STUDIES ON DENITRIFICATION-DEFLUORIDATION OF WATER USING SBR SYSTEM

A THESIS

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By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"STUDIES ON DENITRIFICATION – DEFLUORIDATION OF WATER USING SBR SYSTEM"** in the fulfilment of the requirement for the award of the **Degree of Doctor of Philosophy**, submitted in the Department of Civil Engineering, University of Roorkee, is an authentic record of my own work carried out during the period from December, 1996 to June, 2000 under the supervision of **Dr. Arvind Kumar**, Professor Civil Engineering Department and **Dr. Pradeep Kumar**, Associate Professor Civil Engineering Department.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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ABSTRACT

Nitrate and fluoride concentrations in groundwaters exceed desirable levels at various places throughout the world. According to the WHO guidelines and recommendations, the allowable concentrations of nitrate and fluoride in drinking water are 10 mg/L (as N) and 1.5 mg/L respectively (WHO, 1984). Excessive intake of nitrate and fluoride can cause methemoglobinemia and fluorosis respectively. The Problem is more acute in rural and small urban communities particularly in third world countries. In India, 27845 habitations consisting approximately 25 million people are supposed to have water supply contaminated with fluoride (Paramasivam and Nanoti, 1997; Iyengar and Venkobachar, 1997). Another example is the Rift Valley region in Ethiopia (Ashley and Burley, 1994). Simultaneous occurrence of both nitrate and fluoride in high concentrations in groundwater samples has been noticed at several places. Three such examples are Rajasthan State and Agra region in India, and the Rift Valley region in Ethiopia where nitrate-N and fluoride concentrations as high as (i) 251 mg/L and 3.2 mg/L, (ii) 178 mg/L and 21 mg/L, and (ii) 224 mg/L and 26 mg/L respectively have been reported (Gupta, 1992; Pal, 1983; Ashley and Burley, 1994).

Methods for fluoride and nitrate removal include ion exchange, reverse osmosis, and electrodialysis. Chemical precipitation and adsorption, and chemical reduction and biological denitrification are also used for fluoride and nitrate removal respectively. Of these methods, chemical precipitation by alum and lime and adsorption by activated alumina or bone char are extensively used for fluoride removal (Iyengar and Venkobachar, 1997), whereas ion exchange and biological denitrification are widely used for nitrate removal (Hoek and Klapwijk, 1987; Gayle et al., 1989). In India,

defluoridation technique based on the principle of fluoride precipitation using alum and lime, which could be operated in batch or continuous mode of operation, was developed and referred to as "Nalgonda" technique. This technique is simple with significant cost savings compared to other methods (Bulusu, et al., 1979). It is utilized for defluoridation of water with fluoride concentrations only up to 10 mg/L. Waters containing high fluoride concentrations (≥ 10 mg/L) require high dose of alum which results in an increase of sulfate and aluminum concentrations in the treated water to unacceptable levels (Bulusu, 1984; Gupta et al., 1999).

Alum and powdered activated carbon (PAC) both have been found to remove fluoride from water separately. However, alum and PAC have not been used together. Therefore, in the present investigation their combination as alum-PAC slurry was tried for defluoridation particularly to reduce alum dose requirement at high initial fluoride concentrations.

Although ion exchange and biological denitrification are widely used in nitrate removal from water, the treatment cost of the latter is relatively lower (Kapoor and Viraraghavan, 1997). Fluidized bed, fixed bed, and upflow sludge-blanket reactors have been tried for drinking water denitrification (Richard et al., 1980; Gayle et al., 1989; Green et al., 1994). Sequencing batch reactors (SBRs) have not been tried in drinking water denitrification, although there are many advantages and they are being used in biological wastewater treatment particularly for small communities (Wun-Jern, 1989). Some of the advantages of these reactors include simplicity in operation, cost effectiveness, and suitability to match with the operation of fill-and-draw (sequencing batch) type defluoridation plant working based on the Nalgonda technique. Hence the

possibilities of using an SBR for denitrification of water have been explored in the present investigation.

Although several treatment methods are known for separate nitrate and fluoride removal, there is a need to explore the possibility of a treatment option for water containing relatively high fluorides and nitrates simultaneously. Thus, the objectives of this research work were to explore the defluoridation potential of alum-PAC slurry, to evaluate a dentification SBR unit, and to develop an integrated nitrate and fluoride treatment process using two SBRs for community water supply schemes. Studies were conducted in three phases using jar test apparatus (phase 1) and bench-scale reactors (phase 2 and 3).

In the study on defluoridation by alum-PAC slurry (phase 1), optimum pH and operation procedure were assessed, and alum and PAC doses were optimized for initial fluoride concentrations of 6,10,15, and 20 mg/L. Role of each component (i.e. alum, PAC, and lime) on fluoride removal and kinetics of the process were examined. In addition, effects of some water quality parameters i.e. phosphate, silica, alkalinity, sulfate, nitrate, chloride and dissolved organic matter (ethanol) on the treatment were investigated.

In the denitrfication part of the treatment process (phase 2), using ethanol as external carbon source, the COD/NO_3^--N ratio was optimized, the efficiency of the SBR for initial nitrate concentrations in the range of 40-250 mg/L (as N) was investigated, and kinetics of denitrification was studied. Furthermore, effects of length of idle time and fluoride concentrations on denitrification were also investigated. Lastly in phase 3, treatment integration sequence options were assessed and the overall efficiency of the selected method was evaluated for various combinations of fluoride

(6-20 mg/L) and nitrate (40-250 mg/L as N) by analysing eleven water quality parameters which were considered to be affected by the treatment process.

The optimum pH for defluoridation by alum-PAC slurry was found to be in the range of 5.8 to 6.5. Operation procedure having two-step feeding (at the beginning of rapid and slow mixing) and two-phases of mixing with rapid mixing at 100 rpm for 40 minutes and slow mixing at 30 rpm for 20 minutes was found most appropriate to reduce initial fluoride to the acceptable level. Alum-PAC slurry having 500, 600, and 800 mg/L of alum along with 100 mg/L of PAC were found optimum to reduce initial fluoride concentrations of 6, 10, and 15 mg/L respectively to the acceptable level (1.5 mg/L). Use of alum-PAC in place of alum and lime reduced the requirement of alum dose by 40 and 43% at fluoride concentrations of 10 and 15 mg/L respectively. However, it had no significant advantage for lower fluoride concentrations (≤ 6 mg/L). Fluoride concentration of 20 mg/L also could not be reduced to 1.5 mg/L with alum doses up to 900 mg/L along with 100 mg/L of PAC. Combination of alum with PAC doses greater than 100 mg/L did not provide improvement in fluoride removal. It was found that in this process fluoride is removed by alum during rapid and slow mixing, whereas direct removal by PAC took place only during rapid mixing. In this treatment process lime was used only for adjustment of pH and alkalinity. It did not provide fluoride removal by itself. The kinetics of the treatment process revealed that competitive fluoride removal by alum and PAC took place, which resulted in minor desorptions of fluoride from PAC mainly during the transition to slow mixing. The mechanism of fluoride removal by alum-PAC slurry is possibly adsorption and/or complexation on the aluminum hydroxide floc available in the bulk water and floc available on the surface of the PAC, and by adsorption directly on the surface of the

PAC. Gradual diffusion of fluoride through the floc surrounding the particle to the PAC surface particularly at higher initial fluoride concentrations (higher concentration gradient) is also possible. Sulfate, nitrate, chloride, and organic matter (ethanol) did not show adverse effect on the process, whereas phosphate and silica did in different magnitudes. Sufficient alkalinity (0.5 to 0.63 mg/L as $CaCO_3$ for each mg/L of alum dose) is a prerequisite for the treatment, whereas excess of it would exert demand on extra dose of alum.

In the denitrification treatment process, ethanol at COD/NO_3^--N ratio of 2.00 was found to be sufficient to reduce the initial nitrate to the acceptable level. Length of idle time (1-14 hours) and fluoride concentrations (6-20 mg/L) had no significant effect on the treatment process. Almost at all initial nitrate concentrations significant nitrate removal (85.7- 91.5 %) took place in the first hour of reaction. Nearly in all cases peak nitrite accumulations were noticed within the first six minutes of reaction. It decreased rapidly thereafter. Considering the quality of the treated water in terms of both nitrate and nitrite, the SBR was found to be efficient in denitrification of nitrate in the concentration range of 40 to 250 mg/L at anoxic reaction times (ARTs) of 3, 5, and 7 hours for initial nitrate concentrations of 40-160, 200, and 250 mg/L (as N) respectively. The Monod kinetic parameters i.e. maximum specific denitrfication rate (k_{max}), half saturation coefficient (K_s), yield coefficient (Y), endogenous decay coefficient (k_d), and maximum specific growth rate (μ_m) for denitrifcation were estimated and found to be 0.31 d^{-1}, 0.46 mg NO_3^--N/L, 1.54 mg VSS/mg NO_3^--N, 0.009 d^{-1}, and 0.48 d^{-1} respectively.

Denitrification-defluoridation treatment sequence was found to be a better choice than defluoridation followed by denitrification. This treatment sequence was

found to be promising only for treatment of water with fluoride and nitrate concentrations up to 15 mg/L and 80 mg/L (as N) respectively. Even though the quality of the treated water was within the acceptable limit, slight pH adjustment, filtration, and disinfection will also be additionally required to make sure the safety and potability of the water. At higher nitrate concentrations (≥ 120 mg/L as N), production of excessive alkalinity during preceding denitrification inhibited reduction of fluoride to 1.5 mg/L when alum doses were restricted to 900 mg/L. Use of alum-PAC slurry for defluoridation of denitrified water reduced the alum dose by 40 and 43% (at initial nitrate concentration of 40 mg/L as N), and 20 and 39% (at initial nitrate concentration of 80 mg/L as N) for initial fluoride concentrations of 10 and 15 mg/L respectively, compared to defluoridation by alum and lime alone. Some of the other advantages of this treatment sequence are (i) the alkalinity produced by the denitrification process is used up during defluoridation in raising the pH avoiding the need of lime for the same purpose, and (ii) residual amounts of turbidity, COD, sulfide, nitrogen, and denitrifying microorganisms in the denitrified effluent are removed by alum and PAC along with fluoride at the defluoridation stage.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS AND ABBREVIATIONS	DESCRIPTION
APHA	American Public Health Association
ASCE	American Society of Civil Engineering
AWWA	American Water Works Association
ART	Anoxic Reaction Time
b	Constant in Langmuir Isotherm Equation
B	Constant in BET Isotherm Equation
BET	Brunauer, Emett, and Teller
C	Concentration of Solute at Equilibrium in Solution, mg/L
C_o	Initial Fluoride Concentration, mg/L
C_s	Saturation Concentration of a Solute, mg/L
C/N	Carbon-to-Nitrogen Ratio
COD	Chemical Oxygen Demand, mg/L
COD/NO_3^{-}-N	Chemical Oxygen Demand to Nitrate-Nitrogen Ratio
CPHEEO	Central Public Health and Environmental Engineering Organization
d	Day
EEC	European Economic Commission
Env. Engg.	Environmental Engineering
g/L	Gram Per Liter
GAC	Granulated Activated Carbon
G	Velocity Gradient, s^{-1}
h	Hour
HRT	Hydraulic Retention Time, h (d)
ICMR	Indian Council of Medical Research
J	Journal
k, n	Empirical Constants in Freundlich Isotherm Equation
k_d	Endogenous Decay Coefficient, d^{-}

