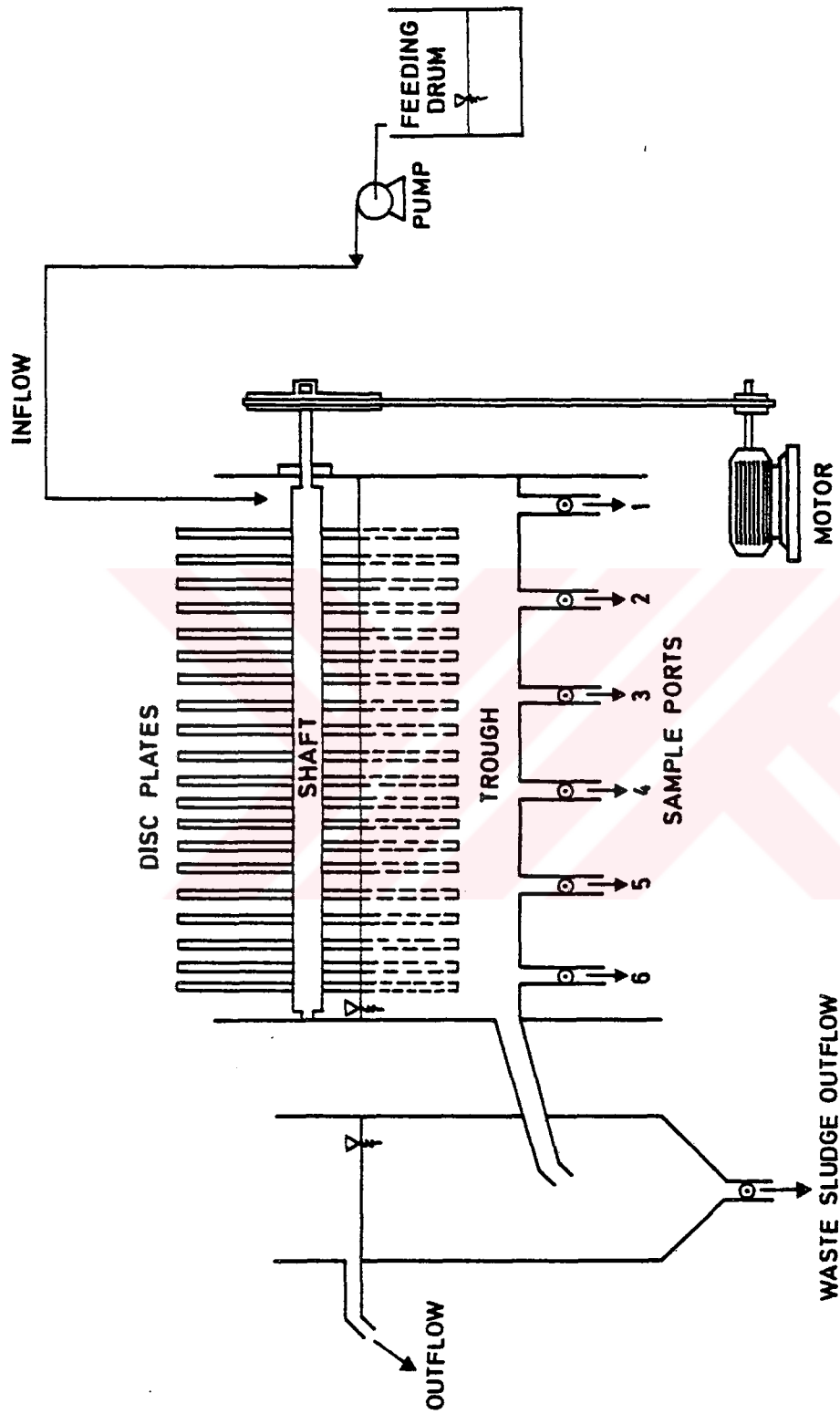


Figure 3.1. Schematic presentation of RBC unit

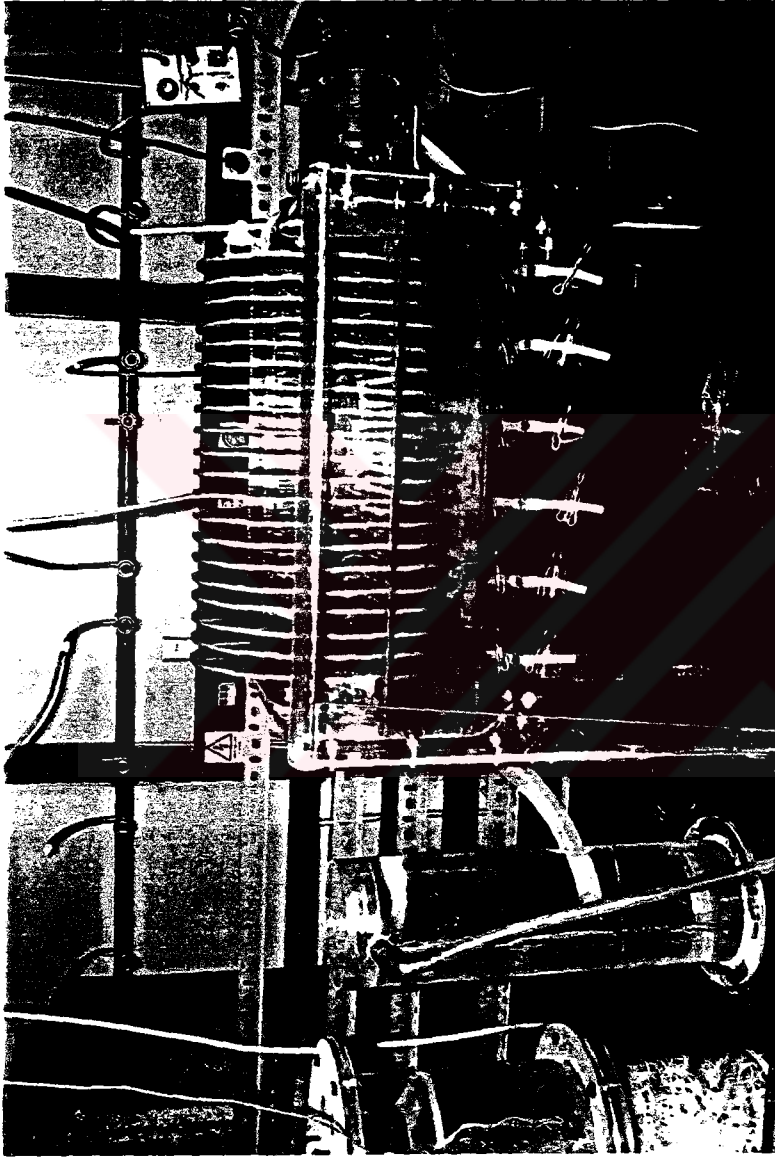


Figure 3.2. The RBC Unit

3.1.3. Instruments Used in The Experiments

In the experimental study, DIGI-SENSE Digital pH Meter (Cole Parmer) was used for pH measurements. YSI Model 54A Oxygen Meter was used for dissolved oxygen and temperature measurements. Gerhardt Vapodst 3S Kjeldahl Nitrogen Analyser was used for ammonium nitrogen analysis. Dionex Ion Chromatography (Series 4000i) was used for nitrite, nitrate, phosphate, sulfate, chloride, fluoride and chromate analysis.

3.1.4. Solutions Used in The Experiments and Compositions

In the experiments, for every mg of $\text{NH}_4\text{-N}$, 10 mg of alkalinity (as CaCO_3) and 0.25 mg of phosphorus were added to the feeding solution.

3.1.4.1. Experiments Performed With $\text{NH}_4\text{-N}$:

60 mg/l $\text{NH}_4\text{-N}$ Solution (30 litre):

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

80 mg/l $\text{NH}_4\text{-N}$ Solution (30 litre):

11.3 g $(\text{NH}_4)_2\text{SO}_4$

40.3 g NaHCO_3

6.9 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

120 mg/l $\text{NH}_4\text{-N}$ Solution (30 litre):

17 g $(\text{NH}_4)_2\text{SO}_4$

60.5 g NaHCO_3

10.4 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

3.1.4.2. Experiments Performed With $\text{NH}_4\text{-N}$ and Fluoride:

60 mg/l $\text{NH}_4\text{-N}$ and 200 mg/l fluoride solution (30 litre):

13.26 g NaF

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

60 mg/l $\text{NH}_4\text{-N}$ and 400 mg/l fluoride solution (30 litre):

26.53 g NaF

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

60 mg/l $\text{NH}_4\text{-N}$ and 800 mg/l fluoride solution (30 litre):

53.05 g NaF

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

80 mg/l $\text{NH}_4\text{-N}$ and 200 mg/l fluoride solution (30 litre):

13.26 g NaF

11.3 g $(\text{NH}_4)_2\text{SO}_4$

40.3 g NaHCO_3

6.9 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

80 mg/l NH₄-N and 500 mg/l fluoride solution (30 litre):

33.15 g NaF

11.3 g (NH₄)₂SO₄

40.3 g NaHCO₃

6.9 g Na₂HPO₄·12H₂O

80 mg/l NH₄-N and 800 mg/l fluoride solution (30 litre):

53.05 g NaF

11.3 g (NH₄)₂SO₄

40.3 g NaHCO₃

6.9 g Na₂HPO₄·12H₂O

120 mg/l NH₄-N and 200 mg/l fluoride solution (30 litre):

13.36 g NaF

17 g (NH₄)₂SO₄

60.5 g NaHCO₃

10.4 g Na₂HPO₄·12H₂O

120 mg/l NH₄-N and 600 mg/l fluoride solution (30 litre):

39.8 g NaF

17 g (NH₄)₂SO₄

60.5 g NaHCO₃

10.4 g Na₂HPO₄·12H₂O

120 mg/l NH₄-N and 1000 mg/l fluoride solution (30 litre):

66.3 g NaF

17 g (NH₄)₂SO₄

60.5 g NaHCO₃

10.4 g Na₂HPO₄·12H₂O

3.1.4.2. Experiments Performed With NH_4 -N and Hexavalent Chromium:

60 mg/l NH_4 -N and 10 mg/l hexavalent chromium solution (30 litre):

848.1 mg $\text{K}_2\text{Cr}_2\text{O}_7$

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

60 mg/l NH_4 -N and 50 mg/l hexavalent chromium solution (30 litre):

4.24 g $\text{K}_2\text{Cr}_2\text{O}_7$

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

60 mg/l NH_4 -N and 100 mg/l hexavalent chromium solution (30 litre):

8.48 g $\text{K}_2\text{Cr}_2\text{O}_7$

8.5 g $(\text{NH}_4)_2\text{SO}_4$

30.2 g NaHCO_3

5.2 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

80 mg/l NH_4 -N and 15 mg/l hexavalent chromium solution (30 litre):

1.27 g $\text{K}_2\text{Cr}_2\text{O}_7$

11.3 g $(\text{NH}_4)_2\text{SO}_4$

40.3 g NaHCO_3

26.9 g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

80 mg/l NH₄-N and 60 mg/l hexavalent chromium solution (30 litre):

5.1 g K₂Cr₂O₇

11.3 g (NH₄)₂SO₄

40.3 g NaHCO₃

6.9 g Na₂HPO₄·12H₂O

80 mg/l NH₄-N and 110 mg/l hexavalent chromium solution (30 litre):

9.3 g K₂Cr₂O₇

11.3 g (NH₄)₂SO₄

40.3 g NaHCO₃

6.9 g Na₂HPO₄·12H₂O

120 mg/l NH₄-N and 10 mg/l hexavalent chromium solution (30 litre):

848.1 mg K₂Cr₂O₇

17 g (NH₄)₂SO₄

60.5 g NaHCO₃

10.4 g Na₂HPO₄·12H₂O

120 mg/l NH₄-N and 75 mg/l hexavalent chromium solution (30 litre):

26.36 g K₂Cr₂O₇

127 g (NH₄)₂SO₄

60.5 g NaHCO₃

10.4 g Na₂HPO₄·12H₂O

120 mg/l NH₄-N and 125 mg/l hexavalent chromium solution (30 litre):

10.6 g K₂Cr₂O₇

17 g (NH₄)₂SO₄

60.5 g NaHCO₃

10.4 g Na₂HPO₄·12H₂O

3.1.5. Build-up of Biofilm

The build-up of biofilm is established by first seeding the system with the activated sludge sample taken from a domestic wastewater treatment unit and feeding the system with a solution made up of $(\text{NH}_4)_2\text{SO}_4$, NaHCO_3 and Na_2HPO_4 for a period of about 6 months. For every 10 mg of ammonia nitrogen 10 mg of alkalinity (as CaCO_3) and 0.25 mg of phosphorus was added into the solution. Results of the experiments performed in the biofilm formation part of the study are given on Table 3.1. Experimental study was started with 100 mg/l initial $\text{NH}_4\text{-N}$ concentration and 15 mg/l feeding rate. After the system has reached to about 90% $\text{NH}_4\text{-N}$ removal rate, then initial $\text{NH}_4\text{-N}$ concentration was increased to 200, 300, 400, 500 and finally to 600 mg $\text{NH}_4\text{-N/l}$ concentrations. Solutions used in the experiments and their compositions are shown as follows;

-100 mg/l initial $\text{NH}_4\text{-N}$ concentration:

471.4 mg/l $(\text{NH}_4)_2\text{SO}_4$,
1680 mg/l NaHCO_3 ,
289 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

-200 mg/l initial $\text{NH}_4\text{-N}$ concentration:

942.8 mg/l $(\text{NH}_4)_2\text{SO}_4$,
3360 mg/l NaHCO_3 ,
2578 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

-300 mg/l initial $\text{NH}_4\text{-N}$ concentration:

1414.2 mg/l $(\text{NH}_4)_2\text{SO}_4$,
5040 mg/l NaHCO_3 ,
8267 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

Table 3.1. Results of the experiments performed in the period of biofilm build up.