k_{max}	Maximum Specific Denitrification Rate, d^-
K_s	Half Saturation Coefficient, mg/L
K_{sp}	Solubility Product
K_t	Temperature Constant
lpcd	Liter Per Capita Demand
MPN	Most Probable Number, MPN index/100 mL
mg/L	Milligram Per Liter
min	Minute
MLVSS	Mixed Liquor Volatile Suspended Solids, mg/L
MLSS	Mixed liquor Suspended Solids, mg/L
NEERI	National Environmental Engineering Research Institute
NOM	Natural Organic Matter
NTU	Nesler Turbidity Unit
PAC	Powdered Activated Carbon
PAHS	Polyaluminum Hydroxy Sulfate
PDP	Package Defluoridation Plant
PNAS	Partially Neutralized Aluminum Sulfate
ppm	Parts Per Million
Q	Maximum Concentration of the Solute Removal Per Unit Weight of the Adsorbent in Forming a Complete Monolayer, mg/mg
q_e	Concentration of Solute Removal Per Unit Weight of Adsorbent, mg/mg
RD_t	Maximum Denitrification Rate at the Given Temperature, d^-
RD_{20}	Maximum Denitrification Rate at 20 °C, d^-
R^2	Correlation Coefficient
rpm	Round Per Minute
SBR	Sequencing Batch Reactor
S_e	Effluent Substrate Concentration, mg/L
S_o	Influent Substrate Concentration, mg/L
SOC	Synthetic Organic Matter

SVI	Sludge Volume Index
t	Temperature
USBR	Upflow Sludge Blanket Reactor
VSS	Volatile Suspended Solids, mg/L
WHO	World Health Organization
X	Biomass Concentration, mg/L
Y	Yield Coefficient, mg VSS/mg substrate
θ_c	Cell Residence Time, d
μ_m	Maximum Specific Growth Rate, d^{-1}

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Chapter 1

INTRODUCTION

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INTRODUCTION

1.1 GENERAL

Best of all things is water. It has always been vital for man's existence. Its use for drinking, agriculture, transport, industry, and recreation show the extent to which it is an integral part of man's life. Some substances dissolved or suspended in it can affect its suitability for its intended use. Quality of drinking water is of vital importance for the wellbeing of mankind. Evidence shows that a substantial part of world's population, particularly in developing countries, does not have access to safe water supply (WHO, 1963).

In most parts of the world, groundwater has generally been considered to be a readily available and relatively good quality water source for drinking. In most of the cases, it is economical to supply groundwater as its quality is better than surface water and cost of the treatment is low. However, its contamination with excess quantity of organic and inorganic (fluoride, nitrate, arsenic, iron, sulfate, chloride, etc.) pollutants is not a rare case. Of these contaminants, fluoride and nitrate are more commonly found in the concentrations more than the WHO permissible limit of 1.5 mg/L and 10 mg/L (as N) respectively (Lenain, 1967; Bell et al., 1970; Gruener and Shuval, 1973; WHO, 1984; Zhaoli et al., 1989; Mathur and Kumar, 1990).

Presence of fluoride in water in small concentration (0.8 to 1 mg/L) is essential for the normal mineralization of bones and development of healthy teeth (WHO, 1969). On the other hand, its excessive intake depending on the concentration causes dental, skeletal, and non-skeletal fluorosis (Leone et al., 1970). Nitrate itself is relatively nontoxic. However, it can be microbially reduced to nitrite, which poses serious health problems to humans including methomoglobinemia and cancers (Gruener and Shuval, 1973; Mirvish, 1977). Except in unusual circumstances, surface waters are generally low in fluoride, the levels being below 1 mg/L. On the other hand, groundwaters may have a greater opportunity to come in contact with fluoriferous material, which results in appreciable quantities of fluoride, depending on the geological conditions. The distribution of water containing excessive fluoride is worldwide. Almost in all the six continents, in majority of cases, fluoride values up to 10 mg/L, in relatively less cases in the range of 10 to 20 mg/L, and in very few cases values exceeding 20 mg/L were reported (Bell et al., 1970; CPHEEO, 1976; Bishop and Sansoucy, 1978; Zhaoli et al., 1989; Ashley and Burley, 1994). In USA 4 million people were exposed to excessive fluoride in their drinking water (Bhattacharya, 1988). Fluoride in drinking water is a common occurrence in the Rift Valley region of several East African countries (Bell et al., 1970; Bhattacharya, 1988). In India, 27845 habitations in 11 states are affected by excess fluoride in drinking water and it is estimated that around 25 million people were suffering from fluorosis (Susheela,1988; Iyengar and Venkobachar, 1997; Paramasivam and Nanoti, 1997).

Nitrate contamination of drinking water is a serious problem in many parts of the world and its concentration in groundwater is ever increasing (Lenain, 1967; Chakravarty, 1990; Mathur and Kumar, 1990; Ashley and Burley, 1994). Among European countries in Bulgaria, Czechoslovakia, France, and United Kingdom, 4%, 1.8%, 2-4%, and 7% of their population has been reported to be exposed to nitrate concentration greater than EEC's recommendation (11.3 mg/L as N) respectively (Mathur and Kumar, 1990). Pollution of water by unacceptable amounts of nitrate has been identified in some areas of Belgium, Denmark, FRG, Netherlands, Sweden, Switzerland, and Israel (Gruener and Shuval, 1973; Mathur and Kumar, 1990). In Mid Western United States nitrate in the ground water exceeds the permissible limit and in one case as high as 690 mg/L (as N) was reported (Hamill and Bell, 1986). In India, in 11 states the nitrate levels in groundwater have been reported to be more than the permissible limit as prescribed by WHO (Chakravarty, 1990). Nitrate concentrations of 120, 164, 183, and 251 mg/L (as N) have been reported in groundwaters in Churu (Rajasthan), Nagpur, Kurnool, and Nagaur districts respectively (Mathur and Kumar, 1990; Gupta, 1992; Joshi et al., 1995). So, barring very few cases, nitrate occur worldwide up to 250 mg/L (as N).

Groundwaters of same eleven states in India, mainly serving small communities have been reported to be affected by the problem of high fluoride (Paramasivam and Nanoti, 1997; Susheela, 1988) and high nitrate (Chakravarty, 1990). Simultaneous presence of fluoride and nitrate in excessive concentrations in groundwaters in India, Ethiopia, and elsewhere also has been reported (Pal, 1983; Gupta, 1992; Ashley and Burley, 1994). Although, the synergistic adverse effects of these contaminants on human health are not known, yet they are suspected to be of great concern.

1.2 JUSTIFICATION OF THE PRESENT RESEARCH

Ion exchange, reverse osmosis, and electrodialysis methods are used for both nitrate and fluoride removal whereas chemical precipitation and adsorption, and chemical reduction and biological denitrification are used for fluoride and nitrate removal respectively. Of these methods, chemical precipitation by alum and lime and adsorption by activated alumina or bone char are extensively used for fluoride removal (Iyengar and Venkobachar, 1997), whereas ion exchange and biological denitrification are widely used for nitrate removal (Hoek and Klapwijk, 1987; Gayle et al., 1989; Kapoor and Viraraghavan, 1997).

In India, defluoridation technique based on the principle of fluoride precipitation using alum and lime popularly known as "Nalgonda" technique is extensively being used for treatment of domestic and community water supplies (Bulusu et al., 1983; Nawlakhe and Rao, 1990). However, despite its simplicity and low cost, its use is limited to waters having fluoride concentrations of less than 10 mg/L (Bulusu, 1984). Water containing high fluoride concentrations (≥ 10 mg/L) require a high dose of alum which results in an increase of sulfate and aluminum concentrations in the treated water to unacceptable levels (Bulusu 1984; Gupta et al., 1999). A combination of coagulation and adsorption processes using alum/ferric chloride and activated carbon improved organic removal compared to the removal when used separately (Stukenberg, 1975; Kassam et al., 1991; Najm et al., 1998). Since, both alum and activated carbon have been reported to have fluoride removal capacities separately (Culp and Stoltenberg, 1958; Sigworth and Smith, 1972; Ramamohan Rao, 1997), this combination also appeared to be feasible for defluoridation. This would improve the applicability of the Nalgonda technique at initial fluoride concentrations of greater than 10 mg/L reducing the alum requirement. Thus, in search for quantifying potential improvement of the Nalgonda technique, the feasibility of incorporation of coagulation and adsorption processes by using alum and powdered activated carbon (PAC) as alum-PAC slurry for defluoridation was studied in this work.

Although ion exchange and biological denitrification are widely used in nitrate removal from water, the treatment cost of the latter is relatively lower (Kapoor and viraraghavan, 1997). Biological denitrification is a biological reaction of oxidation-reduction where nitrates (electron acceptor) are reduced to nitrogen gas and added carbonaceous substrates (electron donor) are oxidized to carbondioxide. Various conventional treatment units such as fluidized bed, fixed bed, and upflow sludge-blanket reactors (Gayle et al., 1989; Traverso and Cecchi, 1989; Green et al., 1994) have been suggested for denitrification of drinking water especially in European countries. Although these reactors have high dentrification rate relative to suspended growth reactors, the fluidized bed has limitation in process flexibility (Traverso and Cecchi, 1989), fixed bed is prone to clogging (Gayle et al., 1989), whereas operation of upflow sludge blanket reactors are affected by hardness of the water (Green et al., 1994). Despite the fact that sequencing batch reactor (SBR) has high efficiency in organic carbon removal and has got practical application particularly for small-scale wastewater treatment (Irvine et al., 1983; Silverstein and Shroeder, 1983; Wun-Jern, 1989), it has not been so far used for biological denitrification of drinking water. It is a cyclically operated batch process consisting of five phases: Fill, React, Settle, Decant, and Idle. Since the reactor also serves as a clarifier, there is no need of additional unit to work as a clarifier, and sludge return system is also not required, which largely decreases the capital cost of the process. Moreover, effluent water quality can be easily controlled by manipulating the reaction and settling time and quantity of sludge solids. Its operation also matches with a cyclically operated batch reactor for defluoridation in the Nalgonda technique. This would eliminate the need of an equalization/storage tank when the two reactors are operated in series for simultaneous defluoridation and denitrification of water having fluorides along with nitrates. Although several methods for purification of water having either fluoride or nitrate individually are available, the treatment of water containing simultaneously fluoride and nitrate has not been tried.

Furthermore, though high values of nitrates are reported in groundwaters and its value is ever increasing, most of the studies in nitrate removal of drinking water were at relatively low nitrate concentrations.

1.3 THE PRESENT WORK

The main objective of this work was to study the feasibility of an integrated nitrate and fluoride treatment scheme using two SBRs in series. Setting this objective, investigations were planned in three phases for the following purposes:

(i) To investigate the possibility of incorporation of coagulation-adsorption processes together using slurry of alum and PAC as a feed solution in the Nalgonda technique for fluoride removal (in the concentration range of 6 to 20 mg/L). This would increase the range of application of the technique when fluoride in water is above 10 mg/L, reduce alum consumption and thus the problems associated with high dose of alum. Furthermore, to study the effect of some water quality parameters on the defluoridation process.