Days	NH ₄ -N, mg/l		Efficiency, %	Feeding Rate, l/day	Effluent pH
	Influent	Effluent			
0	91.8	58.2	37	15	-
3	98	63.8	35	15.3	8.56
4	-	-	-	4	-
5	98	52.4	47	15	-
6	98	51.8	47	13.3	8.48
7	-	-	-	13	-
8	96	54.3	44	14.5	-
10	91	52	43	13.4	-
11	-	-	-	17	8.44
12	92.1	55	40	13.9	8.48
13	-	-	-	13	-
14	95.8	53.5	44.2	13.6	8.54
19	-	-	-	11	8.58
20	-	-	-	13	-
21	96	38.2	60	13	8.54
24	96	44.2	54	13.3	8.56
25	-	-	-	12.3	-
26	96	41	57	13.8	8.36
27	-	-	-	13.8	8.15
28	-	-	-	-	-

Table 3.1. Continue

Days	NH ₄ -N, mg/l		Efficiency, %	Feeding Rate, l/day	Effluent pH
	Influent	Effluent			
30	-	-	-	13.2	8.12
31	83.2	2.2	99	13.2	-
32	-	-	-	13.2	-
33	190.2	6.44	97	13.5	-
34	-	-	-	-	8.01
35	-	1.35	99	13	7.9
38	195.4	45.9	77	13.3	8.35
39	-	-	-	13	8.22
40	-	21.1	89	12.3	-
45	166.3	3.9	98	13.8	-
46	-	-	-	15.7	-
47	289.5	4	99	14	8.12
48	-	-	-	14	-
49	274.4	2.8	99	12	-
52	-	6.7	98	12.7	-
53	275.2	-	-	14	8.34
54	-	-	-	0	-
55	-	-	-	14.2	8.16
56	-	4	98	13.5	-

Table 3.1. Continue

Days	NH ₄ -N, mg/l		Efficiency, %	Feeding Rate, l/day	Effluent pH
	Influent	Effluent			
59	388	-	-	12	-
60	-	-	-	12	-
61	396.8	3.1	99	13.5	-
62	-	-	-	12	-
63	397.6	3.92	99	12	8.15
66	385	3.9	99	16.3	8.16
67	-	-	-	14	-
68	-	4.3	99	13	8.10
69	-	-	-	14	-
70	-	-	-	13.9	8.00
73	479	7.1	99	13.3	-
74	-	-	-	14	-
75	-	-	-	13	8.1
76	-	5.2	99	13	8.00
77	-	-	-	13.4	-
107	476.4	1.4	99	12.6	8.12
111	431.9	2	99	-	7.51
112	475	5.6	99	-	-
113	-	-	-	11	-
115	407.6	5.9	98	11	-
118	-	-	-	11	7.20

Table 3.1. Continue

Days	NH ₄ -N, mg/l		Efficiency, %	Feeding Rate, l/day	Effluent pH
	Influent	Effluent			
119	574	12.3	98	16	7.20
120	-	-	-	14	8.20
121	-	-	-	16	-
122	546	12.3	98	13	-
125	565.6	44.8	92	12.9	8.28
126	-	-	-	13	-
127	554.4	46.5	92	12.5	8.24
128	-	-	-	13.5	-
129	546.2	67.2	88	12.6	8.30
132	571.2	73.9	87	13	-
133	-	-	-	5.4	-
134	-	-	-	12	-
135	-	-	-	16	-
136	529	102	81	14	8.36
139	570.4	128.8	77	13.3	8.06
140	624	142	77	14	8.6
141	-	-	-	14	-
142	-	-	-	14	-
143	591	169	71	14	8.54
146	568.4	209.4	63	14.1	-

Table 3.1. Continue

Days	NH ₄ -N, mg/l		Efficiency, %	Feeding Rate, l/day	Effluent pH
	Influent	Effluent			
147	-	-	-	12.4	-
148	-	-	-	12.7	8.7
149	586	210	64	14	8.74
150	-	209.5	-	13.5	8.74
153	470	126	74	8.25	8.80
154	-	-	-	7.7	-
155	456	134	71	7	8.80
156	-	-	-	8.1	-
157	426.2	103	76	6.35	8.80
160	426	79.5	81	7.8	8.80

-400 mg/l initial NH_4 -N concentration:

1885.6 mg/l $(\text{NH}_4)_2\text{SO}_4$,

6720 mg/l NaHCO_3 ,

1156 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

-500 mg/l initial NH_4 -N concentration:

2356 mg/l $(\text{NH}_4)_2\text{SO}_4$,

8400 mg/l NaHCO_3 ,

1445 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

-600 mg/l initial NH_4 -N concentration:

2828.4 mg/l $(\text{NH}_4)_2\text{SO}_4$,

10080 mg/l NaHCO_3 ,

1734 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

The speed of 15 rpm was chosen as the rotational speed of the disc. This speed was determined to be the optimum value in the previous work (Kinli, 1987) and the system was then kept at this value all through the study.

After 160 days of operation, sufficient amount of biofilm has developed on the discs and therefore RBC unit was decided to be ready for experimental study. In the literature, 2-3 months period was found to be enough for build up of biofilm in RBC (Collins et al, 1988).

3.2. Operation of the Experimental Set-up

After the build-up of biofilm has been completed, three sets of experiments were performed; firstly with NH_4 -N, secondly with NH_4 -N and fluoride and finally with NH_4 -N and hexavalent chromium.

3.2.1. Experiments Performed With $\text{NH}_4\text{-N}$:

In the experiments performed with $\text{NH}_4\text{-N}$, firstly a solution that contains 60 mg/l of $\text{NH}_4\text{-N}$ is filled to the reactor. Later, the system was operated on the basis of the batch reactor. Within the period of 7-7.5 hours, the samples were taken from a port at the bottom of the reactor and analysed for pH, dissolved oxygen, temperature, $\text{NH}_4\text{-N}$, nitrite, nitrate, phosphate, sulfate and chloride. At the end of the experiments, the reactor was emptied and filled again with a solution containing 10-15 mg/l of $\text{NH}_4\text{-N}$ and corresponding amounts of $(\text{NH}_4)_2\text{SO}_4$ and NaHCO_3 . Later, the system was fed continuously with a solution of 200 mg/l initial $\text{NH}_4\text{-N}$ concentration, and again corresponding amounts of $(\text{NH}_4)_2\text{SO}_4$ and NaHCO_3 at a rate of 1.25 l/hr. The solution was composed of 942.8 mg/l $(\text{NH}_4)_2\text{SO}_4$, 3360 mg/l NaHCO_3 , and 578 mg/l $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

Every other day or on the alternate days, samples from the exit of the system were taken and analysed till $\text{NH}_4\text{-N}$ concentration reached to about 5 mg/l (in other words, an efficiency of 97 per cent, $(200-5)/200 * 100 = 97\%$). It took about 2 days to 3 weeks to obtain 5 mg/l effluent $\text{NH}_4\text{-N}$ concentration. Once this value was obtained, the feeding to the reactor was stopped and the reactor was emptied to make it ready for another experiment. These operations were repeated for 80 and 120 mg/l $\text{NH}_4\text{-N}$ concentrations.

Experiments performed with $\text{NH}_4\text{-N}$ are summarized as follows;

- Runs 1,2- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$,
- Run 3 - Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$,
- Run 4 - Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$.

3.2.2. Experiments Performed With $\text{NH}_4\text{-N}$ and Fluoride:

In the experiments performed with $\text{NH}_4\text{-N}$ and fluoride, in order to determine the effect of fluoride concentration on $\text{NH}_4\text{-N}$ oxidation rate, for each 60, 80 and 120 mg/l of $\text{NH}_4\text{-N}$ concentrations, three different concentrations of fluoride in the range of 100-1000 mg/l were tested.

As in the experiments performed with $\text{NH}_4\text{-N}$, the reactor was filled with every $\text{NH}_4\text{-N}$ and fluoride concentrations after the system was stabilized. Then the reactor was operated on the basis of batch reactor. Within the period of 7-7.5 hours, the samples were taken from a port which was at the bottom of the reactor. Then, the samples were analysed for pH, dissolved oxygen, temperature, $\text{NH}_4\text{-N}$, nitrite, nitrate, phosphate, sulfate, chloride and fluoride. At the end of the experiments, the reactor was emptied and then filled with a solution containing 10-15 mg/l $\text{NH}_4\text{-N}$ concentration and corresponding amounts of $(\text{NH}_4)_2\text{SO}_4$ and NaHCO_3 . Later, the system was fed continuously with a solution of 200 mg/l $\text{NH}_4\text{-N}$ and again corresponding amounts of $(\text{NH}_4)_2\text{SO}_4$ and NaHCO_3 at a rate of 1.25 l/hr.

Every other day or on alternate days, the samples were collected at the exit of the reactor till $\text{NH}_4\text{-N}$ concentration reached to about 5 mg/l (in other words, an efficiency of 97 per cent). It took about 2 days to 3 weeks to obtain 5 mg/l effluent $\text{NH}_4\text{-N}$ concentration. Once this value was obtained, the feeding to the reactor was stopped and the reactor was emptied to make it ready for another experiment.

Experiments performed with $\text{NH}_4\text{-N}$ and fluoride are given as follows;

Run 5- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ and 200 mg/l fluoride,

Run 6- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ and 400 mg/l fluoride,

Run 7- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ and 800 mg/l fluoride,
Run 8- Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ and 200 mg/l fluoride,
Run 9- Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ and 500 mg/l fluoride,
Run 10- Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ and 800 mg/l fluoride,
Run 11- Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$ and 200 mg/l fluoride,
Run 12- Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$ and 600 mg/l fluoride,
Run 13- Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$ and 1000 mg/l fluoride.

3.2.3. Experiments Performed With $\text{NH}_4\text{-N}$ and Hexavalent Chromium:

In the experiments performed with $\text{NH}_4\text{-N}$ and hexavalent chromium, in order to determine the effect of hexavalent chromium concentration on $\text{NH}_4\text{-N}$ oxidation rate, for each of 60, 80 and 120 mg/l $\text{NH}_4\text{-N}$ concentration, three different concentration of hexavalent chromium ranging from 0 to 130 mg/l were tested.

As in the experiments with performed with $\text{NH}_4\text{-N}$ and fluoride, the reactor was filled with every $\text{NH}_4\text{-N}$ and hexavalent chromium concentrations after the system was stabilized. Then the reactor was operated on the basis of batch reactor. Within the period of 7-7.5 hours, the samples were taken from a port which was at the bottom of the reactor, and the samples were evaluated for pH, dissolved oxygen, temperature, $\text{NH}_4\text{-N}$, nitrite, nitrate, phosphate, sulfate, chloride and chromate (CrO_4).

At the end of the experiments, the reactor was emptied and then filled with a solution containing 10-15 mg/l $\text{NH}_4\text{-N}$ and corresponding amounts of $(\text{NH}_4)_2\text{SO}_4$ and NaHCO_3 . Later, the system was fed continuously with a solution of 200 mg/l $\text{NH}_4\text{-N}$ and again corresponding amounts of $(\text{NH}_4)_2\text{SO}_4$ and NaHCO_3 at a rate of 1.25 l/hr.

Every other day or on the alternate days, samples from the exit of the system were taken and analysed till $\text{NH}_4\text{-N}$ concentration reached to about 5 mg/l (in other words, an efficiency of 97 per cent). It took about 2 days to 3 weeks to obtain 5 mg/l effluent $\text{NH}_4\text{-N}$ concentration. Once this value was obtained, the feeding to the reactor was stopped and the reactor was emptied to make it ready for another experiment. These operations were repeated for 80 and 120 mg/l $\text{NH}_4\text{-N}$ concentrations.

Experiments performed with hexavalent chromium are given as follows;

Run 14- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ and 20 mg/l hexavalent chromium,

Run 15- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ and 50 mg/l hexavalent chromium,

Run 16- Experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ and 100 mg/l hexavalent chromium,

Run 17- Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ and 30 mg/l hexavalent chromium,

Run 18- Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ and 60 mg/l hexavalent chromium,

Run 19- Experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ and 100 mg/l hexavalent chromium,

Run 20- Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$ and 20 mg/l hexavalent chromium,

Run 21- Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$ and 75 mg/l hexavalent chromium,

Run 22- Experiments performed with 120 mg/l $\text{NH}_4\text{-N}$ and 125 mg/l hexavalent chromium.

CHAPTER 4. EXPERIMENTAL RESULTS

Experimental results are given in three parts; firstly as experimental results obtained with $\text{NH}_4\text{-N}$, secondly as experimental results obtained with $\text{NH}_4\text{-N}$ and fluoride, and finally as experimental results obtained with $\text{NH}_4\text{-N}$ and hexavalent chromium.

In the study, results of the experiments were found somewhat different from the amounts of the chemicals used in the solutions. This may be due to the technical grade chemicals used in the solutions, or dilution error during preparation of 30 l solutions.

4.1. Results of The Experiments Performed With $\text{NH}_4\text{-N}$:

Results of the experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ at an average bulk solution temperature of 12.2°C are given on Table 4.1. Results of the experiments performed with 60 mg/l $\text{NH}_4\text{-N}$ at an average bulk solution temperature of 18.75°C are given on Table 4.2. Results of the experiments performed with 80 mg/l $\text{NH}_4\text{-N}$ at an average bulk solution temperature of 19.7°C are given on Table 4.3. Finally, results of the experiments with 120 mg/l $\text{NH}_4\text{-N}$ at an average bulk solution temperature of 15.35°C are given on Table 4.4.

4.2. Results of The Experiments Performed With $\text{NH}_4\text{-N}$ and Fluoride:

The results of the experiments performed with $\text{NH}_4\text{-N}$ concentration of 60 mg/l and fluoride concentrations of 200, 400, and 800 mg/l are given in Tables 4.5, 4.6, and 4.7, respectively. Similarly, results of the experiments performed for 80 mg/l of $\text{NH}_4\text{-N}$ concentration and 200, 500, and 800 mg/l of fluoride concentrations are given in Tables 4.8, 4.9, and 4.10, respectively. Finally, results of the experiments performed for 120 mg/l of $\text{NH}_4\text{-N}$ concentration and 200, 600, and 1000 mg/l of fluoride concentrations are given in Tables 4.11, 4.12, and 4.13, respectively.

4.3. Results of The Experiments Performed With $\text{NH}_4\text{-N}$ and Hexavalent Chromium:

The results of the experiments performed with $\text{NH}_4\text{-N}$ concentration of 60 mg/l and hexavalent chromium concentrations of 20, 50, and 100 mg/l are given in Tables 4.14, 4.15, and 4.16, respectively. Similarly, results of the experiments performed for 80 mg/l of $\text{NH}_4\text{-N}$ concentration and 30, 60, and 100 mg/l of hexavalent chromium concentrations are given in Tables 4.17, 4.18, and 4.19, respectively. Finally, results of the experiments performed with 120 mg/l of $\text{NH}_4\text{-N}$ concentration and hexavalent chromium concentrations of 20, 75, and 125 mg/l are given in Tables 4.20, 4.21, and 4.22, respectively.

Table 4.1. Experimental results obtained at an average bulk solution temperature of 12.2 °C with 60 mg/l $\text{NH}_4\text{-N}$.

Duration	pH	D.O., mg/l	T, °C	$\text{NH}_4\text{-N}$, mg/l	NO_2^- , mg/l	$\text{NO}_2\text{-N}$, mg/l	NO_3^- , mg/l	$\text{NO}_3\text{-N}$, mg/l	TotalN, mg/l	PO_4^- , mg/l	SO_4^- , mg/l	Cl, mg/l
0	7.93	8.75	-	64.1	6.9	2.1	108.1	24.4	90.6	156.7	321.7	30
2	7.90	7.6	11.6	49.1	28	8.5	152.4	34.4	92	158.3	318.5	25.3
4	7.80	7.4	12.4	31.7	31.7	9.6	217.8	49.2	90.5	165	320.1	24.1
6	7.70	7.3	12.6	14.4	29.6	9	294.7	66.5	89.9	167.9	329.8	25.2
7.5	8.03	7.3	12.2	5	28.6	8.7	338	76.3	90	166.2	358.7	35.1

Table 4.2. Experimental results obtained at an average bulk solution temperature of 18.75°C with 60 mg/l $\text{NH}_4\text{-N}$

Duration	pH	D.O. mg/l	T, °C	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.78	8.50	-	57.1	-	-	72.8	16.4	73.5	131.4	275.8	29.3
2	7.66	8.4	18.6	27	71.6	21.8	99	22.4	71.2	130.5	275.1	23.4
4	7.59	5.85	18.8	2.4	137	41.6	119	27	71	134.5	274.1	31
6	8.06	7.9	18.8	0.9	119	36.3	138	31.2	68.4	132.9	275.8	-
7.5	8.19	8.8	18.8	0	28.9	8.8	275.3	62.2	71	132.4	278.8	28.5

Table 4.3. Experimental results obtained at an average bulk solution temperature of 19.7°C with 80 mg/l of $\text{NH}_4\text{-N}$.

Duration	pH	D.O. mg/l	T, °C	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.85	8.75	-	81.3	-	-	69.7	15.7	97	157.8	370.4	30.7
2	7.86	5.4	20.0	50.6	78.8	24	90.8	20.5	95.1	162.8	375.6	23.6
4	7.77	5.30	19.8	12.6	147.9	45	108	24.4	82	160	372.1	-
6	7.86	5.85	19.8	0.8	162.6	49.5	169.1	38.2	88.5	163.3	379.2	-
7.5	8.19	7.0	19.2	0.3	65.5	19.9	301.6	68.1	88.3	165.8	386	25.3

Table 4.4. Experimental results obtained at an average bulk solution temperature of 15.35°C with 120 mg/l $\text{NH}_4\text{-N}$.