(ii) To investigate the possibility of utilization of an SBR for denitrification of drinking water having relatively high nitrate concentrations in the range of 40 to 250 mg/L (as N), and to study the effect of length of idle time and fluoride concentration on denitrification.

(iii) To evaluate the sequence of treatment and overall efficiency of an integrated nitrate and fluoride treatment processes in order to overcome the problem of simultaneous occurrence of fluorides along with nitrates in excessive concentrations.

Hence, the main goals of this research work were to explore the defluoridation potentials of alum-PAC slurry, evaluate a denitrification SBR unit, and develop an integrated nitrate and fluoride treatment processes using two SBRs for community water supply schemes.

Chapter 2

REVIEW OF LITERATURE

CHAPTER-2

REVIEW OF LITERATURE

2.1 GENERAL

Contamination of water with fluoride and nitrate is a worldwide problem. The World Health Organization (WHO) has set a maximum acceptable fluoride and nitrate concentrations in drinking water of 1.5 and 10 mg/L (as N) respectively (WHO, 1984).

Fluoride has either beneficial or detrimental effects depending on the concentration and total amount ingested. In small range (0.8 to 1 mg/L) it inhibits dental caries and aids in the development of sound teeth in children. Excessive intake of it is a cause for dental, skeletal, and non-skeletal fluorosis (Leone et al., 1970; Paramasivam and Nanoti, 1997).

Nitrate and nitrites in drinking water are potential health hazards when consumed in large amounts. Nitrite formed by reduction of nitrate in water and in the body produces methomoglobinemia in infants (Gruener and Shuval, 1973). Under certain conditions, nitrite reacts with a wide range of secondary and tertiary amines and amides to produce N-nitroso compounds, many of which are carcinogenic in animals and human beings (Shuval and Gruener, 1977). In some cases, its high concentration in drinking water has been found to increase mortality rate in some animals (Lehr et al., 1980).

Simultaneous contamination of community water supplies with fluoride and nitrate also has been reported (Pal, 1983; Gupta, 1992; Ashley and Burley, 1994). Although various defluoridation and denitrification methods are available, an integrated approach for removal of both fluoride and nitrate (when occurring simultaneously) has not been explored.

To fix the targets and scope of present research, the review of literature has been arranged in three main sections viz. dealing with presence and treatment of fluoride and nitrate occurring individually as well simultaneously.

2.2 PRESENCE AND TREATMENT OF FLUORIDE

Fluorine is the most electronegative of all elements. It is rarely or never encountered in nature as elemental fluorine. It forms very strong bond with all elements except oxygen and the lighter noble gases (helium, argon, and neon) to form thermodynamically stable fluorides (Jolly, 1966). Its F-F bond in the fluorine molecule is very weak, which might attribute to its reactivity with other elements. Earth's crust, water, food, and industry are the sources of fluoride as discussed below:

(i) Earth's crust: The earth's crust contains high fluoride content. It is seventeenth in the order of abundance of elements in the earth's crust (Bell et al., 1970). Volcanic and sedimentary rocks contain up to 2500 and 450 ppm fluoride respectively (Bell et al., 1970). Fluoride occurs in a variety of minerals including fluorospar, apatite, cryolite, the micas, hornblende, topaz, and muscovite. It occurs most commonly in fluorospar, which may contain up to 49% fluoride (Bell et al., 1970). Mineral apatite is widely distributed in all igneous rocks. Cryolite, topaz, and muscovite may contain up to 54.88%, 20.37%, and 2.06% fluoride respectively (Kishore, 1988). The size of fluoride ion is similar to that of the hydroxide ion so that it frequently replaces hydroxide ion in minerals (Sherwin and Weston, 1966). Secondary dispersion of fluoride also occurs in soil, river water, groundwater, and atmosphere. The average fluorine content of soils is about 0.02%, increasing in its content towards the subsoil (Vinogradov, 1959).

(ii) Water: Depending on the ionic concentration and on the pH of the solution, fluoride will be present in water as fluoride ion (F^-), HF_2^-, and undissociated HF. In dilute (neutral) pH virtually all fluoride will be present as fluoride ion (F^-). However, as the pH of the solution decreases, the proportion of F^- present decreases while the proportion of HF_2^- and undissociated HF increases (Bell et al., 1970). The fluoride content of surface and underground waters are mainly dependent on availability and solubility of the parent fluoride mineral with which the waters are in contact, the porosity of rocks or soils, flow velocity, temperature, pH, and concentration of calcium ion. Surface waters are generally low in fluorides, the level being below 1 mg/L, whereas groundwaters may have appreciable quantity of fluoride depending on the geological conditions (Bell et al., 1970). The distribution of water containing high fluoride concentration is worldwide (Bell et al., 1970; Zhaoli et al., 1989; Ashley and Burley, 1994). In India, fluoride concentration as high as 36 mg/L have been reported (CPHEEO, 1976). Fluoride content in groundwater is reported to increase with salinity, alkalinity, and concentrations of sodium and potassium ions, and decreases with an increase of calcium and magnesium ions (Pal, 1983; Zhaoli et al., 1989; Ashley and Burley, 1994). The groundwaters in arid and semiarid areas are vulnerable to high fluoride concentrations (Pal, 1983; Zhaoli et al., 1989).

(iii) Food: The amount of fluoride in food is very important because combined ingestion of fluoride-containing water and high fluoride foods may be either harmful or useful nutritional practice. Almost every known food contains traces of fluoride since fluorine is one of the more abundant elements in the earth's crust. Among those foods which have high fluoride content are fish (up to 84.5 ppm), cabbage (up to 15.4 ppm), garlic (up to 17.7 ppm), black tea (52 to 161 ppm), and green tea (336 ppm) (Bell et al., 1970).

(iv) **Industry:** Some industries emit fluoride in their production processes. These include aluminum smelters, steel works, vitreous enamel making, brick making, phosphorous and fertilizers manufacture, cement manufacture, petroleum and magnesium refining, uranium processing, glass and ceramic processing, electroplating, and some rubber processing plants (Coker and Davis, 1981; Eilbech, 1987).

Fluoride concentration in excess of the permissible limit depending on its concentration causes dental, skeletal, and non-skeletal fluorosis. Dental fluorosis is characterized by the formation of paper white areas and deep brown or black stains on the dental enamel. The effect of skeletal fluorosis ranges from stiffness and rheumatism to permanent crippling skeletal rigidity, which includes rigidity in spines and neck, constraints of movements of joints, and deformity of legs. Non-skeletal fluorosis includes the abnormality of functions of kidneys and parathyroid glands, and gastrointestinal and neurological problems (Leone et al., 1970). The severity of fluorosis is dependent on concentration of fluoride in water, length of time of ingestion, climate, nutritional habit, and physical activity. Fluorosis is enhanced generally by poor diet, high fat intake, and calcium and vitamin deficiencies. In India, it is estimated that 25 million people are suffering from fluorosis (Iyengar and Venkobachar, 1997).

2.2.1 Defluoridation Methods

Several physicochemical methods are tried/practiced for defluoridation of drinking water. Mainly these can be divided into two categories: (i) methods based on precipitation, and (ii) methods based on adsorption, ion exchange, and others.

2.2.1.1 Methods Based on Precipitation

The precipitation method includes the use of lime, alum, polyaluminum coagulants, iron salts, tricalcium phosphate, and magnesium compounds. Of these chemicals, in India, alum is widely used in the defluoridation technique referred to as "Nalgonda" technique. When alum is added to water, many chemical and physical parameters determine which aluminum species are formed. Of these, pH and ionic content of the water have significant influence. The cation Al^{3+} predominates at pH less than 4. In the pH range of 5.5 to 7.5, which is relatively favorable for fluoride removal by alum, the principal species is $Al(OH)_3$ (Mc Comic et al., 1993). It is formed within 1 to 7 seconds after addition of alum to the water (Amirtharajah and Mills, 1982). And it has minimum solubility in the pH range of 6 to 6.5 (Murrey and Roddy, 1993). In the presence of fluoride along with aluminum in water, mainly depending on the pH: (i) aluminum may form hydroxoaluminum complex precipitate with fluoride such as $Al(OH)_{2.32}F_{0.68}$ (Buffle et al., 1985), (ii) fluoride may be adsorbed or incorporated on to aluminum hydroxide precipitate (Zabban and Helwick, 1975), (iii) fluoride may react with aluminum ion and precipitate as AlF_3 (Sherwin and Weston, 1966), and (iv) in the presence of sodium ion, fluoride may be precipitated as cryolite, $NaAlF_6$ (Bodek et al., 1988).

The anionic content of the water could affect the pH of precipitation of aluminum hydroxide depending on the basicity of the anion, its affinity to bind with aluminum, and its resistance to displacement by hydroxide ion (Hanna and Rubin, 1970). If the anion has a strong affinity to aluminum and not replaced by hydroxide ion, the pH of optimum precipitation will drop sharply with increase in anion concentration. The same but if can be displaced by hydroxide ion, the pH of optimum precipitation increases with a very basic anion and decreases with a weakly basic anion. Anion having weak affinity to aluminum exerts slight effect on optimum precipitation in the direction of lower pH values. Letterman et al. (1979) reported that the mole ratios [anions (all species combined)/aluminum] required to move the pH range corresponding to effective turbidity removal by approximately one unit are PO_4^{3-}, 1; SiO_3^{2-}, 2; SO_4^{2-}, 3; F^-, 5; HCO_3, 8; Cl^-, 30; and NO_3^-, 50. This ranking appears to be related to the electronegativities of the anions. Thus, the presence of these anions in water could have impact on defluoridation by alum.

(1) Lime

Fluoride can be precipitated by adding calcium to the fluoride solution to form calcium fluoride precipitate.

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2\downarrow + 2OH^-$$

For precipitation of calcium fluoride, the solubility product which is expressed as $[Ca^{++}][F^-]^2 = K_{sp}$, $K_{sp} = 3.4 \times 10^{-11}$ at 18°C or $K_{sp} = 3.95 \times 10^{-11}$ at 26°C must be exceeded. The minimum solubility of calcium fluoride is 7.8 mg/L as F^- at 18°C (Link and Rabosky, 1976). Hence, this method theoretically can reduce initial fluoride concentration to about 8 mg/L. However, based on 10 years operating experience of defluoridation plant, compliance of the following conditions could enable to reduce the fluoride concentration below the solubility level (Link and Rabosky, 1976).

(i) high calcium concentration and rigid pH control,

(ii) long detention time for lime precipitation,

(iii) polyelectrolyte addition during precipitation,

(iv) exclusion of materials or ions which interfere with calcium ion precipitation.