Duration	pH	D.O. mg/l	T, °C	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.82	8.9	-	116.1	-	-	72.1	16.3	132.4	168.2	494.7	31.4
2	7.93	6.1	15	89.2	75.9	23.1	99.7	22.5	134.8	184.2	529.5	29.9
4	7.91	6	15.5	64.7	134.3	40.9	119.4	27	132.6	183.2	503.5	-
6	7.84	5.96	16.3	39.3	192.4	58.6	140.1	31.6	129.5	186.5	534.9	-
7.5	7.82	6.05	14.6	18.3	229.1	69.7	156.1	35.2	123.2	185.3	522.4	-

Table 4.5. Experimental results obtained at 60 mg/l $\text{NH}_4\text{-N}$ concentration and 200 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.80	9.10	-	221	64	43.8	13.3	67.8	15.3	92.6	171.6	323	-
2	7.77	5.75	16.6	187.1	43.8	74.6	22.7	108	24.4	90.9	159	332.7	-
4.5	7.63	5.55	16.6	179.3	12.5	129.1	39.3	146.2	33	84.8	192.2	322.6	-
6	7.80	6.60	16.6	169.9	1.1	134	40.8	216.1	48.8	90.7	161.4	327.5	-
7.5	8.5	8.25	15	190.3	0.3	71.3	21.7	312.3	70.6	92.6	162.4	317.7	-

Table 4.6. Experimental results obtained at 60 mg/l $\text{NH}_4\text{-N}$ concentration and 400 mg/l fluoride concentration

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.77	9.35	-	420.7	58.5	26.6	8.1	66.7	15.1	81.7	131.7	290.5	-
2	7.80	5.65	17.5	387.8	30.8	94.6	28.8	98	22.1	81.7	148	294.6	-
4	7.60	5.55	17.8	340.4	4.9	141.9	43.2	148.8	33.6	81.7	191.1	320.5	-
6	8.02	7.60	18	370	0.98	65.5	19.9	269.2	60.8	81.7	164.1	293.6	-
7.5	8.20	8.95	17.8	350.2	0.28	50.7	15.4	292.5	66	81.7	154.4	282	-

Table 4.7. Experimental results obtained at 60 mg/l $\text{NH}_4\text{-N}$ concentration and 800 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.75	8.6	-	750.6	54.6	-	-	158.6	35.8	90.4	132	272.8	-
2	7.80	5.95	17.2	713.9	29.8	62.1	18.9	186.5	42.1	90.8	101.7	276.6	-
4	7.74	6	17	668.4	8	109.7	33.4	218.8	49.4	90.8	173.13	275	-
6	8.06	8	16.5	691.2	0.6	100.9	30.7	263.7	59.5	90.8	181.3	274.2	-
7.5	8.25	9.1	16.6	689.7	0.7	76.2	23.2	296.1	66.9	90.8	179.3	276.2	-

Table 4.8. Experimental results obtained at 80 mg/l $\text{NH}_4\text{-N}$ concentration and 200 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.89	9.20	-	166.8	81.6	14.1	4.3	75.2	17.1	103	156.4	378.3	-
2	7.88	6.20	15.5	162.5	58.1	84.5	25.7	100.1	22.6	106.4	161.4	387.1	42.8
4	7.84	6.05	15.6	158.4	35.2	125.8	38.8	127.6	28.8	102.3	166.9	384.2	41.4
6	7.75	6.30	15.6	159.1	14.5	166.5	50.7	163.1	36.8	102	165.7	394.6	38.6
7.5	7.76	6.95	16.5	159.5	1.68	171.1	52.1	209.2	47.3	101.1	166.3	390.8	36.8

Table 4.9. Experimental results obtained at 80 mg/l $\text{NH}_4\text{-N}$ concentration and 500 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.91	8.85	-	513.2	81.9	6.9	2.1	103.1	23.3	107.3	232.9	394.8	-
2	7.9	5.75	16.0	490.2	57.7	69.3	21.1	126	28.5	107.3	248.7	390.8	-
4	7.82	5.70	16.5	442.6	31.6	158.8	48.3	126.5	28.6	108.5	182.1	385	-
6	7.71	5.59	16	426.4	6.72	219	66.7	148.6	33.6	107	186.5	382.9	-
7.5	8.01	7.65	15	435.5	0.84	178.2	54.2	273.4	51.3	106.3	191.5	387.4	-

Table 4.10. Experimental results obtained at 80 mg/l $\text{NH}_4\text{-N}$ concentration and 800 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.81	8.50	-	783	84.4	71	21.6	69.9	15.8	121.8	170.9	400.5	-
2	7.87	5.55	16.5	762.1	56.4	77.2	23.5	185.4	41.9	121.8	174.2	390.1	-
4	7.82	5.60	17	686.9	31.1	178.5	54.3	193.6	43.7	129.1	215.4	380	-
6	7.70	5.59	16.8	671	5.6	227	69.1	178.1	40.2	114.9	238.4	382.7	-
7.5	8.00	7.15	16.8	710.4	0.8	194.8	59.3	273.4	61.7	121.8	208.8	388.7	-

Table 4.11. Experimental results obtained at 120 mg/l $\text{NH}_4\text{-N}$ concentration and 200 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.97	9.4	-	174.8	105.7	83.4	25.4	62.7	14.2	145.3	198.8	462.9	-
2	8.02	6.45	13.2	186.8	83.5	137.3	41.8	64.5	14.6	139.9	192.1	466.8	-
4	7.96	6.30	14.5	182.7	60.7	192	58.4	76.5	17.3	136.4	189.2	456.3	-
6	7.94	6.30	13.9	181.1	38.6	260.6	79.3	85.8	19.4	137.3	189.4	454.6	-
7.5	7.88	6.20	14.7	184.3	19.2	313.3	95.4	101. 5	22.9	137.5	199.3	475.9	-

Table 4.12. Experimental results obtained at 120 mg/l $\text{NH}_4\text{-N}$ concentration and 600 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.93	9.9	-	566.4	116.2	53.6	16.3	51.2	11.6	144.1	178.4	484	-
2	7.98	7.3	12	598.1	92.1	116.3	35.4	73.7	16.6	144.1	178.4	484	-
4	7.92	7.0	13	602.2	73.4	166.4	50.6	96.5	21.8	145.8	192.6	481.2	-
6	7.94	6.7	14	545.6	51.5	220.5	67.1	118.4	26.7	145.3	203.4	493	-
7.5	7.85	6.55	14	539.7	34.4	257.7	78.4	126.9	28.7	141.2	201.7	482.4	-

Table 4.13. Experimental results obtained at 120 mg/l $\text{NH}_4\text{-N}$ concentration and 1000 mg/l fluoride concentration.

Duration	pH	D.O. mg/l	T, °C	F, mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.85	10.6	-	989.7	114.5	-	-	69.7	15.7	130.2	179.2	479	-
2	8.03	8.15	9	945	94	30.9	9.4	118.5	26.8	130.2	-	474	-
4	8.00	8.05	9.6	939	80.4	69.3	21.1	127.1	28.7	130.2	216.1	477.5	-
6	7.97	7.85	9.6	948.6	62.9	107.4	32.7	153.3	34.6	130.2	218.8	469.6	-
7.5	7.94	7.85	9.5	943.5	49.6	132.1	40.2	178.7	40.4	130.2	222.5	465.9	-

Table 4.14. Experimental results obtained at 60 mg/l $\text{NH}_4\text{-N}$ concentration and 20 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.81	9.7	-	46.7	20.9	61.04	13.8	4.2	87.6	19.8	85	120.4	314.8	29.5
2	7.85	7.7	12	36.2	16.2	47.7	19.9	6.1	137.3	31	84.7	121	324.8	21.1
4	7.82	7.35	12.5	45	20.2	29.1	30.5	9.3	205.8	46.5	84.9	128.4	336.7	25.4
6	7.71	7.3	-	44	19.7	15.7	29.4	8.9	269	60.7	85.3	131.1	315.4	21.6
7.5	7.82	8.0	12	44	19.7	6.45	12.2	3.7	331.7	74.9	85	133.2	322.6	27.3

Table 4.15. Experimental results obtained at 60 mg/l $\text{NH}_4\text{-N}$ concentration and 50 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.44	7.75	-	121.2	54.3	54.5	33.2	10.1	68.1	15.4	80	104.6	-	-
2	7.50	7.70	19.2	121.2	54.6	30.8	69.2	21.1	114.5	25.9	77.8	113.8	311	24.1
4	7.55	5.95	19	113.9	51.1	9.1	103.4	31.5	166.8	37.7	78.3	114.6	306.5	23.8
6	7.90	8.20	19	118.5	53.1	0.56	28.1	8.6	328.1	74.1	83.3	114.6	310.4	25.4
7.5	8.04	9.75	19	138.4	62	0.17	4.6	1.4	352.6	79.6	81.2	114.2	310.8	32.7

Table 4.16. Experimental results obtained at 60 mg/l $\text{NH}_4\text{-N}$ concentration and 100 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.31	9.3	-	227.2	101.8	58.88	4.9	1.5	59.2	13.4	73.8	99.8	293.2	28.5
2	7.67	9.7	14.9	237.3	106.4	39.9	25.7	7.8	111.9	25.3	73	111.2	282.1	23
4	7.71	9.6	15.3	228.6	102.5	30.8	17.1	5.2	181.7	41	77	116	274.7	19.8
6	7.62	9.4	15.5	238.5	106.9	14	15	4.6	248	56	74.6	123.5	310	42.3
7.5	7.63	8.4	16.2	209	93.7	6.16	14.2	4.3	266.4	60.2	70.7	116.5	286.5	30.3

Table 4.17. Experimental results obtained at 80 mg/l $\text{NH}_4\text{-N}$ concentration and 30 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.73	8.75	-	69.1	31	85.4	-	-	116.9	26.4	111.8	121.9	379.9	29.2
2	7.90	6.05	16.6	51.1	22.9	61	29	8.8	188.1	42.5	112.3	119.9	388.1	23.3
4	7.85	6.10	16.6	47	21.1	43.5	33.7	10.3	277.7	62.7	116.5	119.3	388.5	23.8
6	7.82	5.95	16.1	37.9	17	25.2	31.2	7.1	367.3	82.9	115.2	122.5	390.2	29.8
7.5	7.75	6.2	16	43.3	19.4	11.6	21.3	4.8	437.5	98.8	115.2	116.2	386.9	22.8

Table 4.18. Experimental results obtained at 80 mg/l $\text{NH}_4\text{-N}$ concentration and 60 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.48	8.55	-	146.8	65.8	79.6	-	-	156.4	35.3	114.9	122.1	380.9	27.9
2	7.92	6.80	14.8	129.5	58.1	61.5	22.9	7	216.8	49	117.5	123	389.3	22.9
4	7.88	6.7	15.2	134.4	60.3	46.7	20.1	6.1	286.5	64.7	117.5	120.6	384.9	23.5
6	7.82	6.75	15.2	135.8	60.9	29	39.4	12	336.6	76	117	121.8	391	26.7
7.5	7.78	6.78	15	148.8	66.7	17.4	18	9.6	398.6	90	117	121	394.2	34.8

Table 4.19. Experimental results obtained at 80 mg/l $\text{NH}_4\text{-N}$ concentration and 100 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.47	9.3	-	238.6	107	80.1	14.8	4.5	99.1	22.4	107	139.4	412.5	21.9
2	7.88	6.45	16.3	244.2	109.5	60.8	24.9	7.6	174.1	39.3	107.7	141.1	419.7	22.4
4	7.88	6.4	16.4	223.5	100.2	41.9	23.2	7.1	245.5	55.4	104.4	138.5	412.8	21.6
6	7.83	6.4	16.5	248.6	111.4	27.4	19.3	5.9	332.3	76.4	109.7	138.8	418.7	22.1
7.5	7.76	6.32	16.5	245.2	109.9	14	17.7	5.4	407.9	92.1	111.5	137.6	417.8	22.3

Table 4.20. Experimental results obtained at 120 mg/l $\text{NH}_4\text{-N}$ concentration and 20 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.84	9.8	-	41.9	18.8	107.5	3.6	1.1	63.7	14.4	123	151.8	498.1	29.6
2	7.96	6.85	11.2	48.1	21.6	86.5	68.6	20.9	77.5	17.5	124.9	149.1	504.4	19.5
4	7.93	6.65	12.5	44.7	20	62.2	124.5	37.9	90.7	20.5	120.6	148.8	504.9	20.3
6	7.92	6.25	14	38.7	17.3	39.2	197.8	60.2	104.7	23.6	123	148.8	503.8	-
7.5	7.76	6.45	13.5	38.7	17.3	17.1	260.2	79.2	117.5	26.5	122.8	152.8	503.8	-

Table 4.21. Experimental results obtained at 120 mg/l $\text{NH}_4\text{-N}$ concentration and 75 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.67	8.7	-	186.6	83.6	112.6	18.7	5.7	55	12.4	130.7	150.7	517.3	20.9
2	7.87	6.2	13.5	184.8	82.8	92.4	78.5	23.9	69.7	15.7	132	158.8	518.7	17.2
4	7.87	6.5	13.5	169.6	76	66.9	140.7	42.8	98.6	22.3	132	162.8	513.5	-
6	7.89	6.9	14.5	181.7	81.5	50.4	159	48.4	140.8	31.8	130.6	162.4	505.4	-
7.5	7.85	7.0	14.5	179.4	80.4	38.4	167.5	51	188.6	42.6	132	165.5	514.1	-

Table 4.22. Experimental results obtained at 120 mg/l $\text{NH}_4\text{-N}$ concentration and 125 mg/l hexavalent chromium concentration.

Duration	pH	D.O. mg/l	T, °C	CrO_4 mg/l	Cr^{+6} mg/l	$\text{NH}_4\text{-N}$ mg/l	NO_2 mg/l	$\text{NO}_2\text{-N}$ mg/l	NO_3 mg/l	$\text{NO}_3\text{-N}$ mg/l	Total N,mg/l	PO_4 mg/l	SO_4 mg/l	Cl mg/l
0	7.55	8.95	-	279.1	125.1	111.4	22.9	7	49.4	11.2	129.6	137.3	504.7	21.7
2	7.93	6.5	14	281.9	126.4	91	73.3	22.3	68.7	15.5	128.8	144.6	500	19.5
4	7.92	6.6	15	285.4	127.9	72.8	103.6	31.5	110.4	24.9	129.2	154.8	511.9	19.3
6	7.92	6.45	15.5	286.5	128.4	56.6	111	33.8	166.5	37.6	128	155	518	20.8
7.5	7.90	6.6	15.5	280.7	125.8	46.8	110.3	33.6	210.7	47.6	128	155.1	519.9	19.8

CHAPTER 5. DISCUSSION OF RESULTS

5.1. $\text{NH}_4\text{-N}$ Oxidation Rate

The residual $\text{NH}_4\text{-N}$ concentration versus reaction time for four experimental runs performed at 60, 60, 80 and 120 mg/l initial $\text{NH}_4\text{-N}$ concentrations are shown on Figure 5.1. Experimental results related with these runs (Table 4.1 to 4.4) are summarized on Table 5.1. It can be seen from Figure 5.1 that the change of residual $\text{NH}_4\text{-N}$ concentration against reaction time is linear up to 5 to 10 mg/l $\text{NH}_4\text{-N}$ concentration. And then, it becomes nonlinear.

Another thing that can be seen from Figure 5.1 is that, the slopes of the lines are not equal to each other. Beg and Others (1982) have found that nitrification reaction is a zero order reaction at 60 and 120 mg/l initial $\text{NH}_4\text{-N}$ concentrations in their similar study performed with fixed-bed reactor at ambient temperature of $26 \pm 1^\circ\text{C}$. Also in this case, nitrification reaction can be accepted as a zero order reaction. It can be seen from Table 5.1 that nitrification rates do not increase or decrease with the increase in initial $\text{NH}_4\text{-N}$ concentrations and nitrification reaction rates for two experiments performed with 60 mg/l initial $\text{NH}_4\text{-N}$ concentrations are different from each other. Nitrification reaction rate changes independently from the initial $\text{NH}_4\text{-N}$ concentrations. Therefore in this case nitrification can be accepted as a zero order reaction in parallel with Beg and Others (1982).

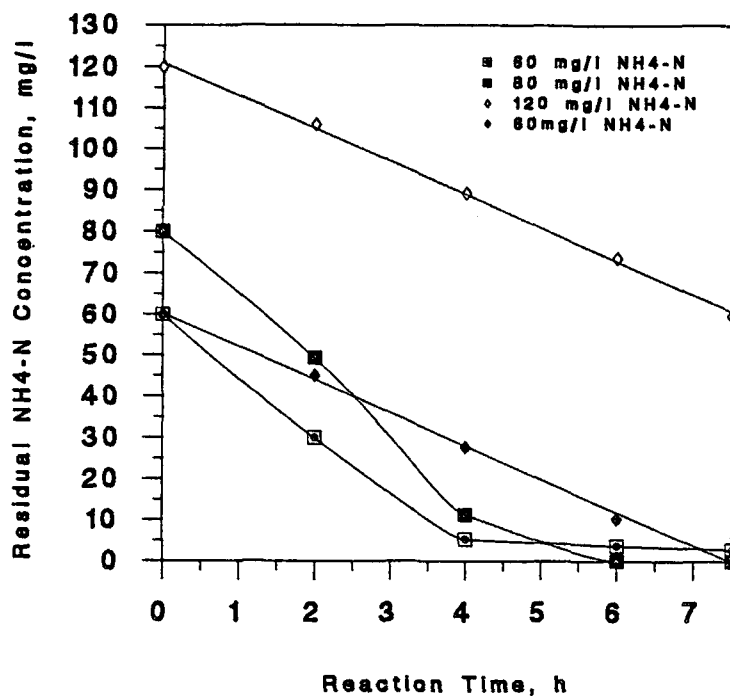


Figure 5.1. Typical $\text{NH}_4\text{-N}$ oxidation profile

Table 5.1. Experimental results related with Figure 5.1.

$\text{NH}_4\text{-N}$, mg/l	pH	Dissolved Oxygen,mg/l	Temperature, $^{\circ}\text{C}$ (Avg.)	Rate of oxidation mg $\text{NH}_4\text{-N}$ /l.hr
60	7.70-8.03	7.3-8.75	12.2	8
60	7.59-8.20	5.85-8.8	18.75	13.68
80	7.77-8.19	5.3-8.75	19.7	17.17
120	7.82-7.93	5.96-8.9	15.35	12.91

It can be seen from Table 5.1 that bulk solution pH and dissolved oxygen concentrations at each experimental run varied at the levels in which nitrification reaction rate is not affected. Therefore, it can be concluded that nitrification reaction rate is independent of initial $\text{NH}_4\text{-N}$ concentrations and depends on bulk solution temperature. It increases with increase in temperature.

Change of $\text{NH}_4\text{-N}$ oxidation rate against bulk solution temperature are shown on Figure 5.2. It can be seen from Figure 5.2 that $\text{NH}_4\text{-N}$ oxidation rate increases linearly with the bulk solution temperature.

In the experimental study, RBC was placed on a laboratory and operated at room temperature. For this reason, any change at room temperature caused a change on the $\text{NH}_4\text{-N}$ oxidation rate. This was a great problem faced in the experimental study. In order to solve this problem, Figure 5.2 was used as a reference plot for the whole experimental study including experiments performed with fluoride and experiments performed with hexavalent chromium. By using average bulk solution temperature for the experimental runs performed with fluoride or hexavalent chromium, reference $\text{NH}_4\text{-N}$ oxidation rates were found from Figure 5.2 and compared with the experimental $\text{NH}_4\text{-N}$ oxidation rates.

5.2. Effect of Fluoride on $\text{NH}_4\text{-N}$ Oxidation Rate

In the experiments performed with fluoride, residual $\text{NH}_4\text{-N}$ concentration changed linearly against reaction time and was found as dependent on the temperature of bulk solution, as it was the case in Section 5.1.

Change in residual $\text{NH}_4\text{-N}$ concentration against reaction time for the experimental runs with 60, 80 and 120 mg/l of initial $\text{NH}_4\text{-N}$ concentrations are

shown on Figures 5.3, 5.4, and 5.5, respectively. The experimental results related with these runs (Table 4.5-4.13) are summarized on Table 5.2. As can be seen from Table 5.2, the effect of fluoride on $\text{NH}_4\text{-N}$ oxidation was found to be dependent on initial $\text{NH}_4\text{-N}$ concentration in the system. By using the average bulk solution temperature for each experimental runs with fluoride, reference $\text{NH}_4\text{-N}$ oxidation rates was found from Figure 5.2. Experimental and corresponding reference $\text{NH}_4\text{-N}$ oxidation rates against fluoride concentration are shown schematically on Figures 5.6, 5.7, and 5.8.

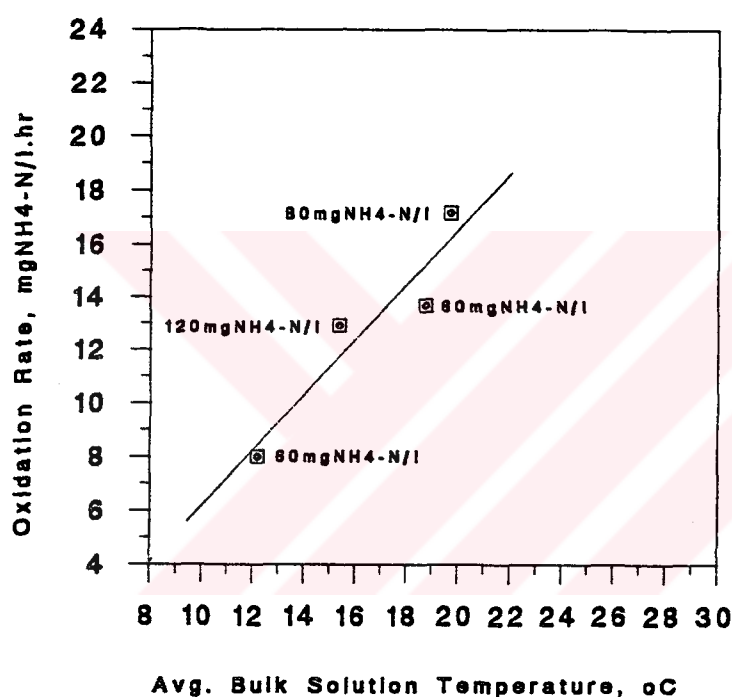


Figure 5.2. Change of $\text{NH}_4\text{-N}$ oxidation rate against average bulk solution temperature in the solutions which do not contain fluoride and hexavalent chromium.

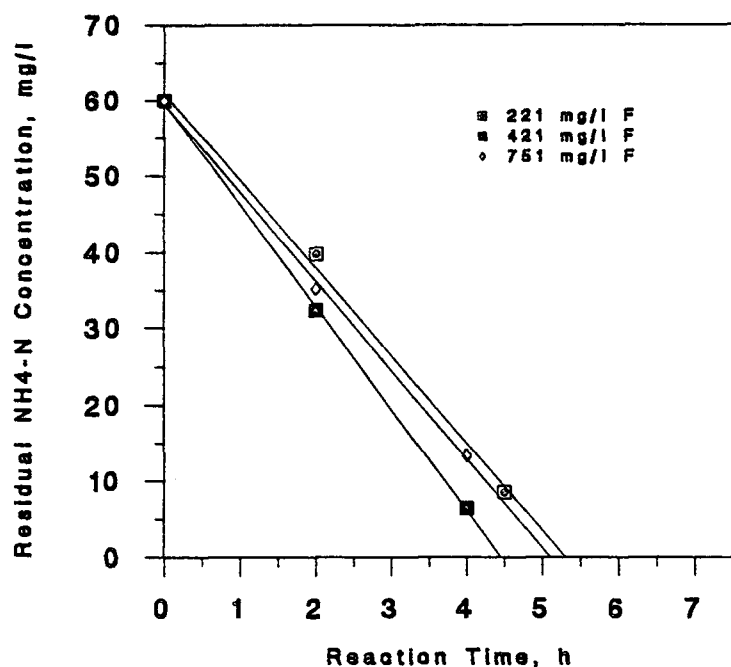


Figure 5.3. Effect of fluoride on $\text{NH}_4\text{-N}$ oxidation profile for an initial $\text{NH}_4\text{-N}$ concentration of 60 mg/l.

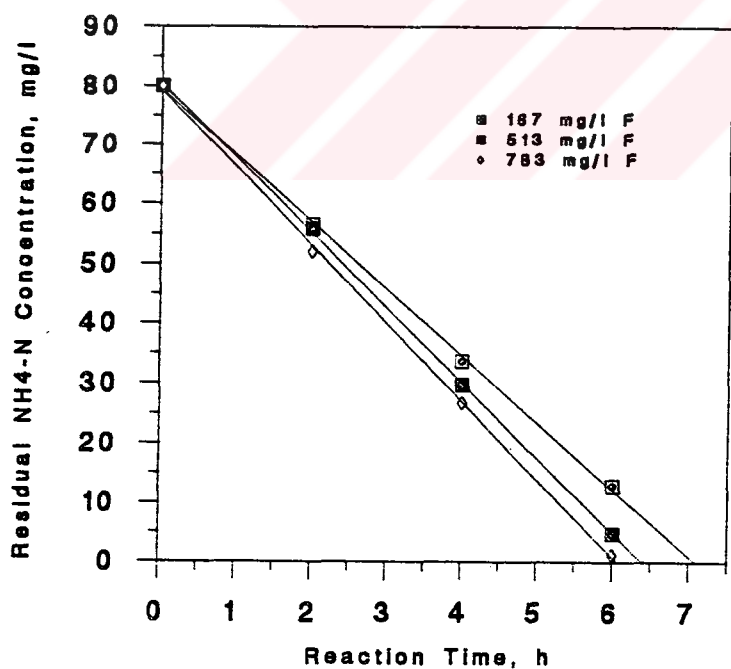


Figure 5.4. Effect of fluoride on $\text{NH}_4\text{-N}$ oxidation profile for an initial $\text{NH}_4\text{-N}$ concentration of 80 mg/l.

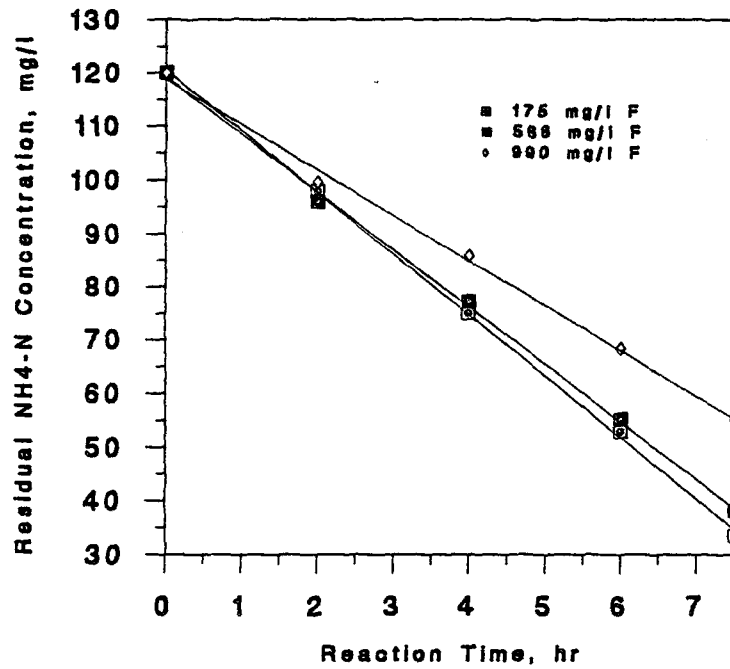


Figure 5.5. Effect of fluoride on $\text{NH}_4\text{-N}$ oxidation profile for an initial $\text{NH}_4\text{-N}$ concentration of 120 mg/l.

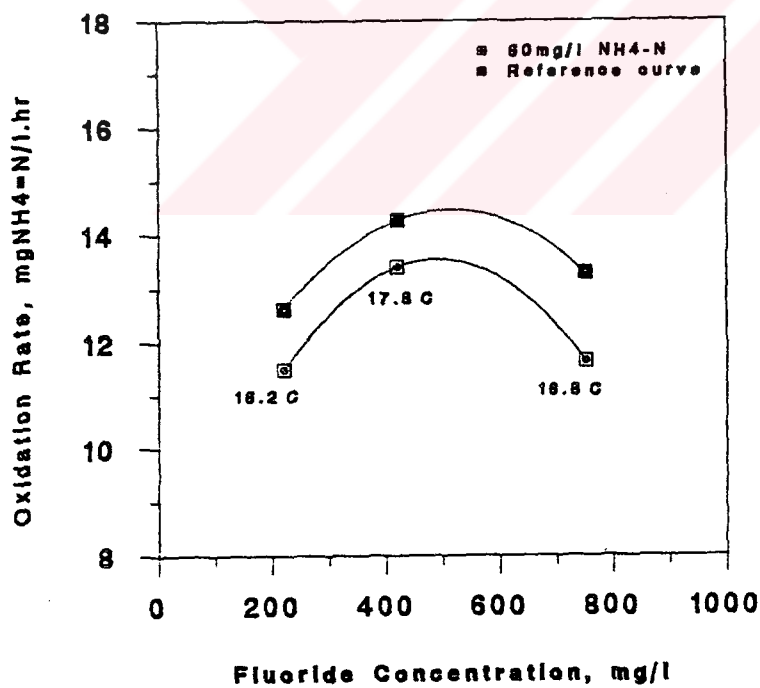


Figure 5.6. Experimental and reference oxidation rates in the solutions which contain 60 mg/l $\text{NH}_4\text{-N}$ and fluoride.

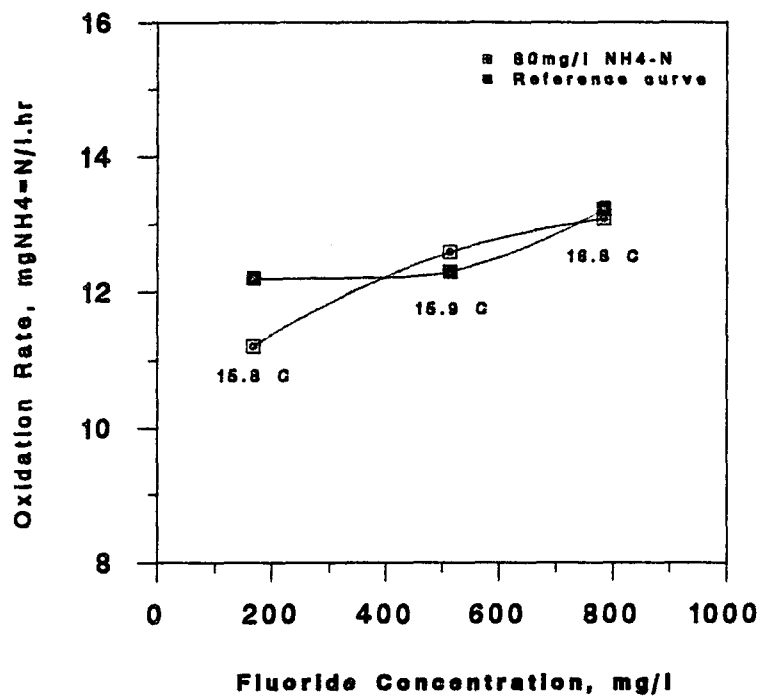


Figure 5.7. Experimental and reference oxidation rates in the solutions which contain 80 mg/l NH₄-N and fluoride.

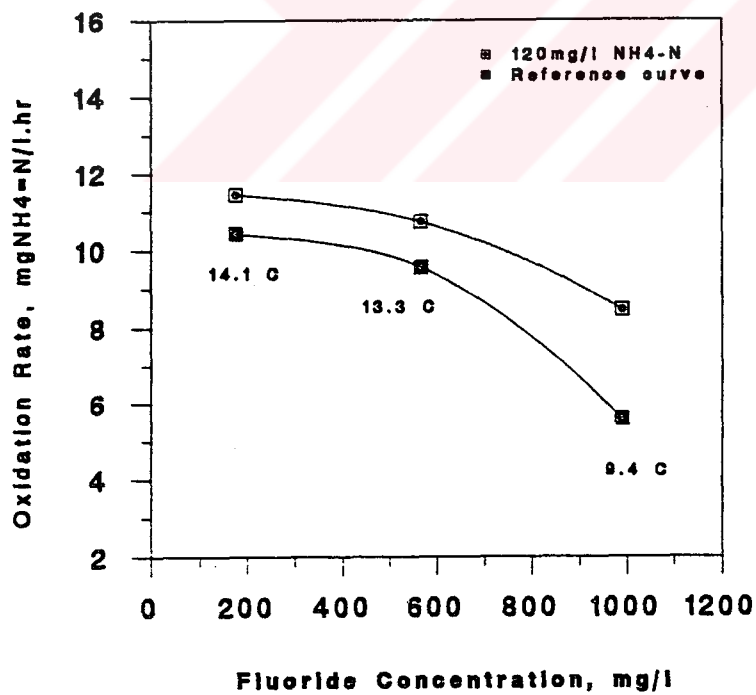


Figure 5.8. Experimental and reference oxidation rates in the solutions which contain 120 mg/l NH₄-N and fluoride.