The optimum pH for calcium fluoride precipitation is greater than pH of 12. However, the more sensitive parameter is calcium ion concentration rather than pH (Rabosky and Miller, 1974). In the presence of a suitable excess of calcium ion, precipitation can occur in the pH range of 8 to 9 (Zabban and Helwick, 1975). Combination of lime-calcium chloride in approximately a 1:1 to 2:1 weight ratio can reduce the optimum pH range to 5.7 to 8 (Link and Rabosky, 1976). This also decreases the quantities of sludge produced compared to the treatment by lime only. In continuous treatment process recirculation of precipitated calcium fluoride to the reaction tank, maintaining as high a concentration of suspended solids as practicable, leads to enhanced performance (Eilbech, 1987). This method is mainly used in defluoridation of industrial wastewater where there is high concentration of fluoride (Rabosky and Miller, 1974).

(2) Alum

The usefulness of alum used alone or along with lime in the reduction of fluoride in water is well documented (Culp and Stoltenberg, 1958; Rabosky and Miller, 1974; Nawlakhe et al., 1974 and 1975; Zabban and Helwick, 1975). Culp and Stoltenberg (1958) reported that 250 mg/L of alum were required to reduce the fluoride concentration in a groundwater from 3.6 mg/L to 1.5 mg/L and 350 mg/L were needed to reduce it to 1 mg/L. It was also observed that fluoride removal is proportional to alum dosage, incremental feeding of alum decreases its requirement by 10%, and duration of mixing time and use of recirculated sludge have no effect on fluoride removal. The optimum pH range was found to be from 6.5 to 7.5. Rabosky and Miller (1974) reported that by using lime, alum, and polyelectrolytes, fluoride concentration was reduced from 132.12 mg/L to 6.58 mg/L and from 123.96 mg/L to 1.75 mg/L.

The mechanism of fluoride removal by alum was suggested to be formation and precipitation of hydroxylated aluminum complex with fluoride ion or adsorption of fluoride ion on the alum floc (Zabban and Helwick, 1975). Studies on species of products of fluoride removal by aluminum hydroxide polymers (which also could form during alum coagulation) also revealed that fluoride was precipitated with the polymer and had empirical formula of $Al(OH)_{2.32}F_{0.68}Na_{0.01}$ or $Na_{0.4}O_{1.2}AlF.3H_2O$ depending on F/Al ratio (Buffle et al., 1985). In the presence of sodium ion, fluoride could be precipitated as cryolite, Na_3AlF_6 (Bodek et al., 1988). Aluminum also forms more stable complexes with fluorine viz. AlF^{2+}, AlF_2^{+}, AlF_3, AlF_4^{-}, AlF_5^{2-} and AlF_6^{3-} (Sherwin and Weston, 1966). Despite these suggestions, the precise mechanism of fluoride removal by alum is not yet well established (Nawlakhe et al., 1975).

Based on alum and lime treatment, three major successful achievements in India have been identified viz. (i) Nalgonda technique was developed for defluoridation of domestic and community water supplies by NEERI (Nawlakhe et al., 1975), (ii) a full scale package defluoridation plant for hand pump installations was developed (Alagarsamy et al., 1986), and (iii) alum floc sludge-blanket technique was studied (Purushotaman and Rao, 1986). These are briefly discussed below:

(i) Nalgonda technique: It comprises addition in sequence of lime, bleaching powder, and filter alum to the fluoride containing water followed by flocculation, sedimentation, and filtration. Nawlakhe et al. (1975) conducted extensive laboratory studies on the amount of alum dose required for reduction of fluoride in the range of 2-10 mg/L to excessive (2 mg/L) and permissive (1 mg/L) limits at various alkalinity (Table 2.1). Approximate alum doses required by this technique for reduction of fluoride to 1.5 mg/L (WHO, 1984) was also similarly compiled in a table by this author from the same data (Table 2.2).

Table 2.1 Approximate Alum Doses (mg Al (III)/L) Required to Reduce Fluoride Concentration to the Excessive (E, 2 mg/L) and to the Permissive (P, 1 mg/L) Limits at Various Alkalinity and Initial Fluoride Concentrations (Nawlakhe et al., 1975)

Fluoride concent., mg/L	Alkalinity, mg/L as $CaCO_3$																	
	80		125		200		310		400		510		600		820		1070	
	Alum doses, mg Al (III)/L																	
	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P
2	0	8	0	11	0	17	0	21	0	24	0	27	0	31	0	36	0	40
3	6	**	9	17	12	23	16	27	20	31	24	39	27	40	29	45	33	59
4	11		15	**	16	31	22	32	23	36	30	43	31	46	37	53	43	72
5	*		19		22	**	26	39	29	46	36	53	37	55	50	68	51	80
6			*		31		30	47	35	55	40	60	46	72	54	82	59	93
8					*		46	**	51	**	48	76	57	86	67	100	72	110
10							*		*		59	**	64	**	78	116	89	130

Notes: 1) To obtain alum dose in mg/L multiply the values of mg Al (III)/L by a factor of 13.

2) * Not possible to obtain excessive limit of 2 mg/L because of low alkalinity.

3) ** Not possible to obtain permissive limit of 1 mg/L because of low alkalinity.

Table 2.2 Approximate Alum Doses (as mg Al (III)/L) Required to Reduce Fluoride Concentrations to 1.5 mg/L (WHO, 1984) at Various Alkalinity and Initial Fluoride Concentrations (Compiled from the Data of Nawlakhe et al., 1975)

Fluoride concent., mg/L	Alkalinity, mg/L as $CaCO_3$								
	80	125	200	310	400	510	600	820	1070
	Alum dose, mg Al (III) /L								
2	4.9	5.6	11.2	16.8	16.8	21.0	25.2	22.4	26.0
3	11.2	14.0	16.8	21.0	22.4	32.0	33.6	33.6	42.0
4	*	*	22.4	29.4	33.6	35.0	42.0	44.8	56.0
5			*	33.6	39.2	42.0	50.4	59.7	63.0
6				42.0	44.8	49.0	58.8	67.2	70.0
8				*	*	63.0	67.2	78.4	84.0
10						77.0	84.0	100.8	112.0

Notes: 1) To obtain alum dose in mg/L multiply the values of mg Al (III)/L by a factor of 13.

2) * Not possible to obtain acceptable limit of 1.5 mg/L (WHO, 1984) because of low alkalinity.

These studies showed that:

- The dose of alum mainly depends on the concentration of fluoride, alkalinity, and total dissolved solids in raw water. Waters with 2 to 10.5 mg/L fluorides, and 80 to 1070 mg/L alkalinity were used to evaluate the quantities of alum required to lower the fluoride concentration to 1 mg/L. The doses of alum were worked out to be in the range of 138 to 1825 mg/L depending on initial fluoride concentrations and alkalinity.
- Adequate alkalinity is necessary in raw water to achieve a 1 mg/L of fluoride concentration in the treated water. The presence of sulfate, calcium, chloride, organic matter, nitrate, polyphosphate, and chlorine had no effect on the removal of fluoride. Whereas the adverse effect of silica was observed.
- The proportion of fluoride removed per unit quantity of alum varied considerably with the test water characteristics. Alkalinity remaining constant, the proportion of fluoride removal per unit amount of alum increased with the test water fluoride concentrations.
- The mechanism of fluoride removal by alum could not be conclusively explained. The precise mechanism of removal still remains to be understood.
- The cost per capita (annum) at the rate of 50 lpcd consumption varies between Rs. 5 to Rs. 16 (1975) depending on the raw water characteristics.
- Field experience confirmed that the technique is simple to be adopted in villages either at domestic level or at community water supply level.

Community defluoridation plants working based on this technique at Kadiri and at Tartatur are functioning efficiently (Bulusu et al., 1983; Nawlakhe and Rao, 1990). It can be operated in sequencing batch (fill-and-draw) or continuous mode. Technoeconomical evaluation studies conducted on several defluoridation plants in the State of Rajasthan (India) (Kumar, 2000) revealed that the Nalgonda technique is most economical for fluoride concentrations up to 5 mg/L. It was also found that sequencing batch (fill-and-draw) type and hand pump attached defluoridation plants of this technique are effective at community and village levels respectively. The other advantage of the Nalgonda technique is simultaneous removal of color, odor, turbidity, bacteria, and organic matter along with fluoride (Kumar, 2000). However, water containing high fluoride concentrations ($\geq$ 10 mg/L) require a high dose of alum (Tables 2.1 and 2.2) which results in an increase of sulfate and aluminum concentrations in the treated water (Bulusu, 1984; Gupta et al., 1999), and in large quantity of sludge production (Bishop and Sansoucy, 1978; Choi and Chen, 1979). To alleviate these problems it was proposed to treat the water with split (two-stage) treatment method which reduced the alum consumption (Bulusu et al., 1979). To solve the problem of excess sulfate ion in the treated water because of the high dose of alum, Bulusu (1984) studied the possibility of using aluminum chloride alone or in combination with aluminum sulfate. Doses of aluminum chloride alone and in combination with aluminum sulfate required for reduction of various concentrations of fluoride (2 to 21 mg/L) to 0.5, 1.0, 1.5, and 2.0 mg/L at various alkalinity (200 to 1200 mg/L as $CaCO_3$) were worked out. The doses required for reduction of fluoride to 1.5 mg/L (WHO, 1984) and to excessive (2 mg/L) and permissive (1 mg/L) limits are shown in Tables 2.3 and 2.4 (for aluminum chloride alone) and Tables 2.5 and 2.6 (for aluminum chloride in combination with alum) respectively. Comparison of doses of aluminum chloride (Tables 2.3 and 2.4) and doses of combination of alum and aluminum chloride (Tables 2.5 and 2.6) with doses of alum alone (Tables 2.1 and 2.2)

Table 2.3 **Aluminum Chloride ($AlCl_3$) Doses (as mg Al (III)/L) Required to Reduce Fluoride Concentrations to 1.5 mg/L (WHO, 1984) at Various Alkalinity and Initial Fluoride Concentrations (Compiled from the Data of Bulusu, 1984)**

Fluoride concent., mg/L	Alkalinity, mg/L as $CaCO_3$					
	200	400	600	800	1000	1200
	Aluminum chloride dose (as mg Al (III)/L)					
2	7.2	8.2	12.3	15.3	25.6	38.8
3	15.3	17.4	24.5	32.7	45.0	73.6
4	25.6	29.6	32.7	59.3	62.4	81.8
5	28.6	35.8	53.2	65.4	81.8	103.3
6	33.7	44.0	---	---	---	116.6
7	---	---	66.5	80.8	92.0	---
8	*	---	---	---	---	149.3
9	---	55.2	76.7	86.9	102.2	---
11	---	---	---	---	108.4	---
12	*	64.4	86.9	98.2	112.5	165.6
16	*	71.6	---	109.4	---	---
17	---	---	93.0	---	126.8	184.0
21	*	*	99.0	124.7	156.4	210.6

Notes: 1) To express the doses of aluminum chloride (mg/L) in terms of mg Al(III)/L they have been divided by a factor of 4.89 [4.89 mg aluminum chloride ($AlCl_3$) is equivalent to 1 mg Al (III)].

2) * Not possible to reduce fluoride concentrations to 1.5 mg/L because of low alkalinity.