Table 5.2. Experimental results related with Figures 5.3, 5.4, 5.5, 5.6, 5.7 and 5.8.

NH ₄ -N mg/l	F, mg/l	pH	D.O., mg/l	T,°C (Avg.)	Rate of Oxidat. <u>mgNH₄-N</u> l.hr	Ref. Rate, <u>mgNH₄-N</u> l.hr
60	221	7.63-8.50	5.55-9.10	16.2	11.49	12.63
	421	7.60-8.20	5.55-9.35	17.78	13.40	14.27
	751	7.74-8.25	5.95-9.10	16.83	11.65	13.29
80	167	7.75-7.89	6.05-9.20	15.8	11.21	12.2
	513	7.71-8.01	5.59-8.85	15.88	12.59	12.3
	783	7.70-8.00	5.55-8.50	16.78	13.09	13.23
120	175	7.94-8.02	6.20-9.40	14.08	11.45	10.43
	566	7.85-7.98	6.55-9.90	13.25	10.74	9.57
	990	7.85-8.03	7.85-10.6	9.42	8.42	5.59

As it can be seen from Figure 5.6, in the experimental runs performed with 60 mg/l initial NH₄-N concentration, fluoride caused inhibition on NH₄-N oxidation rate at all tried fluoride concentrations. Due to this reason, the plot of the reference NH₄-N oxidation rates was found above the plot of the experimental NH₄-N oxidation rates. At fluoride concentrations of 221, 421, and 753 mg/l, the inhibition values were found as 9.6 and 14 per cent, respectively.

However, as it can be seen from Figure 5.7, in the experimental runs performed with 80 mg/l initial NH₄-N concentration, the inhibition effect of fluoride on NH₄-N oxidation rate was found to be decreased and even disappeared. This case can be observed if fluorides 5.6 and 5.7 are

compared. At 167 mg/l of fluoride concentration, the inhibition was 8%, 513 mg/l fluoride concentration increased the oxidation by 2.3%, and 783 mg/l fluoride concentration again caused 1% inhibition. Depending on the experimental results, it was concluded that the effect of fluoride concentration on inhibition is minor. In other words, it does not effect the $\text{NH}_4\text{-N}$ oxidation rate neither in positive nor in negative manner. As can be seen from Figure 5.8, in the experiments performed with 120 mg/l initial $\text{NH}_4\text{-N}$ concentration, the effect of fluoride was found in the positive manner. At fluoride concentrations of 175, 566, and 990 mg/l, the $\text{NH}_4\text{-N}$ oxidation rates was found to be increased by 9, 11, and 33.6%, respectively.

As a summary, in the experiments which were carried out in the existence of fluoride in the bulk solution, residual $\text{NH}_4\text{-N}$ concentration was found to be decreasing linearly with the reaction time and $\text{NH}_4\text{-N}$ oxidation rate has been affected from the average temperature of the bulk solution. Besides, it was also observed that, the inhibition effect of fluoride was very closely related to the initial $\text{NH}_4\text{-N}$ concentration. As the initial $\text{NH}_4\text{-N}$ concentration was increased from 60 to 120 mg/l, the inhibition effect of fluoride was decreasing, disappearing and finally increasing, respectively. Therefore it was concluded that inhibition effect of fluoride depends on initial $\text{NH}_4\text{-N}$ concentration and decreases with increase in initial $\text{NH}_4\text{-N}$ concentration.

5.3. Effect of Hexavalent Chromium on $\text{NH}_4\text{-N}$ Oxidation Rate

In the experiments performed with hexavalent chromium, residual $\text{NH}_4\text{-N}$ concentration changed linearly against reaction time and was found as dependent on bulk solution temperature, as it was the case in Section 5.1 and 5.2. Change in residual $\text{NH}_4\text{-N}$ concentration against reaction time for the experimental runs with 60, 80, and 120 mg/l initial $\text{NH}_4\text{-N}$ concentrations are

shown on Figures 5.9, 5.10 and 5.11, respectively. The experimental results related with these runs (Tables 4.14-4.22) are summarized on Table 5.3.

As it can be seen from Table 5.3, the effect of hexavalent chromium on $\text{NH}_4\text{-N}$ oxidation was found to be dependent on the initial $\text{NH}_4\text{-N}$ concentration in the system. However, this relation was not so clear as it was the case for fluoride. By using the average bulk solution temperature for each experimental run with hexavalent chromium, reference $\text{NH}_4\text{-N}$ oxidation rates were found from Figure 5.2. Experimental and corresponding reference $\text{NH}_4\text{-N}$ oxidation rates against hexavalent chromium concentration are shown schematically on Figures 5.12, 5.13, and 5.14.

As it can be seen from Figures 5.12 and 5.13, for the initial $\text{NH}_4\text{-N}$ concentrations of 60 and 80 mg/l, hexavalent chromium concentrations in the

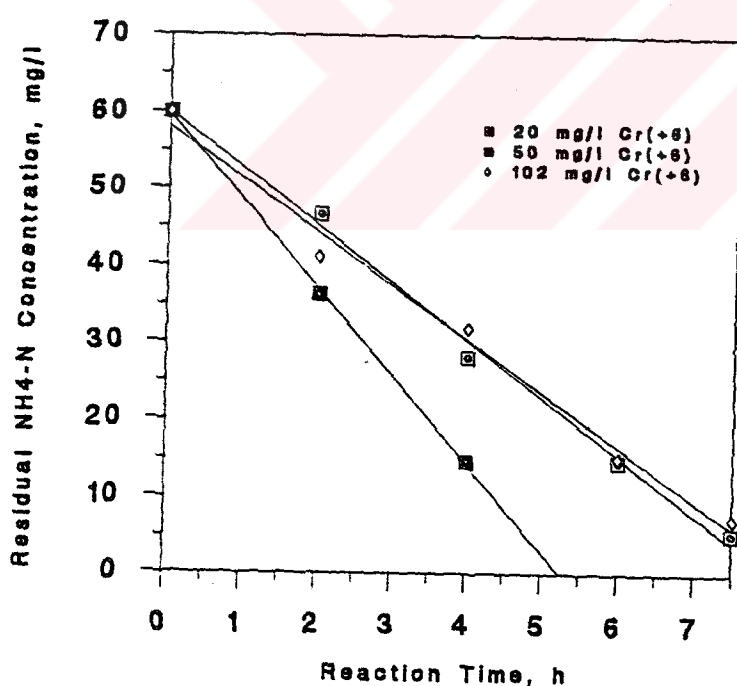


Figure 5.9. Effect of hexavalent chromium on $\text{NH}_4\text{-N}$ oxidation profile for an initial $\text{NH}_4\text{-N}$ concentration of 60 mg/l.

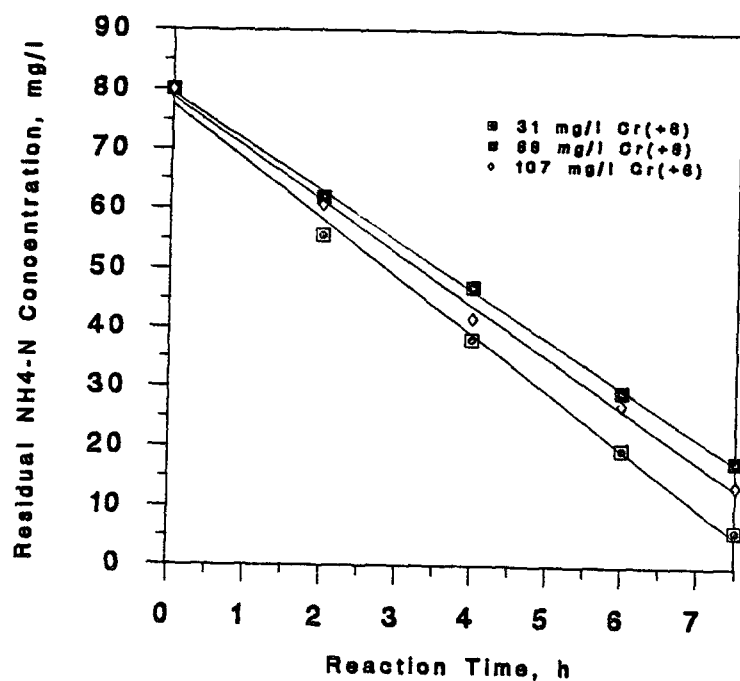


Figure 5.10. Effect of hexavalent chromium on $\text{NH}_4\text{-N}$ oxidation profile for an initial $\text{NH}_4\text{-N}$ concentration of 80 mg/l.

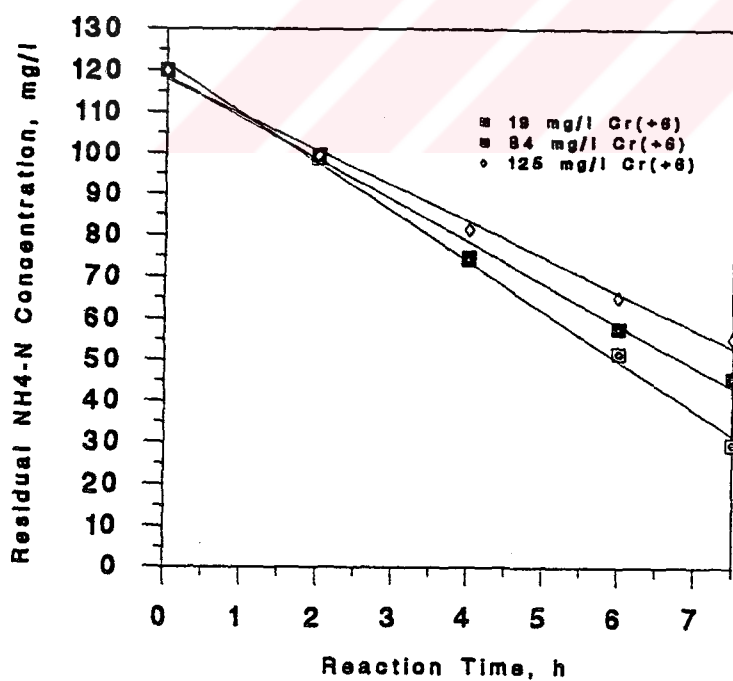


Figure 5.11. Effect of hexavalent chromium on $\text{NH}_4\text{-N}$ oxidation profile for an initial $\text{NH}_4\text{-N}$ concentration of 120 mg/l.

Table 5.3. Experimental results related with Figure 5.9, 5.10, 5.11, 5.12, 5.13 and 5.14.

NH ₄ -N mg/l	Cr ⁺⁶ mg/l	pH	D.O. mg/l	T.°C (Avg.)	Rate of Oxidat. <u>mgNH₄-N</u> l.hr	Ref. Rate, <u>mgNH₄-N</u> l.hr
60	21	7.71-7.82	7.3-9.7	12.17	7.43	8.44
	54	7.44-8.04	5.95-9.75	19.10	11.40	15.64
	102	7.31-7.71	8.4-9.3	15.48	6.92	11.88
80	31	7.73-7.90	5.95-8.75	16.33	9.67	12.77
	66	7.48-7.92	6.70-8.55	15.05	8.26	11.44
	90	7.47-8.88	6.32-9.3	16.43	8.72	12.87
120	19	7.76-7.96	6.25-9.8	12.8	11.98	9.10
	84	7.67-7.89	6.20-8.7	14	10.05	10.35
	125	7.55-7.93	6.45-8.95	15	8.64	11.39

experiments. Due to this reason, the plot of the reference NH₄-N oxidation rates was found to be above the plot of the experimental NH₄-N oxidation rates. In the experiments performed with 60 mg/l initial NH₄-N concentration, the inhibition values were found as 12, 27, and 42% for hexavalent chromium concentrations of 21, 54 and 102 mg/l, respectively. Similarly, in the experiments performed with 80 mg/l initial NH₄-N concentration, the inhibition values were found as 24, 28, and 31% for hexavalent chromium concentrations of 31, 66 and 90 mg/l, respectively.

As it can be seen from Figure 5.14, in the experiments performed with 120 mg/l initial NH₄-N concentration, the NH₄-N oxidation rate was found to be either increased, or unaffected, or inhibited dependent on the average bulk

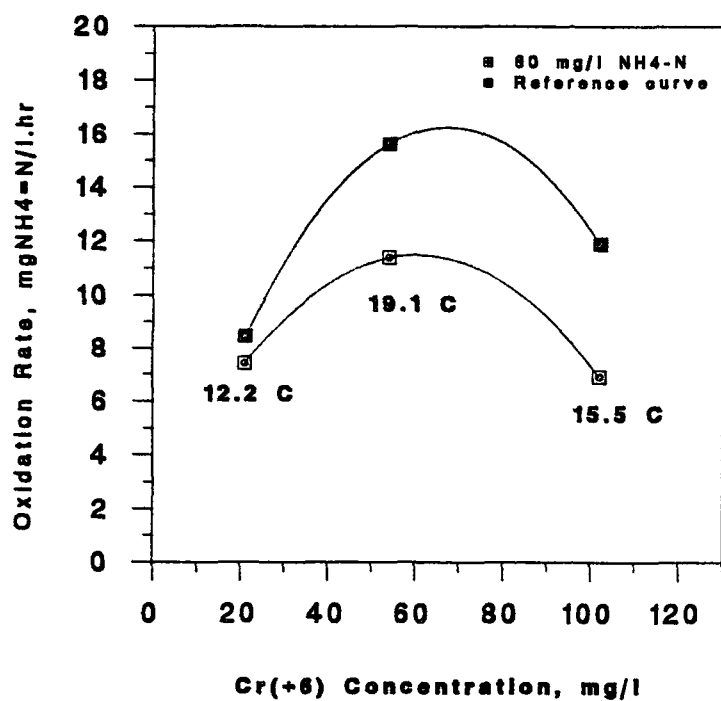


Figure 5.12. Experimental and reference oxidation rates in the solutions which contain 60 mg/l NH₄-N and hexavalent chromium.

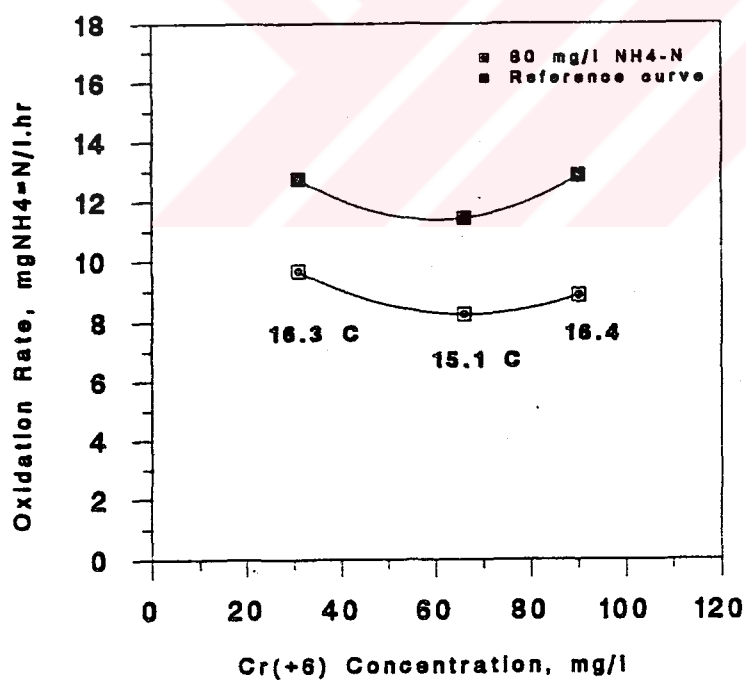


Figure 5.13. Experimental and reference oxidation rates in the solutions which contain 80 mg/l NH₄-N and hexavalent chromium.