Table 2.4 Aluminum Chloride Doses (as mg Al (III)/L) Required to Reduce Fluoride Concentrations to the Excessive (E, 2 mg/L) and Permissive (P, 1 mg/L) Limits at Various Alkalinity and Initial Fluoride Concentrations (Bulusu, 1984)

Fluoride concent., mg/L	Alkalinity, mg/L as Ca CO$_3$											
	200		400		600		800		1000		1200	
	Aluminum chloride doses, mg Al(III) /L											
	E	P	E	P	E	P	E	P	E	P	E	P
2	0.0	17.4	0.0	22.5	0.0	29.6	0.0	37.8	0.0	49.1	0.0	68.5
3	14.3	24.9	19.4	32.7	24.5	45.0	35.8	54.2	----	69.5	49.1	97.1
4	18.4	31.7	20.4	40.9	31.7	51.1	47.0	72.6	55.2	76.7	71.6	104.3
5	25.6	34.8	28.6	42.9	37.8	68.5	55.2	77.7	67.5	85.9	90.0	116.6
6	29.6	37.8	36.8	51.1	48.0	---	---	61.3	---	---	104.3	130.9
7	34.8	*	40.9	---	55.2	79.8	71.6	91.0	81.8	102.2	---	---
8	*	*	---	55.2	---	---	---	---	---	---	135.0	163.6
9	---	---	49.1	61.3	67.5	85.9	77.7	96.1	94.1	110.4	---	---
11	---	---	---	---	---	---	---	---	100.2	116.6	---	---
12	*	*	59.3	68.5	79.8	93.0	90.0	105.3	106.3	119.6	153.4	177.9
16	*	*	67.5	*	---	---	102.2	114.5	---	---	---	---
17	---	---	---	---	87.9	98.2	---	---	120.6	130.9	177.9	192.2
21	*	*	*	*	94.0	105.3	118.6	130.1	149.3	163.6	200.4	218.8

Notes: 1) To obtain aluminum chloride dose in mg/L, multiply the values of mg Al (III)/L by a factor of 4.89.

2) * Not possible to get the excessive/permissive limits because of low alkalinity.

Table 2.5 Doses of Combination of Alum and Aluminum Chloride at a Ratio of 1:2.4 (as mg Al (III)/L) Required to Reduce Fluoride Concentrations to 1.5 mg/L (WHO, 1984) at Various Alkalinity and Initial Fluoride Concentrations (Compiled from the data of Bulusu, 1984)

Fluoride concent., mg/L	Alkalinity, mg/L as $CaCO_3$					
	200	400	600	800	1000	1200
	Alum + Aluminum chloride doses (mg Al (III) /L)					
2	6.1	8.4	10.7	12.5	18.3	36.3
3	13.1	18.6	22.3	29.0	63.9	71.1
4	22.3	33.4	37.7	50.8	---	78.4
5	---	---	47.9	---	85.6	95.8
6	30.5	45.0	---	---	---	116.1
7	---	---	61.0	82.7	97.2	---
8	36.3	---	---	---	---	---
9	---	59.5	75.4	90.0	107.4	---
11	*	---	---	---	113.2	---
12	*	72.5	81.3	101.6	119.0	152.4
16	*	*	---	114.6	---	---
17	---	---	91.4	---	149.5	175.6
21	*	*	98.7	130.6	171.2	200.3

Notes: 1) To express the doses of alum (mg/L) and aluminum chloride (mg/L) in terms of mg Al(III)/L they have been divided by factors of 11.66 and 4.89 respectively [11.66 mg alum ($Al_2(SO_4)_3.16H_2O$) and 4.89 mg aluminum chloride ($AlCl_3$) are equivalent to 1 mg Al (III) respectively].

2) * Not possible to reduce fluoride concentrations to 1.5 mg/L because of low alkalinity.

Table 2.6 Doses of Combination of Alum and Aluminum Chloride at a Ratio of 1:2.4 (as mg Al (III)/L) Required to Reduce Fluoride Concentrations to the Excessive (E, 2 mg/L) and Permissive (P, 1 mg/L) Limits at Various Alkalinity and Initial Fluoride Concentrations (Bulusu, 1984)

Fluoride concent., mg/L	Alkalinity, mg/L as $CaCO_3$											
	200		400		600		800		1000		1200	
	Alum + Aluminum chloride doses (mg Al (III) /L)											
	E	P	E	P	E	P	E	P	E	P	E	P
2	0.0	14.5	0.0	30.4	0.0	33.3	0.0	37.7	0.0	52.2	0.0	60.9
3	11.0	21.7	16.5	37.7	24.6	43.5	33.3	55.1	40.6	85.5	46.4	95.6
4	16.2	29.0	21.7	44.9	34.8	50.7	40.6	75.4	55.1	87.0	71.0	98.6
5	21.2	30.4	29.0	49.3	37.7	58.0	50.7	---	71.0	101.4	78.3	113.0
6	26.1	33.3	36.2	52.2	46.4	60.9	58.0	78.3	---	---	95.6	131.9
7	---	---	---	56.5	50.7	71.0	68.1	97.1	84.0	110.1	---	---
8	31.9	37.7	43.5	---	---	---	---	---	---	---	104.3	---
9	---	40.6	53.6	66.7	66.7	82.6	81.2	100.0	95.6	117.4	---	143.5
11	---	---	---	---	---	---	---	---	102.9	123.2	---	---
12	37.7	*	68.1	*	73.9	88.4	95.6	110.1	110.1	129.0	142.0	162.3
16	*	*	72.5	*	---	---	107.2	120.3	---	---	---	---
17	---	---	---	---	82.6	97.1	---	---	142.0	39.5	168.1	184.0
21	*	*	*	*	91.3	*	121.7	139.1	162.3	*	188.4	*

Notes: 1) To express the doses of alum (mg/L) and aluminum chloride (mg/L) in terms of mg Al(III)/L they have been divided by factors of 11.66 and 4.89 respectively [11.66 mg alum ($Al_2(SO_4)_3.16H_2O$) and 4.89 mg aluminum chloride ($AlCl_3$) are equivalent to 1 mg Al (III) respectively].

2) * Not possible to get the Excessive/Permissive limits because of low alkalinity.

for fluoride concentrations in the range of 2-10 mg/L having similar/approximately similar alkalinity show that in most cases doses of aluminum chloride alone and its combination with alum were almost similar or more than doses of alum (Tables 2.1 and 2.2). This indicates that the doses were not reduced in terms of aluminum. Hence, although the risk of contamination of treated water by sulfate could be avoided in this case; the risk of aluminum contamination is still persisting. However, based on these data the other advantage of aluminum chloride and its combination with alum could be the possibility of reduction of fluoride to the required level at relatively low alkalinity using relatively higher doses in comparison to alum alone viz. the process requires relatively low alkalinity.

In summary, the merits of Nalgonda technique can be identified as simple in construction and operation, cost effective for water having fluoride concentration up to 5 mg/L, applicable to batch and continuous system design and simultaneous removal of color, odor, turbidity, bacteria, and organic contaminants. The demerits are also noteworthy viz. high alum dose results in higher sludge and deterioration of treated water quality with sulfate and aluminum ions, which limits its application to relatively low fluoride concentrations.

(ii) Package Defluoridation Plant (PDP) for Handpump Installation: Alagarsamy et al. (1986) developed a package defluoridation plant for instantaneous use during hand pump operation. The plant module consists of different units i.e. pebble bed flocculator, tube settlers, inbuilt filters, solution tank, constant head box, and chemical dose controlling device. The overall size of the module excluding the solution tank and dosing system was 2.15m x 0.6m x 1.8m and costed about Rs.33000. According to the result of investigation conducted on full-scale unit, initial fluoride concentration of 2.94

to 3.9 mg/L was reduced to 0.8 to 1.2 mg/L with alum and lime dose of 800 and 60 mg/L respectively. Improvement of fluoride removal at constant alum dose with increasing lime dose was also noted.

(iii) Alum Floc Sludge-Blanket Technique: Purushotaman and Rao (1986) reported that fluoride concentrations were reduced from 6 mg/L to 1.6 mg/L, 3 mg/L to 0.7 mg/L, 4 mg/L to 1 mg/L, and 5 mg/L to 1.2 mg/L using 40 mg/L of alum and 20 mg/L of lime by alum sludge blanket technique. The percentage of fluoride removal has been found to be in the range of 70 to 76%. The technique comprises round stone media filter through which coagulated water flows upward and forms a sludge blanket at the junction of the media and free water zone. The dose of alum required in this technique was very low compared to the Nalgonda technique and moreover it has been observed that the fluoride removal was more dependent on the alum to lime ratio rather than their individual quantity. Efficient utilization of alum due to more intimate mixing was suggested to be responsible for the reduction of the alum dose. This technique has proved to be suitable for treatment of water with initial fluoride concentration up to 5 mg/L.

(3) Polyaluminum Coagulants

Coagulants that contain performed polymeric aluminum species such as polyaluminum-hydroxy-sulfate (PAHS), polyaluminum chloride, and partially neutralized aluminum sulfate (PNAS) are reported to be effective in clarification of water and removal of inorganic contaminants including fluoride (Parthasarathy and Buffle, 1985; Koether et al., 1997). Although fluoride removal by polyaluminum chloride is not yet well established, a recent study showed its efficiency to reduce initial fluoride concentration in the range of 2-10 mg/L to a value of 1 mg/L with doses of 143-800 mg/L (Chhabra, 1997).

(4) Iron Salts

Link and Rabosky (1976) reported fluoride concentration of 500 to 600 mg/L was reduced to 3 - 5 mg/L using 350 to 400 mg/L of ferric iron. And 50 mg/L of fluoride was reduced to 12.6 mg/L by adding 50 mg/L of ferric chloride along with 5 mg/L of an anionic polyelectrolyte and 0.7 mL of 5% lime solution at pH of 8.1.

(5) Tricalcium Phosphate

This process is based on changing fluorine compounds into low soluble fluoraptite, which precipitates from water.

$$3Ca_3(PO_4)_2 + CaF_2 \rightarrow 3Ca_3(PO_4)_2.CaF_2$$

Studies on defluoridation of water by freshly precipitated tricalcium phosphate showed that the amount of tricalcium phosphate for removing 1 mg of fluoride was in the range of 23 to 30 mg (Nikoladze et al., 1989). Good results were obtained by passing water through a layer of suspended tricalcium phosphate precipitate with up flow velocity of 0.6 to 0.8 mm/s.

Based on this method package defluoridation plant called "Andco" process was developed by Andco Environmental Process Inc. for small water supply facilities. The fluoride in raw water was precipitated as fluorapatite by addition of phosphoric acid, calcium chloride, and lime to the water and then it was mixed, clarified, and filtered. The optimum ranges of pH were 6.2 to 7 and 7.5 to 9.5 (O'Brien, 1983).

(6) Magnesium Compounds

Fluoride can also be removed from water by coprecipitation with magnesium hydroxide during lime softening. Based on the results of laboratory investigation the following relationship between magnesium and fluoride removal was established (Nikoladze et al., 1989).

$$F_r = F_i - (0.07F_i \times \sqrt{Mg}) \qquad (2.1)$$

where F_r - residual fluoride, mg/L

F_i - initial fluoride, mg/L

Mg - magnesium removed during lime softening, mg/L

To reduce the fluoride concentration by 1 mg/L, 45 to 65 mg/L magnesium was required (Nikoladze et al., 1989; Maier, 1953). This process is primarily adaptable to low fluoride (3 to 4 mg/L) waters requiring softening. It has got practical application in USA at Alger and Beltimore water treatment plants (Nikoladze et al., 1989).

2.2.1.2 Methods Based on Adsorption, Ion Exchange, and Others

Adsorption method includes the use of activated alumina, activated carbon, etc. The driving force for adsorption may be a consequence of hydrophobic (water disliking) character of solute or high affinity of the solute for the solid or a combination of the two. The degree of solubility of dissolved substance is the most significant factor in determining the intensity of the first of the two driving forces. The more hydrophobic the substance is, it will be more likely be adsorbed. The affinity of the solute for the solid may be a result of electrical attraction of the solute to the adsorbent (exchange adsorption), of Vander Waals attraction (physical adsorption) or of a chemical nature (chemical adsorption). There are many factors, which influence both the rate and magnitude of adsorption. These include: nature of adsorbate and adsorbent, solution pH, temperature, concentration of the solute, presence of competing adsorbates, and formation of new surface phases (Weber, 1972; Benjamin et al., 1982; Faust and Aly, 1987; Ching et al., 1994). Fluoride removal by exchange of ions/radicals with fluoride ion (ion-exchange) includes the use of bone char, ion exchange resins, etc.

(1) Activated Alumina

Activated alumina (Al_2O_3) is calcined granules of hydrated alumina. Choi and Chen (1979) reported that activated alumina and activated bauxite were superior to activated carbon for fluoride removal. Activated alumina was the best because of its wider pH range (5 to 8), higher removal capacity, lower water and mechanical wear. Salinity and sulfate also do not affect adsorption of fluoride by activated alumina and activated bauxite.

Bishop and Sasnsoucy (1978) reported that higher removal capacity with activated alumina was achieved in water with low pH (<6) and low alkalinity. The removal efficiency also increased with increase of initial fluoride concentration. However, Choi and Chen (1979) in contrast observed increase of removal efficiency with decrease of initial fluoride concentration. Observation on a laboratory batch test showed that adsorption was relatively more rapid the more dilute the solution (Bulusu and Nawlakhe, 1988). At optimum pH of 5 to 6 the removal capacity of activated alumina exceeds 4.6 kg F^-/m^3 alumina (Rubel and Woosley, 1979). It can be used for water having fluoride concentrations as high as 20 mg/L (Hao and Huang, 1986; Ramamohan Rao, 1997) regenerating with a 1-2% sodium hydroxide solution and rinsing with acid and water. Its capacity also has a linear relationship to the amount of regenerant used (Gillies, 1978). Regenerant disposal, bed clogging, and possible leaching of alumina at low pH were identified as the disadvantages of this method (Bishop and Sansoucy, 1978; Hao and Huang, 1986; Ramamohan Rao, 1997).

Activated alumina has been applied in many developed countries for municipal plants. Domestic defluoridation unit and hand pump attachable community defluoridation plants based on adsorption by indigenously manufactured activated alumina (AA) were developed in India and successfully tested in a laboratory and at the field (Iyengar and Venkobachar, 1997). In case of domestic defluoridation unit, initial fluoride concentration of 10.7 mg/L was reduced to 0.3 mg/L from raw water having alkalinity of 472 mg/L, hardness of 174 mg/L as $CaCO_3$, and total dissolved solids of 636 mg/L. The treatment process is dependent on alkalinity and initial fluoride concentration, whereas hardness in the range of 200-800 mg/L as $CaCO_3$ has no effect. With increase of alkalinity from 400 to 800 mg/L as $CaCO_3$, fluoride removal capacity of activated alumina decreased from 1900 to 1337 mg/kg. With increase of initial fluoride concentrations from 3 to 11 mg/L, its capacity increased in the range of 1550 to 1992 mg/kg. Hand pump attachable defluoridation plant consisting cylindrical tank of 0.5 m diameter and 1.5 m height with hopper bottom filled with 110 kg of AA G-87 (0.3-0.8 mm size) has been studied in the field at raw water fluoride concentration of 5.5 mg/L. The three years experience showed that the plant produced around 25000 liters of treated water per defluoridation cycle reducing initial fluoride to below 1.5 mg/L. Studies on existing defluoridation plants conducted in the State of Rajasthan (India) showed that activated alumina was better at fluoride concentrations greater than 5 mg/L, techno-economically. However, handling of regeneration chemicals (acids and alkalis) was noted as the main problem at community water supply level (Kumar, 2000).

(2) Activated Carbon

Fluoride could be removed by activated carbon at pH of 3 (Sigworth and Smith, 1972). Removal of 72% and 84% was also noted from diluted seawater and from deionized distilled water respectively at pH of 6.2 (Choi and Chen, 1979). Bhargava and Killedar (1992) had studied the feasibility of fluoride adsorption on fish bone charcoal and reported a removal of 80% at an initial fluoride concentration of 10 mg/L. Granular activated charcoal pretreated with aluminum sulfate solution was also reported to have fluoride removal capacity at pH values of 4.8 to 5.5. The removal was achieved by formation of a complex compound with aluminum ion and consequence sorption of both the free and bound fluoride ions by the products of hydrolysis of aluminum sulfate and at the surface of the activated charcoal (Ramamohan Rao, 1997). Activated carbon is also known for its removal of color, odor, bacteria, and organic contaminants (Faust and Aly, 1987) which could be used as an advantage in defluoridation of such waters.

(3) Indigenous Carbonaceous Materials

Saw dust, rice husk, and corn cobs were studied for fluoride removal. Saw dust carbon showed a defluoridating capacity of 350 to 450 mg F^-/kg of dry material but it has poor attritional and hydraulic properties (Thergaonkar et al., 1969). The removal efficiencies of rice husk and corn cobs with optimum doses of 70 mg/L and 30 mg/L were 75% and 65% of the initial fluoride concentrations respectively (Sharma, 1991). Paddy husks digested in 1% potassium hydroxide and soaked in 2% alum solution have fluoride removal capacity of 320 mg F^-/kg of the medium (Ramamohan Rao, 1997). Sulphonated carbonaceous material prepared from coconut shell using sulfuric and fuming sulfuric acids was reported to have fluoride removal capacity of 780 mg F^-/kg (Ramamohan Rao, 1997). It can be regenerated with 2-4% aluminum sulfate solution. Activated carbon prepared from cotton, coffee, and coconut wastes were also studied but the results were not encouraging for practical application (Bulusu et al., 1979).

(4) Defluoron – 1

It is sulphonated saw dust impregnated with 2% alum solution. Its fluoride removal capacity at pH of 6.6 was rated at 600 mg F^-/kg of the medium reducing initial fluoride concentration from 4.5 to 1 mg/L (Bulusu et al., 1979). It has poor hydraulic properties and suffered from heavy attritional loses.

(5) Defluoron – 2

It is sulphonated coal which is regenerated with one bed volume of 4% alum solution. Its average fluoride removal capacity has been found to be 484 mg F^-/L (Bulusu et al., 1979) or 362 mg F^-/L (Thergaonkar et al., 1969) of the medium. Continuous field tests for about four years showed a reduction of defluoridating capacity by about 60% (Bulusu et al., 1979).

(6) Clay and Sand Particles

Kaolinite, serpentine, china clay, clay pot chips, semi-calcined dolomite particles, gypsum particles, and reddish-brown sand had been tested for defluoridation. Studies on green and yellow varieties of serpentine showed that a dose of about 80 mg/L could reduce fluoride from 6.2 to 1.8 mg/L. However, the cost was prohibitive (Bulusu et al., 1979). Clay pot chips have defluoridation capacity of 80 mg F^-/kg of material (Solsona, 1985). Filters filled with semi-calcined dolomite particles were reported to have defluoridation capacity of 400 g F^-/m^3 (Ramamohan Rao, 1997). It is regenerated using 1% sodium hydroxide. Solsona (1985) reported that reddish brown sand reduced fluoride concentration from 6 to 1.7 mg/L in two runs, and it has good hydraulic conditions. Application of some of these locally available defluoridation materials at house hold and community level is promising.

(7) Bone Meal and Bone Char

Fluoride concentration was reduced from 3.5 to 0.2 mg/L on the surface of degreased, caustic and acid treated bone (Gillies, 1978). The removal mechanism suggested was an exchange of the carbonate radical with fluoride. Bone char produced by carbonizing bone at high temperature was also reported to have fluoride removal capacity of 102 g F^{-}/m^{3} when removing 5 mg/L of fluoride and has been utilized in several full-scale defluoridation plants (Gillies, 1978). Nevertheless, since arsenic is irreversibly adsorbed on bone char it will not be practical for fluoride waters that also contain arsenic. Fluoride removal by bone char increases with decreasing pH but because of the problem of solubility (bone is soluble in acid) and for reasons of consumption and distribution, a pH of 7 or greater is recommended. It is regenerated with caustic soda.

(8) Synthetic Bone Material (Tricalcium Phosphate)

It is prepared in powder and granulated form by reacting phosphoric acid with lime. The granulated form is similar to other ion exchange media that require regeneration. It is regenerated with a caustic solution usually sodium hydroxide, and then rinsed with a dilute acid solution. The material has fluoride removal capacity of 685 g F^{-}/m^{3}. However, this capacity decreases by 3% for each 100 mg/L of sulfate in the raw water (Gillies, 1978). Moreover, it has high attrition losses and needs frequent regeneration.

(9) Ion Exchange Resins

Commercially available resins such as Zeocarb 225, Tulsion, and Carboin are reported to have fluoride removal capacity of 1650 mg F^{-}/kg, 960 mg F^{-}/kg, and 820 mg F^-/kg respectively (Ramamohan Rao, 1997). The materials are regenerated with 2-4% aluminum sulfate solution.

(10) Miscellaneous Defluoridation Methods

(i) Reverse Osmosis: A wide fluoride removal range, 40 to 96% was reported by reverse osmosis and it was noted that the process is pH dependent (Gillies, 1978). Reduction of initial fluoride concentration from 5.3 mg/L to less than 1 mg/L was also reported (Ramamohan Rao, 1997). In spite of its high operating costs, it may be used for defluoridation of small community water supplies.

(ii) Electrodialysis: In electrodialysis process fluoride is removed through ion selective membranes by a direct current electrical field. It was described to have about 80% removal efficiency (O'Brien, 1983).

The drawbacks of both reverse osmosis and electrodialysis are removal of part or all dissolved ions present in the raw water, production of concentrated brine, and relatively high energy consumption.

2.2.1.3 Discussion

Various treatment methods and materials have been tried for fluoride removal. However, of these, adsorption/ion exchange by activated alumina or bone char and precipitation by alum and lime are extensively used. Activated alumina is a choice of many developed countries for municipal plants. Handling of chemicals (acids and alkalis) for regeneration, bed clogging, and regenerant disposal are the main problems of this method. Because of its simplicity and low cost (for fluoride concentrations up to 5 mg/L), in India, the Nalgonda technique is widely used for treatment of domestic and community water supplies. It is utilized for fluoride concentrations up to 10 mg/L.