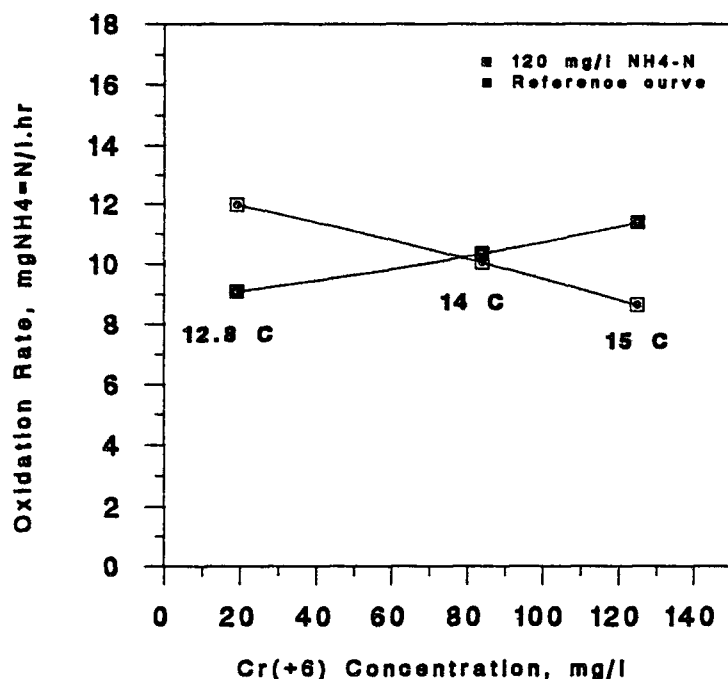


Figure 5.14. Experimental and reference oxidation rates in the solutions which contain 120 mg/l $\text{NH}_4\text{-N}$ and hexavalent chromium.

solution temperature. At hexavalent chromium concentration of 19 mg/l and the average bulk solution temperature of 12.8°C , the $\text{NH}_4\text{-N}$ oxidation rates found as 24% higher than the reference. However, when the hexavalent chromium concentration is increased to 84 mg/l and the average bulk solution temperature is 14°C , the $\text{NH}_4\text{-N}$ oxidation rate was inhibited 2.9% compared to the reference. And again, when the hexavalent chromium concentration is increased to 125 mg/l and at the average bulk solution temperature of 15°C , the $\text{NH}_4\text{-N}$ oxidation rate inhibited compared to the reference $\text{NH}_4\text{-N}$ oxidation rate.

As a summary, the experiments carried out with hexavalent chromium showed a dependence on the bulk solution temperature. The inhibition effect of hexavalent chromium was found to be related to the initial concentration of $\text{NH}_4\text{-N}$ given to the system. However, the experimental results of hexavalent

chromium case were somewhat different compared to the fluoride case. In the experiments performed with 60 and 80 mg/l initial $\text{NH}_4\text{-N}$ concentrations, $\text{NH}_4\text{-N}$ oxidation rates were inhibited. In the experiments performed with 120 mg/l initial $\text{NH}_4\text{-N}$ concentration, the $\text{NH}_4\text{-N}$ oxidation rate was found to be either increased, or unaffected, or inhibited dependent on the average bulk solution temperature. Therefore it was concluded that inhibition effect of hexavalent chromium depends on initial $\text{NH}_4\text{-N}$ concentration and decreases with increase in initial $\text{NH}_4\text{-N}$ concentration.

5.3. Evaluation of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ Results

$\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and Total-N results of the whole experimental study are given in three sections. Results of the experiments performed with $\text{NH}_4\text{-N}$ are shown on Figures 5.15, 5.16, 5.17, and 5.18. Results of the experiments performed with $\text{NH}_4\text{-N}$ and fluoride are shown on Figures 5.19, 5.20, 5.21, 5.22, 5.23, 5.24, 5.25, 5.26, and 5.27. Finally, results of the experiments performed with $\text{NH}_4\text{-N}$ and hexavalent chromium are shown on Figures 5.28, 5.29, 5.30, 5.31, 5.32, 5.33, 5.34, 5.35, and 5.36. In the Figures, T.(Avg) stands for average bulk solution temperature, N.O.R. stands for $\text{NH}_4\text{-N}$ Oxidation Rate, and R.O.R. stands for Reference Oxidation Rate.

It can be seen from Figures 5.15 to 5.36 that Total-N results in the solutions do not change in considerable amounts against reaction time. This result shows that there was any significant losses on $\text{NH}_4\text{-N}$ concentration sourced from stripping during the experimental study.

It can be observed from Figures 5.15 to 5.36 that when the residual $\text{NH}_4\text{-N}$ concentration in the bulk solution reaches to 5-10 mg/l level, the nitrite nitrogen concentration in the bulk solution decreases rapidly whereas the nitrate nitrogen concentration in the bulk solution increases rapidly.

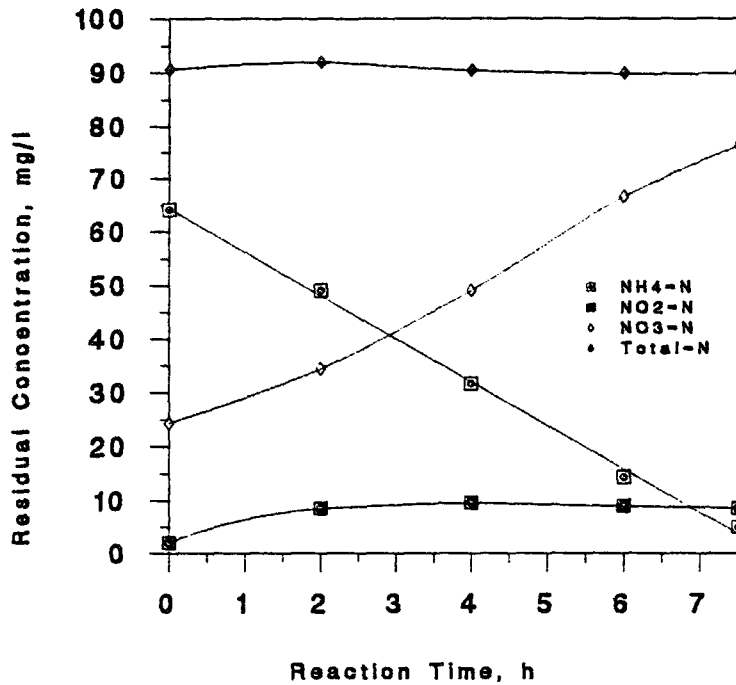


Figure 5.15. Experimental $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and Total-N values
($T(\text{Avg})=12.2^\circ\text{C}$, $\text{N.O.R.}=8\text{mgNH}_4\text{-N/l.h.}$)

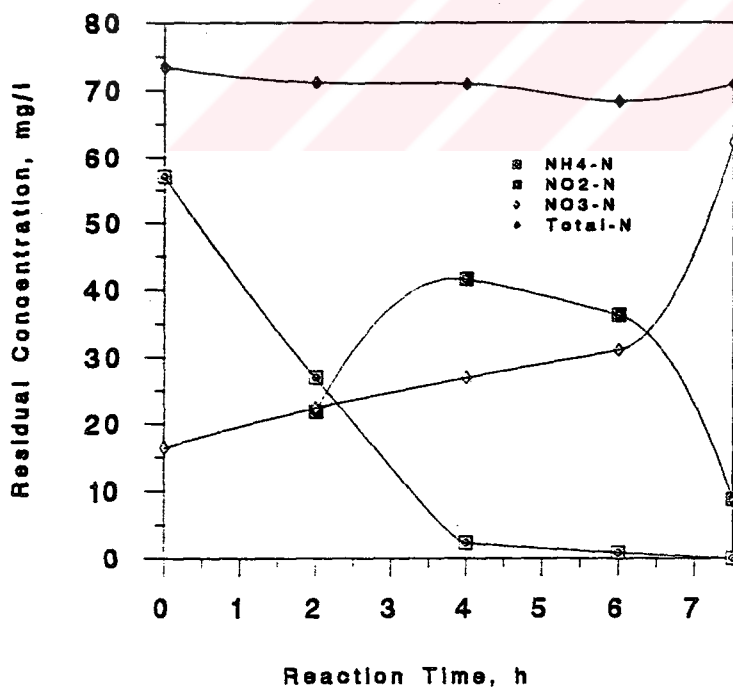


Figure 5.16. Experimental $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and Total-N values
($T(\text{Avg.})=18.75^\circ\text{C}$, $\text{N.O.R.}=13.68\text{ mgNH}_4\text{-N/l.h.}$)

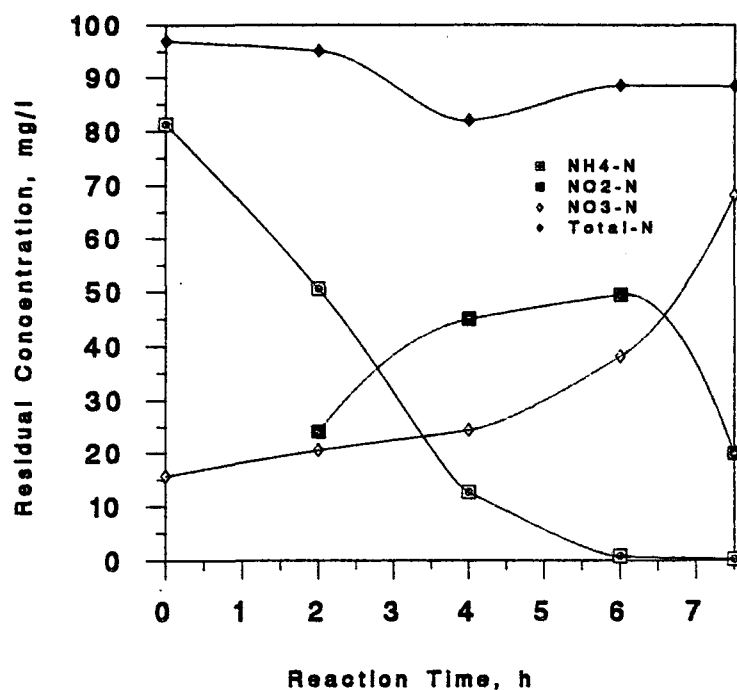


Figure 5.17. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (T.(Avg.)=19.7°C, N.O.R.=17.17mgNH₄-N/l.h.)

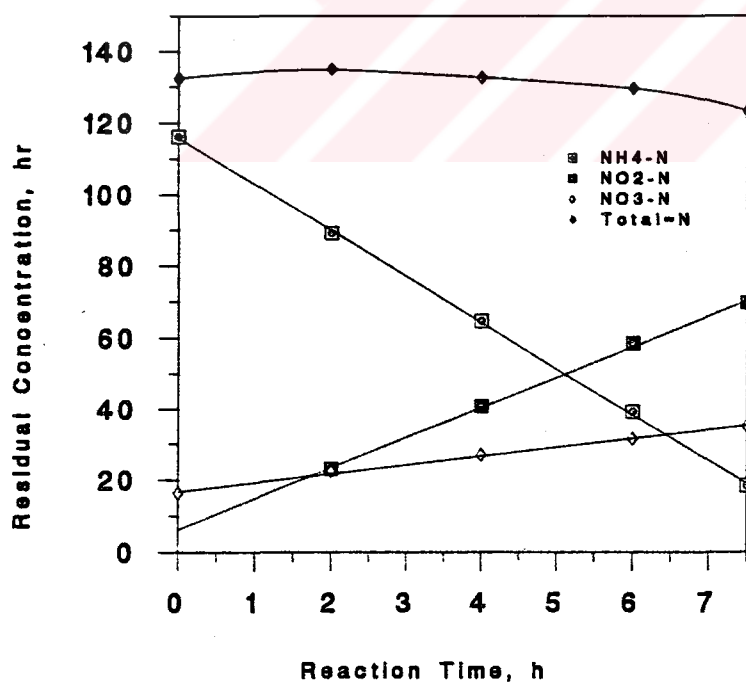


Figure 5.18. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (T.(Avg.)=15.35°C, N.O.R.=12.91 mgNH₄-N/l.h.)

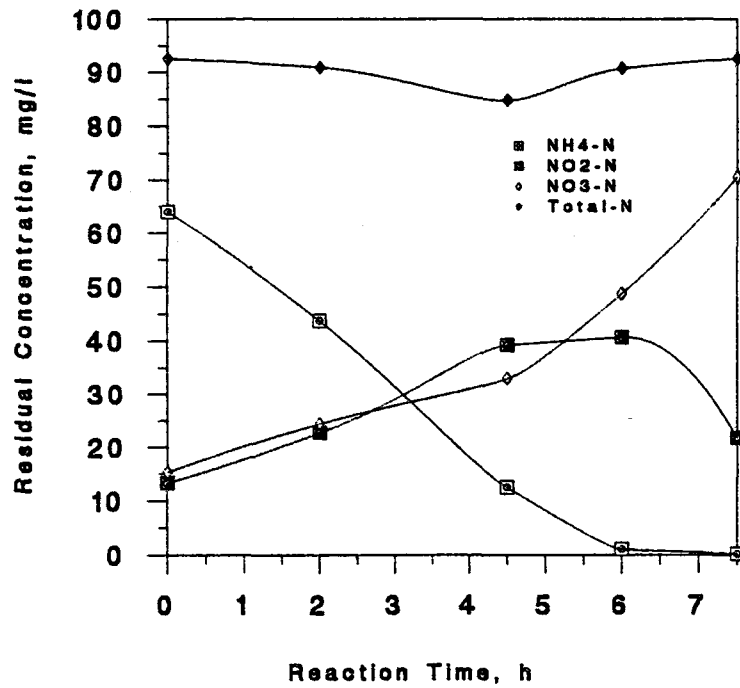


Figure 5.19. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (F=221mg/l, T(Avg.)=16.2°C, N.O.R.=11.49 and R.O.R.= 12.63mgNH₄-N/l.hr)

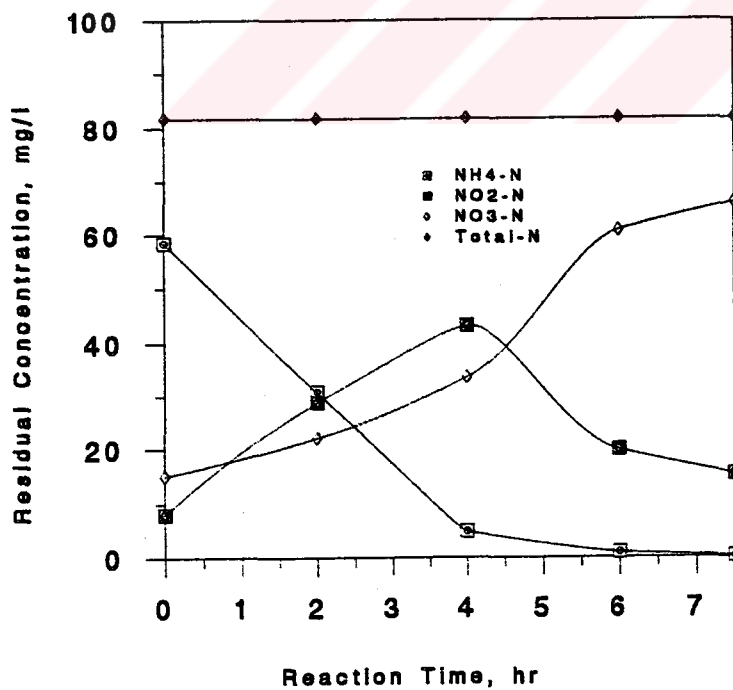


Figure 5.20. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (F=421mg/l, T.(Avg.)=17.78°C, N.O.R.=13.40 and R.O.R.=14.27mgNH₄-N/l.hr)