Sequencing batch (fill-and-draw) type and hand pump attached defluoridation plants of this technique are effective at community and village levels respectively. However, at fluoride concentrations more than 10 mg/L, this method requires a high dose of alum, which could result in increase of sulfate and aluminum concentration in the treated water to unacceptable level. Therefore, there is a need to search for potential improvement of this technique at higher fluoride concentrations.

2.3 PRESENCE AND TREATMENT OF NITRATE

Nitrogenous materials may enter the aquatic environment from either natural or man-caused sources. Natural sources of nitrogenous substances include precipitation, dust fall, non-urban run-off, and biological fixation. The great continental glaciers are believed to be the causes of groundwater nitrate concentration in the Mid Western United States, Southern California, and Central Provinces of Canada (Lenain, 1967). Nitrate pollution of water is derived from various point and non-point sources, such as excessive use of fertilizers, feed lots, industrial wastes, wastewater treatment effluents, septic tanks, and refuse dumps. Since nitrate is neither adsorbed nor precipitated in soil, it is easily leached by rainfall and infiltrating water to the water table. The main cause for increasing nitrate concentration in groundwater of European and North American countries is extensive application of nitrogenous fertilizers and manure in agriculture (Appelo and Postma, 1993). In India, the consumption of nitrogenous fertilizers has grown by three folds in a decade and become a source of pollution in some areas (Pande et al., 1986; Mathur and Kumar, 1990). The nitrate problem in groundwater of the Rift Valley region in Ethiopia is also the result of extensive application of fertilizers to the sugar cane plantation (Ashley and Burley, 1994). Feedlot run-off constitute a source of nitrogen which has become significant as a result of concentrated and centralized feed lots (Lenain, 1967). Animal manure is the main source of pollution of groundwater in Netherlands (Scheltinga, 1985). Industrial wastewater from fertilizer manufacturing, food processing, dairy and meet production, and petroleum refineries contain high nitrogen which significantly contribute to the pollution of groundwater (Pande et al., 1986).

In Netherlands, 25% of the groundwater well-fields have been estimated to have nitrate associated problems (Hoek and Klapwijk, 1987) and nitrate level in the groundwater has been found to be steadily increasing due to intensive animal husbandry (Scheltinga, 1985). In Belgium, 40% of the wells had nitrate levels greater than EEC's recommendation. In United Kingdom, 20% of groundwater bore holes had nitrate concentration greater than 10 mg/L (as N) and its level has been found to be increasing at the rate of 0.01 to 0.02 mg/L per year (Mathur and Kumar, 1990). It is estimated that approximately 1% of the population in USA had been using public water supplies, derived primarily from groundwater having excessive nitrates (Lenain, 1967). In groundwater of West Central Texas (USA) nitrate concentration as high as 690 mg/L (as N) was reported (Hamill and Bell, 1986). And generally the level of nitrate in the groundwater has been found to be increasing at the rate of 0.06 to 0.35 mg/L per year (Mathur and Kumar, 1990). In India, 1290 groundwater samples collected from 11 states showed nitrate concentration more than 45 mg/L (as NO_3^-). The states include Rajasthan, Gujarat, Tamil Nadu, Andhra Pradesh, Haryana, Karnataka, Lakhshdweep, Madhya Pradesh, Bihar, Maharastra, and Orissa (Chakravarty, 1990). Nitrate level in groundwaters of some cities in India such as Meerut, Jaipur, Nagpur, and Hyderabad have also been reported as high as 156, 180, 77, and 78 mg/L respectively (Mathur and Kumar, 1990).

According to the WHO guidelines and recommendations the maximum allowable concentration in drinking water is 45 mg/L (WHO, 1984). In India according to ICMR (1975) recommendation the permissible limit is 45 mg/L but is acceptable if not exceeded 100 mg/L (as NO_3^-). One of a serious medical problems often caused by nitrates is a condition that develops in the blood stream of babies under 6 months called infant cyanosis, methomoglobinemia, or blue babies. In this case hemoglobin loses its property to carry oxygen due to oxidation of iron in the blood from ferrous to ferric form by nitrite which is reduced from nitrate by bacteria (Lenain, 1967; Gruener and Shuval, 1973; Shuval and Gruener, 1977). Cases of methemoglobinemia was reported from many parts of the world, particularly from the Mid Western United States and Central Provinces of Canada, Israel, Czechoslovakia, and Russia (Lenain, 1967). The combination of nitrates and amines through the action of bacteria in the digestive tract results in the formation of nitrosamines, which are potentially carcinogenic (Mirvish, 1977).

2.3.1 Treatment Methods

Several treatment methods, which could broadly classified as (i) physicochemical, and (ii) biological have been studied for nitrate removal from drinking water.

2.3.1.1 Physicochemical Methods

Physicochemical method includes chemical reduction, electrodialysis, reverse osmosis, and ion exchange.

(1) Chemical Reduction

The possibilities of reducing nitrate chemically using ferrous hydroxide precipitated in situ and by powdered aluminum have been discussed in a recent review on denitrification of drinking water by Kapoor and Viraraghavan (1997). The reaction for reduction of nitrate by ferrous hydroxide is induced under basic pH conditions and it is enhanced by the presence of cupric or silver ion.

$$NO_3^- + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + OH^-$$

Experimental results showed that a $Fe:NO_3^-$ ratio of about 15:1 was required in the presence of copper catalyst for the reaction to proceed. The time required for the reaction, the variability of possible end product, which further requires removal by air stripping, and the voluminous sludge produced made the method look unattractive as practical treatment option.

During chemical denitrification by powdered aluminum, ammonia was found to be the principal reaction product (60 to 95%) that could be removed by air stripping. Optimum nitrate removal was observed at pH 10.25. The denitrification was explained on the basis of the following:

$$3NO_3^- + 2Al + 3H_2O \rightarrow 3NO_2^- + 2Al(OH)_3$$

$$NO_2^- + 2Al + 5H_2O \rightarrow NH_3 + 2Al(OH)_3 + OH^-$$

$$2NO_2^- + 2Al + 4H_2O \rightarrow N_2 + 2Al(OH)_3 + OH^-$$

This process can be effectively used if incorporated with lime softening in the pH range of 9 to 10.5. Selective reduction of nitrate relative to sulfate was possible and 1.16 g of aluminum was required for the reduction of 1g of nitrate.

(2) Electrodialysis

Studies were conducted on irrigation water containing 26 mg/L (as N) and secondary wastewater effluent with 12.4 mg/L (as N). A single stage electrodialysis system produced nitrate removal of 46% and 39% respectively (Gillies, 1978).

(3) Reverse Osmosis

Since ion rejection by reverse osmosis is directly related to the size and valence of the ion or molecule, monovalent nitrate is not as efficiently removed from water as divalent ions, such as sulfate. Although various equipment manufacturers have reported that it has nitrate removal efficiency in the range of 60 to 95%, economically it may be competitive with other methods when the total dissolved solids content exceed about 1000 mg/L (Gillies, 1978; Kapoor and Viraraghavan, 1997).

(4) Ion Exchange

The availability of variety of new resins has expanded the application of ion exchange to the treatment of water supply and specifically for removal of nitrate. But most of commercially available resins exhibit a greater selectivity for sulfate than for nitrate (Gillies, 1978) and it is not possible to remove nitrate without completely removing sulfate at the same time. To overcome this problem, nitrate selective ion exchangers have been developed (Hiscock et al., 1991). Currently, fixed-bed and continuous loop system ion exchange plants are being used in UK and other countries (Croll and Hayes, 1988). In continuous loop system the resin is periodically pulsed round the loop. In one section of the loop the resin removes the nitrate whereas in the other sections the exhausted resin is regenerated and rinsed. Its main advantages compared with the fixed bed plant are less variation in water quality and less resin requirement per unit flow. However, the design of the continuous loop system is much complex, requiring considerable maintenance, moreover, compaction and loss of resin has been experienced.

Studies conducted in laboratory indicated that nitrate-nitrogen could be consistently lowered from as high as 50 mg/L to 5 mg/L and less (Gillies, 1978). Water with low total dissolved solids (500 mg/L) and with sulfate concentration less than 300 mg/L can also be effectively treated using this process. However, the main problem of this method was its high regenerant consumption associated with its high disposal cost. To minimize this problem Hoek and Klapwijk (1987) developed a new nitrate removal process combining ion exchange and biological methods. In this process, nitrate was removed by ion exchange and regeneration of the resin in a closed circuit was achieved with denitrification reactor. Because the regenerant bicarbonate is an end product of the biological denitrification, the system itself produces the salt necessary for regeneration of nitrate loaded resin. Thus production of voluminous brine was minimized in this closed circuit.

Kapoor and Viraraghavan (1997) noted that plant installation and operating cost (not including cost of regenerant disposal) for ion exchange is less than biological denitrification. However, the total cost of treatment by ion exchange per pound of nitrate-nitrogen removal was more than heterotrophic denitrfication. The main drawback of this method is the problem associated with concentrated brine production and its disposal.

2.3.1.2 Biological Denitrification

The microbial reduction of nitrate to gaseous nitrogen products is termed dissimilatory denitrification or nitrate respiration. It occurs when nitrate instead of oxygen is used as a terminal electron acceptor. The process proceeds through a series of four steps, from nitrate to nitrogen gas ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_20 \rightarrow N_2$). The pH has influence upon the end product of the process. If it is above 7.3, nitrogen is the end product, if below this value, nitrous oxide production will be the result (Christensen and Harremoës, 1977 ; Traverso and Cecchi, 1989).

Denitrification is accomplished (i) by heterotrophic microorganisms that require a reduced organic substrate for energy and cell synthesis such as methanol, ethanol, or acetic acid, and (ii) by autotrophic bacteria which can use hydrogen or various reduced sulfur compounds as energy sources, and carbon dioxide or bicarbonate as a carbon source for cell synthesis (Gayle et al., 1989). Most bacteria in sewage and sewage sludge are capable of respiratory nitrate reduction (Christensen and Harremoës, 1977; Fang and Zhou, 1999).

(1) Factors Affecting Biological Denitrification

Oxygen content: Oxygen competes with nitrate as a terminal electron acceptor. Its concentration ranging from 0.1 to 0.2 mg/L have been indicated to have inhibitory effects on denitrfication. Particularly suspended cultures are more vulnerable to this effect than fixed microorganisms (Christensen and Harremoës, 1977; Traverso and Cecchi, 1989). Denitrification with the presence of oxygen with accumulation of nitrite in the effluent was also observed (Christensen and Harremoës, 1977).

Temperature: Denitrification rate is a function of temperature and is described by a bell shaped curve, with a minimum (0 °C), an optimum (approximately 40 °C), and a maximum (approximately 50 °C). This dependency is described by the following equation (Christensen and Harremoës, 1977).

$$RD_t = RD_{20}.10^{K_t(t-20)} \quad (2.2)$$

where RD_t –maximum denitrification rate at t °C,

RD_{20}- maximum denitrification rate at t = 20 °C,

K_t - temperature constant (for suspended cultures, experimentally it is found to be in the range of 0.03 to 0.07),

t - temperature.