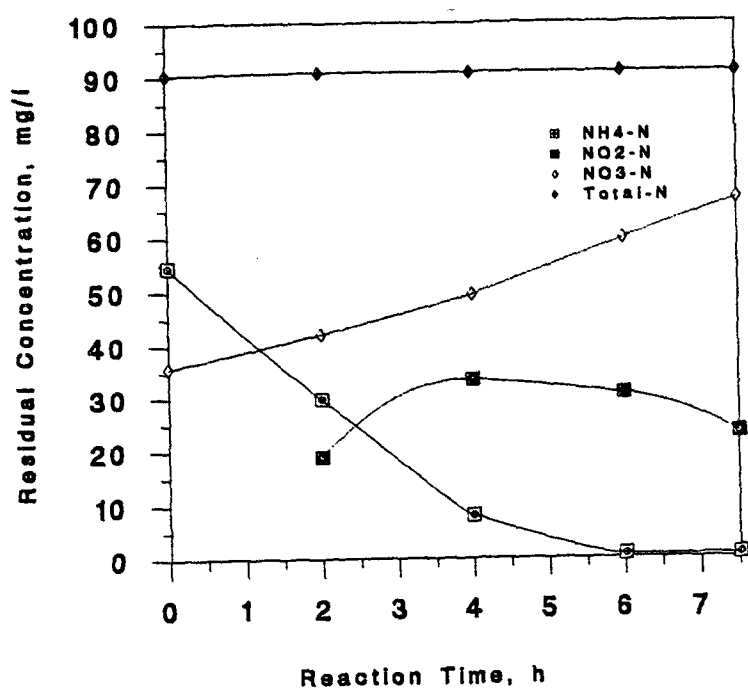


Figure 5.21. Experimental $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and Total-N values ($F=751\text{mg/l}$, $T(\text{Avg.})=16.83^\circ\text{C}$, $\text{N.O.R.}=11.65$ and $\text{R.O.R.}=13.29\text{mgNH}_4\text{-N/l.hr}$)

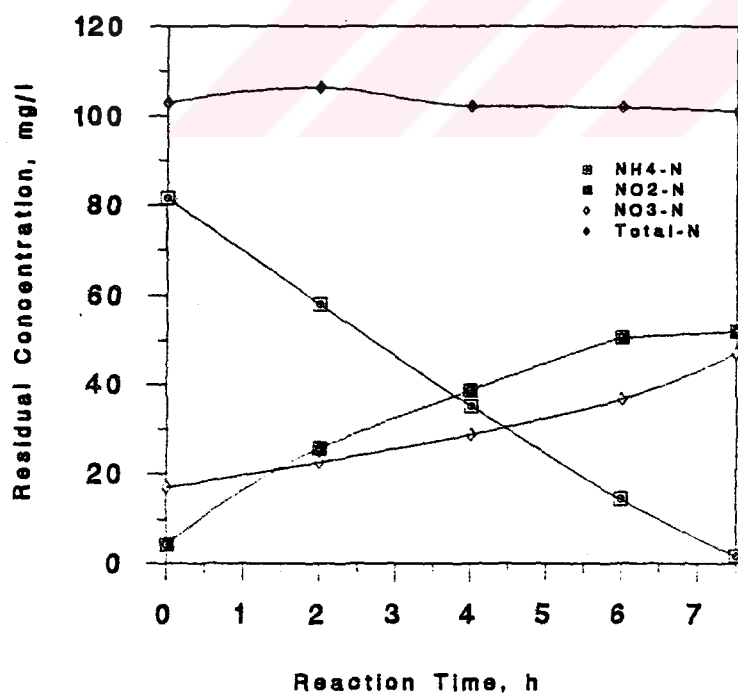


Figure 5.22. Experimental $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and Total-N values ($F=167\text{mg/l}$, $T(\text{Avg.})=15.8^\circ\text{C}$, $\text{N.O.R.}=11.21$ and $\text{R.O.R.}=12.2\text{mgNH}_4\text{-N/l.hr}$)

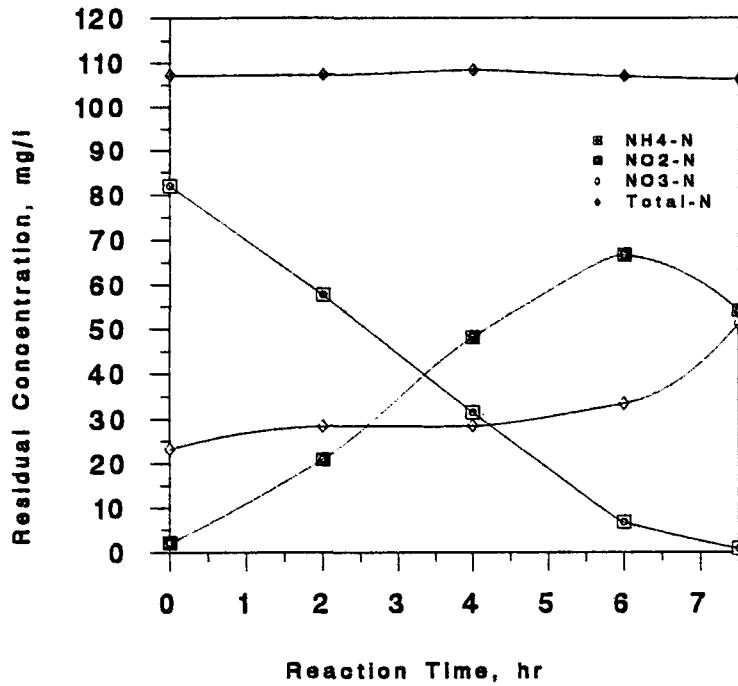


Figure 5.23. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values reaction (F=513mg/l, T.(Avg.)=15.88°C, N.O.R.=12.59 and R.O.R.=12.3mgNH₄-N/l.h)

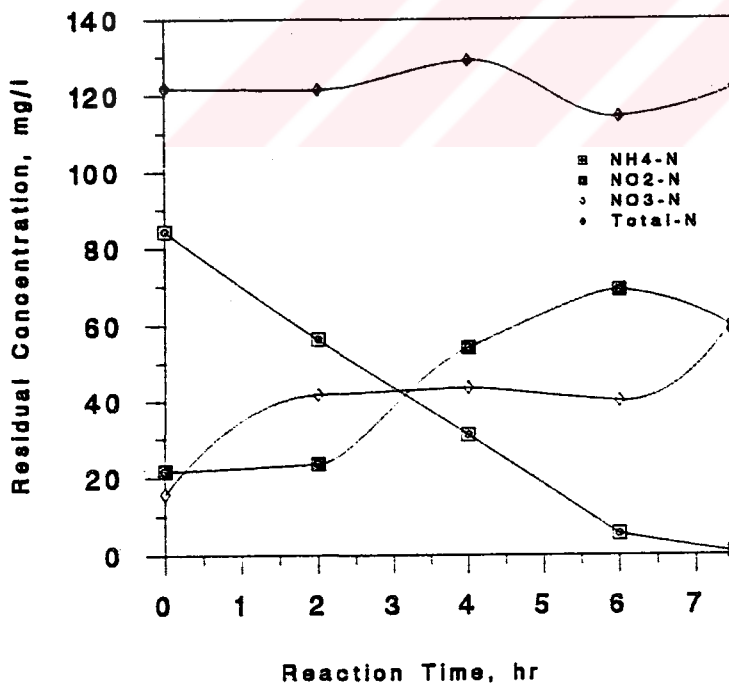


Figure 5.24. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (F=783mg/l, T.(Avg.)=16.78°C, N.O.R.=13.09 and R.O.R.=13.23mgNH₄-N/l.h)

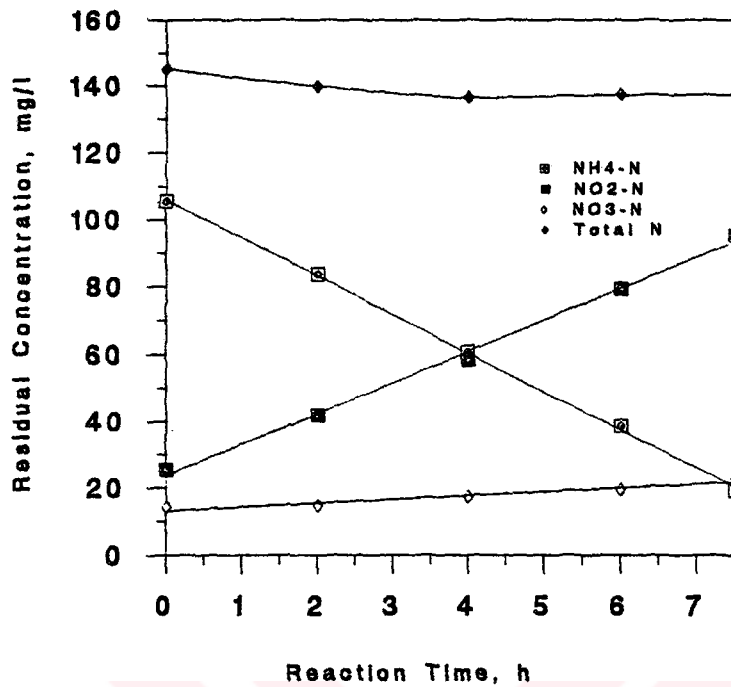


Figure 5.25. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (F=175mg/l, T.(Avg.)=14.08°C, N.O.R.=11.45 and R.O.R.=10.43mgNH₄-N/l.h)

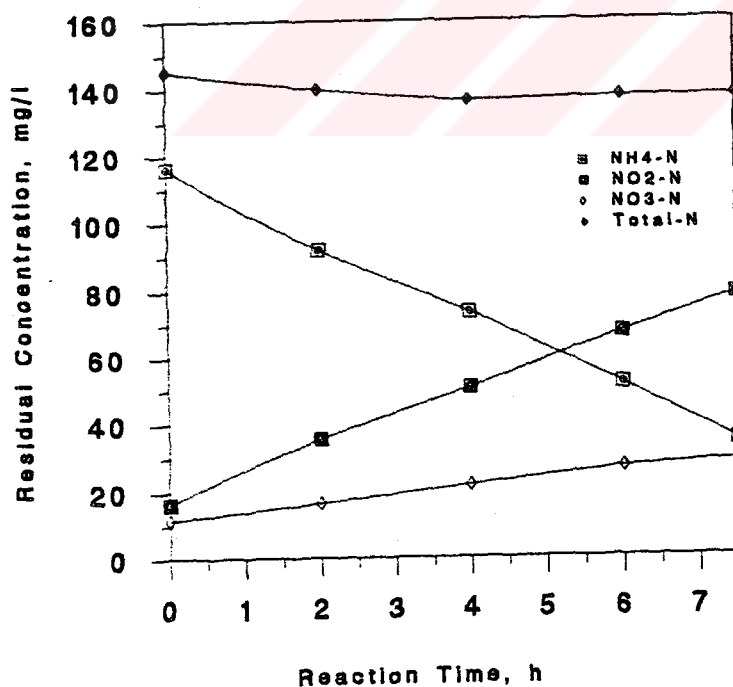


Figure 5.26. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (F=566mg/l, T.(Avg.)=13.25°C, N.O.R.=10.74 and R.O.R.=19.57mgNH₄-N/l.h)

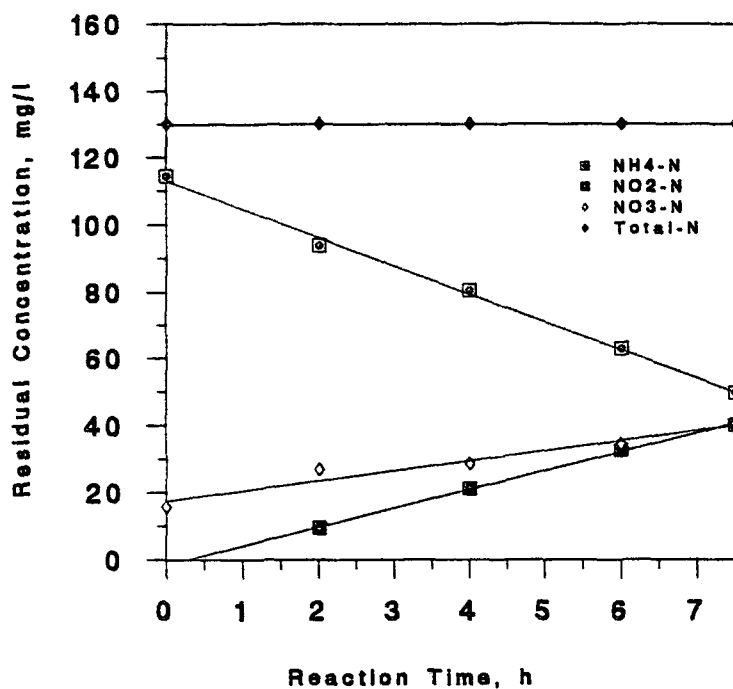


Figure 5.27. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (F=990mg/l, T.(Avg.)=9.42°C, N.O.R.=8.42 and 5.59mgNH₄-N/l.h)

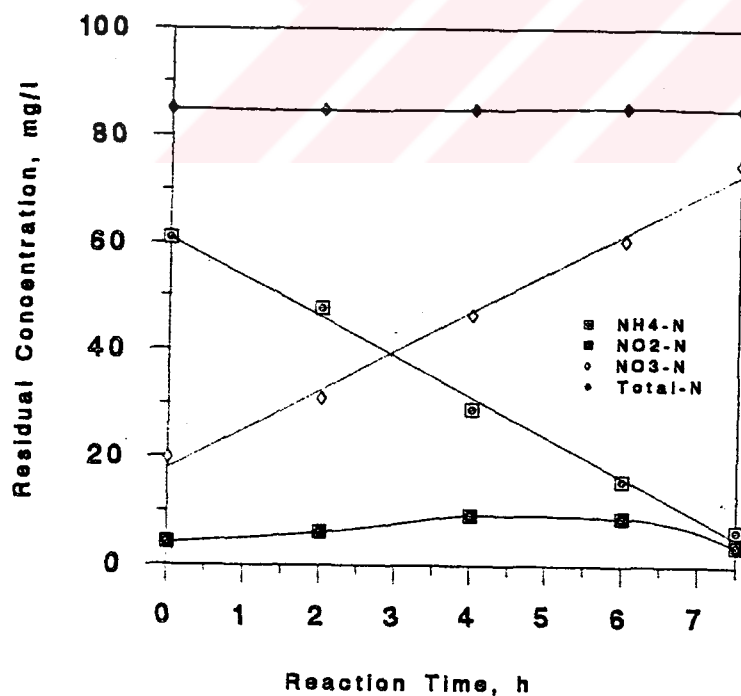


Figure 5.28. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=21mg/l, T.(Avg.)=12.17°C, N.O.R.=7.43 and 8.44mgNH₄-N/l.h)

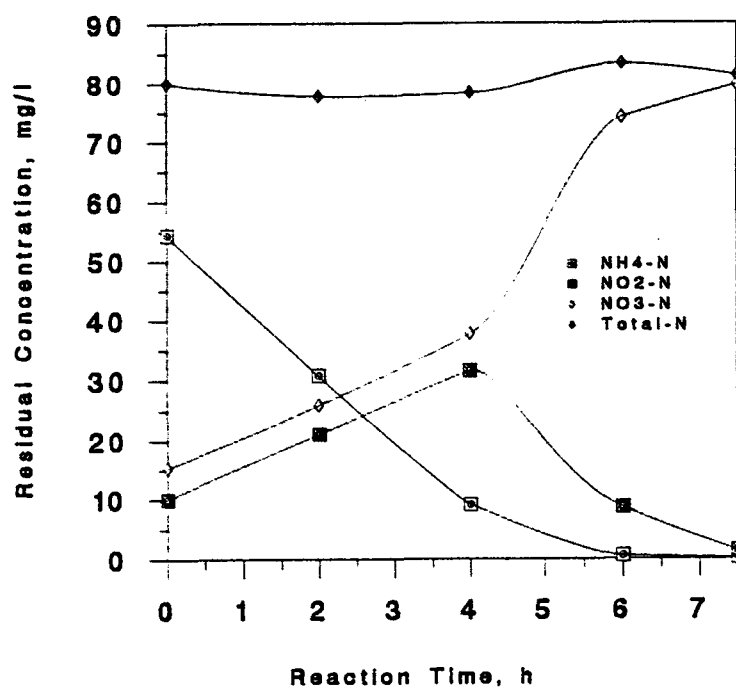


Figure 5.29. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=50mg/l, T.(Avg.)=19.1°C, N.O.R.=11.4 and 15.6mgNH₄-N/l.h)

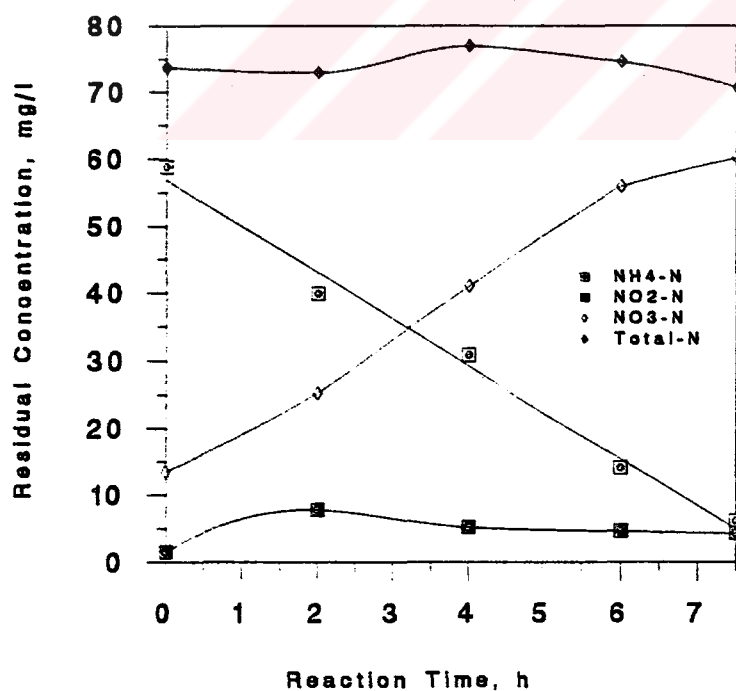


Figure 5.30. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=102mg/l, T.(Avg.)=15.48°C, N.O.R.=6.92 and 11.88mgNH₄-N/l.h)

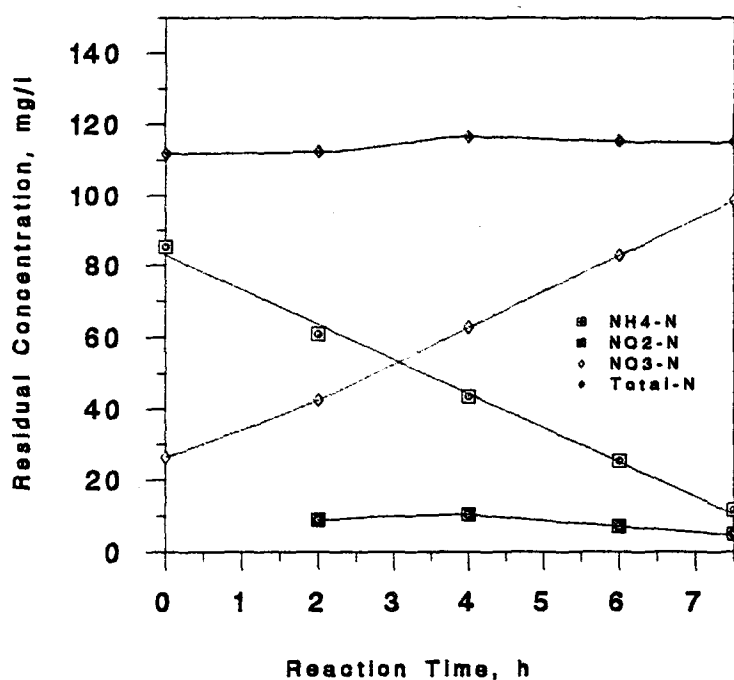


Figure 5.31. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=31mg/l, T.(Avg.)=16.33°C, N.O.R.=9.67 and 12.77mgNH₄-N/l.h)

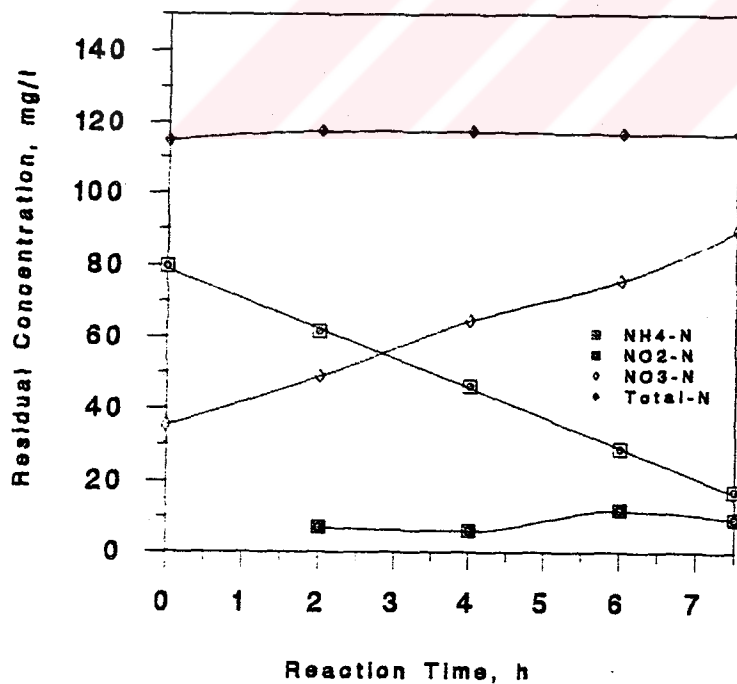


Figure 5.32. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=66mg/l, T.(Avg.)=15.05°C, N.O.R.=8.26 and 11.44mgNH₄-N/l.h)

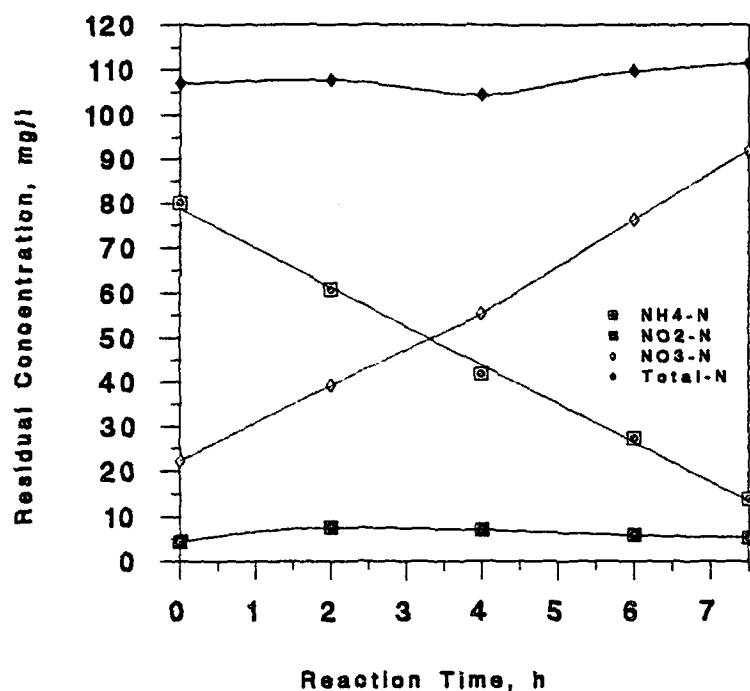


Figure 5.33. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=90mg/l, T.(Avg.)=16.43°C, N.O.R.=8.72 and 12.87mgNH₄-N/l.h)

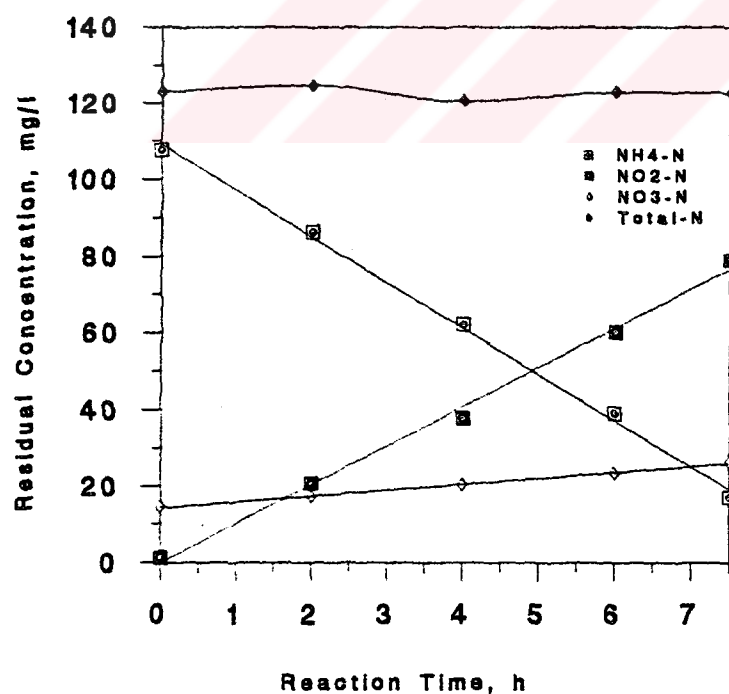


Figure 5.34. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values (Cr(+6)=19mg/l, T.(Avg.)=12.8°C, N.O.R.=11.98 and R.O.R.=9.10mgNH₄-N/l.h)

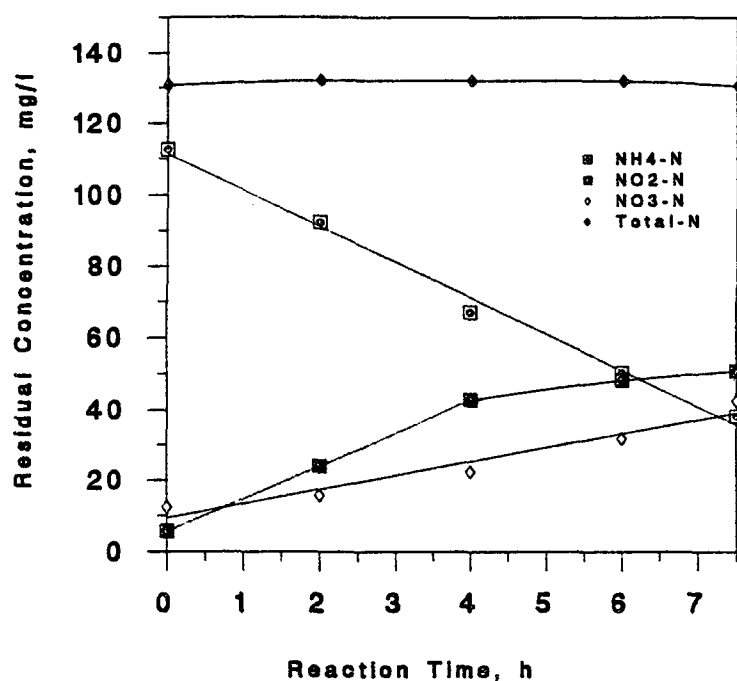


Figure 5.35. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values
(Cr(+6)=84mg/l, T.(Avg.)=14°C, N.O.R.=10.05 and 10.35mgNH₄-N/l.h)

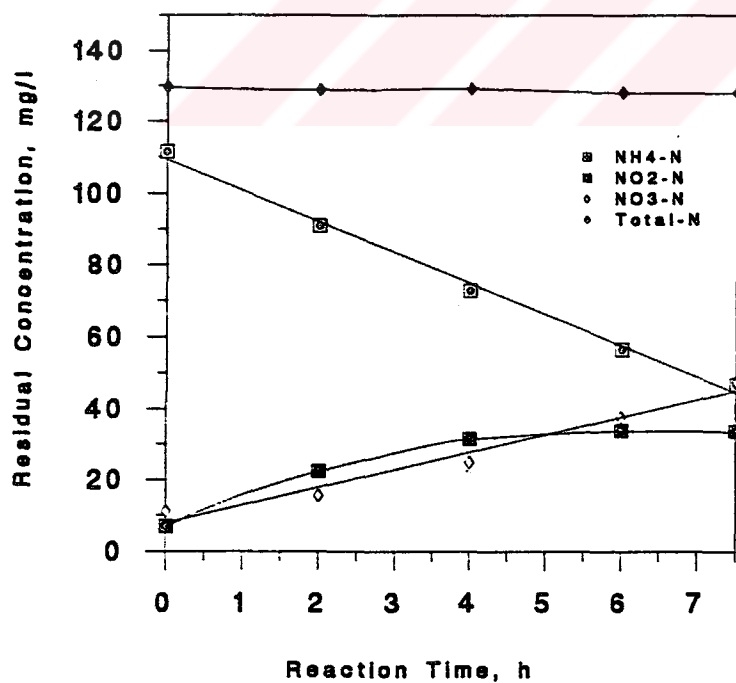


Figure 5.36. Experimental NH₄-N, NO₂-N, NO₃-N and Total-N values
(Cr(+6)=125mg/l, T.(Avg.)=15°C, N.O.R.=8.64 and 11.39mgNH₄-N/l.h)

CONCLUSIONS

Following conclusions can be drawn from this study;

1. Residual $\text{NH}_4\text{-N}$ concentration changes linearly with the reaction time up to 5 to 10 mg/l $\text{NH}_4\text{-N}$ concentration. After this point, it changes exponentially. When the residual $\text{NH}_4\text{-N}$ concentration reaches to 5-10 mg/l level, the $\text{NO}_2\text{-N}$ concentration in the bulk solution decreases rapidly whereas the $\text{NO}_3\text{-N}$ concentration in the bulk solution increases rapidly.
2. Nitrification was a zero order reaction in the experimental conditions. $\text{NH}_4\text{-N}$ oxidation rates were not increase or decrease with the increase in the initial $\text{NH}_4\text{-N}$ concentrations.
3. Change in the average bulk solution temperatures reflected as a change on $\text{NH}_4\text{-N}$ oxidation rate. It has been found that $\text{NH}_4\text{-N}$ oxidation rate increases linearly with the increase in average bulk solution temperature.
4. In the experiments performed with $\text{NH}_4\text{-N}$ and fluoride, the inhibition effect of fluoride was very closely related to the initial $\text{NH}_4\text{-N}$ concentration. In the experiments performed with 60 mg/l initial $\text{NH}_4\text{-N}$ concentrations, fluoride caused inhibition on $\text{NH}_4\text{-N}$ oxidation rate at all tried fluoride concentrations. However, in the experiments performed with 80 mg/l initial $\text{NH}_4\text{-N}$ concentration, the inhibition effect of fluoride on $\text{NH}_4\text{-N}$ oxidation rate was found to be decreased and even disappeared. In the experiments performed with 120 mg/l initial $\text{NH}_4\text{-N}$ concentration, the effect of fluoride

was found in the positive manner, that means, it increased $\text{NH}_4\text{-N}$ oxidation rate at all tried fluoride concentrations.

5. In the experiments performed with hexavalent chromium, the effect of hexavalent chromium on $\text{NH}_4\text{-N}$ oxidation rate was also found to be dependent on the initial $\text{NH}_4\text{-N}$ concentration in the system. However, experimental results of hexavalent chromium case were somewhat different compared to the fluoride case. In the experiments performed with 60 and 80 mg/l initial $\text{NH}_4\text{-N}$ concentrations, hexavalent chromium caused inhibition on $\text{NH}_4\text{-N}$ oxidation rate at all tried hexavalent chromium concentrations. In the experiments performed with 120 mg/l initial $\text{NH}_4\text{-N}$ concentrations, $\text{NH}_4\text{-N}$ oxidation rate was found to be either increased or unaffected or inhibited depending on hexavalent chromium concentration and the average bulk solution temperature.

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RESUME

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