Fairly good denitrification is observed at 20 °C, and a significant increase can be expected for a modest increase to 25-30 °C (Gaudy, jr. and Gaudy, 1981).

pH: As it is illustrated in the following stochiometric relationships for methanol and ethanol respectively, denitrification produces alkalinity.

$$5CH_3OH + 6NO_3^- \rightarrow 5HCO_3^- + 3N_2 + OH^- + 7H_2O$$

$$5C_2H_5OH + 12NO_3^- \rightarrow 6N_2 + 10CO_2 + 9H_2O + 12OH^-$$

The stoichiometric quantity of alkalinity produced is 3.57 mg as $CaCO_3$ per mg of nitrate or nitrite-N reduced to nitrogen gas (Miyajic et al., 1980; Gayle et al., 1989). Therefore, pH increase would be expected in denitrification process. The optimum pH ranges noted for denitrifcation are 7 to 8 (Hiscock et al., 1991), 7 to 7.5 (Gaudy, Jr. and Gaudy, 1981), and 7 to 9 (Christensen and Harremoës, 1977).

Type and quantity of carbon source: This factor has influence on denitrifying activity and its rate. However, if there is an excess of carbon source over the requirement to achieve denitrification, the rate is non-dependent on carbon source concentration (Barnes and B~~u~~liss, 1983). The carbon: nitrogen ratios for methanol, ethanol, and acetic acid was found to be 0.93, 1.05, and 1.32 respectively. Thus methanol is more effective in terms of C/N ratio (Kapoor and Viraraghavan, 1997). Tam et al. (1992) studied methanol, glucose, and sodium acetate as external carbon source at the concentration equivalent to theoretical values of 100 and 200 mg O_2/L and reported their efficiency in the order of sodium acetate, methanol, and glucose. Quantity of sludge produced is also dependent on type of carbon source. Twice as much sludge is produced per mg of nitrogen reduced when saccharose is used rather than methanol is employed (Gaudy, Jr. and Gaudy, 1981). Although ethanol and acetic acid are more expensive than methanol, they are in full-scale use for drinking water denitrification due to potential toxicity of methanol (Christensen and Harremoës, 1977; Clifford and Liu, 1993).

Nitrate concentration: The rate of denitrification is dependent on the minimum concentration value of nitrate. If the concentration is greater than 1 mg/L, the rate will be independent of it (zero order) (Barness and Buss, 1983). Some researchers have also observed inhibition of nitrate reduction due to high nitrate concentration (Traverso and Cecchi, 1989). This was suggested to be due to the toxicity of accumulated nitrite which could result from oxygen availability, nutrient deficiencies, type of denitrifying microorganisms, and the pH condition (Gayle et al., 1989; Lazarova et al., 1994).

Miscellaneous inhibitors: Some substances were described to have inhibitory effects on denitrification. These include sulfide, sulfate, acetylene, nitrite, sodium, calcium, nickel, aluminum, and free ammonia (Hiscock et al., 1991; Christensen and Harremoës, 1977; Traverso and Cecchi, 1989). Nitrite might inhibit at concentration above 30 mg/L (as NO_2^- -N), whereas high concentration of sodium enhances nitrite concentration. Calcium reacts with phosphorous in solution; hence high calcium concentration limits denitrification rates because of limited phosphorus availability. Aluminum solution of 4.4% exhibit toxic effects. Free ammonia has toxicity that can be avoided at pH < 7.8.

(2) Denitrification Kinetics

Denitrification kinetics can be described by an equations (Eq. 2.3 and 2.4) derived from the Monod kinetics relationship (Metcalf & Eddy, Inc., 1991; Dague et al., 1998).

$$\frac{X.HRT}{S_o - S_e} = \frac{K_s}{k_{\max}} \cdot \frac{1}{S_e} + \frac{1}{k_{\max}} \qquad (2.3)$$

where X- biomass concentration (MLVSS), mg/L

HRT- hydraulic retention time, d

S_o- influent substrate concentration, mg/L

S_e-effluent substrate concentration, mg/L

K_s- half saturation coefficient, mg/L

k_{max}- maximum specific substrate removal rate, d^-

This equation is used to determine the Monod's kinetics parameters viz. the half velocity constant (K_s), and the maximum rate of substrate utilization (k_{max}), from a linear plot of $\frac{X.HRT}{S_o - S_e}$ versus $\frac{1}{S_e}$. The slope of this plot is equal to $\frac{K_s}{k_{\max}}$, and the y intercept is equal to $\frac{1}{k_{\max}}$.

$$\frac{1}{\theta_c} = Y\frac{S_o - S_e}{X.HRT} - k_d \tag{2.4}$$

where θ_c-cell residence time = HRT (without recycle), d

Y - Yield coefficient, mg VSS/mg substrate

k_d-endogenous decay coefficient, d^{-1}

This equation is used to determine the yield (Y) and the endogenous decay (k_d) coefficients from a linear plot of $\frac{1}{\theta_c}$ versus $\frac{S_o - S_e}{X.HRT}$. The slope of this plot is equal to Y and the y intercept is equal to ($-k_d$).

(3) Biological Denitrification Units

Various conventional unit processes have been adopted and used for the denitrification of drinking water particularly in European countries. These include fluidized bed, fixed bed, and upflow sludge-blanket reactor (USBR) (Gayle et al., 1989; Green et al., 1994; Traverso and Cecchi, 1989). Further, though sequencing batch reactor (SBR) is not used in denitrification of drinking water so far, it is being used in biological wastewater treatment. They are discussed below:

Fluidized-bed reactor: It is a recent process innovation in water technology. Its important features are the fixation of microorganisms on the surface of small sized particles leading to the high content of active microorganisms and large surface area available for reaction with the liquid. Its high flow rate leads to high degree of mixing, reduction in size of the plant, and avoids risk of clogging. It was reported to have high volumetric loading rate. But the rate of flow in the bed needs strict control to retain the biomass, which restricts the process flexibility (Traverso and Cecchi, 1989). Richard et al. (1980) evaluated a pilot-scale fluidized-bed reactor for denitrification of groundwater with average nitrate concentration of 100 to 150 mg/L using ethanol or acetic acid as a substrate. Accordingly the maximum specific nitrate utilization rate was found to be 250 mg NO_3^- /hr/g VSS.

Fixed-bed reactor: This reactor with various supporting media have been studied for denitrification. In their literature survey Gayle et al. (1989) noted that nitrate concentration was reduced from 80 to 30 mg/L and nitrite decreased to less than 0.1 mg/L by upflow fixed bed reactor using acetic acid as a substrate. Pilot-scale bioreactor packed with polystyrene beads using methanol or ethanol as a carbon source reduced nitrate concentration from 55 mg/L to 3 mg/L. At a filter-loading rate of 1 kg NO_3^- /m^3.day, 95% removal efficiency was obtained by a fixed-film reactor packed with floating styropor spheres using ethanol as a substrate. Sison et al. (1996) reported that fixed film reactor with activated carbon as a support media has demonstrated 89 to 95% removal efficiency with intermittent and injection mode of substrate feeding. The main drawback of fixed film reactors is their susceptibility to clogging, which necessitates back washing. In order to minimize the problem of product water contamination with microorganisms, substrates, and metabolites, Reising and Schroeder (1996) studied the possibility of denitrification incorporating microporous (0.02 µm pore size) polytetrafluoroethylene membrane, which separates the water from microorganisms and substrates. Fixed and free cell microorganisms were investigated and the result showed that nitrate removal rate of the latter was better.

USBR: Green et al. (1994) studied upflow sludge blanket reactor (USBR) for groundwater denitrification and reported stable operation with volumetric loading rates of 4 kg N/m^3.day using ethanol as a carbon source. However, deterioration of settling characteristics of the sludge and biomass washout was also observed for water having low hardness. Hoek and Klapwijk (1987) reported that sodium chloride (10 to 15 g/L) and sodium bicarbonate (25 to 30 g/L) solutions could be denitrified by USBR using methanol as a carbon source with about 80% efficiency.

SBR: In recent years, sequencing batch reactor (SBR) system has found favour with the design of wastewater treatment system. Comparative features of conventional reactor design vis-à-vis the SBR system are presented in Table 2.7. It is a batch process operating cyclically. Each cycle consists of five phases: Fill, React, Settle, Decant, and Idle. Since the reactor also serves as a clarifier, there is no need of additional clarifier and sludge return systems, which largely decreases the capital cost. Moreover, they behave as ideal plug-flow reactors with respect to kinetic response (Silverstein and Schroeder, 1983; Irvine et al., 1983). Clifford and Liu (1993) reported that 0.5 N sodium chloride spent regenerant solution containing up to 835 mg/L NO_3^--N was denitrified by SBR with an efficiency of more than 95% using methanol as a carbon source. Full-scale operation of SBR at Culver demonstrated to be a viable alternative to conventional continuous flow activated sludge treatment of domestic waste waters for BOD and suspended solid removal, nitrification and denitrification, and chemical precipitation of phosphorous (Irvine et al., 1983). SBRs also have got full-scale application for wastewater treatment in USA, Canada, Australia, and Malaysia. In 1987

Table 2.7 Advantages/Disadvantages of Biological Denitrification Units

Biological units	Merits	Demerits
Fluidized bed	(a) High denitrification rate (b) Small volumes of waste biomass sludge (c) Possible elimination of settling tank (d) Not susceptible to bed clogging	(a) Limited process flexibility
Fixed bed	(a) Good denitrification rate (b) Small volume of waste biomass sludge (c) Possible elimination of settling tank	(a) Susceptible to clogging (b) Backwashing may be required
Upflow sludge blanket reactor (USBR)	(a) Good denitrification rate (b) Small volume of waste biomass sludge (c) Possible elimination of settling tank	(a) Not much known in denitrification of drinking water (b) Granule formation is affected by hardness of the water (c) Biomass washout for water having low hardness
Sequencing batch reactor (SBR)	(a) Well known in small scale biological wastewater treatment (b) No need of settling tank (c) Simple in operation (d) Settling in quiescent conditions (e) Simple manipulation of treated water quality (f) Relatively low cost	(a) Not known in denitrifcation of drinking water (b) Relatively high volume of waste biomass sludge

in USA 15 SBRs were operational with a capacity of 151 to 22860 m^3/day (Wun-Jern, 1989). Fill-and-draw (sequencing batch) type reactors are also being used in the Nalgonda technique for defluoridation at community water supply level (Bulusu et al., 1979).

2.3.1.3 Discussion

Although suspended growth reactors have low denitrification rate compared to the fluidized bed and fixed film reactors, they are capable of denitrifying high nitrate with high efficiency (Clifford and Liu, 1993). Despite the fact that sequencing batch reactors (SBRs) have high efficiency in organic carbon and nitrogen removal (Irvine et al., 1983; Silverstein and Schroeder, 1983; Wun-Jern, 1989) and have got practical application particularly for small scale waste water treatment, it has not been tried for biological denitrification of drinking water so far. Its good record in wastewater treatment of small-scale plants points towards its potential in denitrification of drinking water.

2.4 SIMULTANEOUS PRESENCE OF FLUORIDE AND NITRATE AND TREATMENT

Fluoride and nitrate are found simultaneously in groundwater in some parts of the world including India. In some cases they are high in concentrations. In India, since groundwaters of same eleven states have both fluoride and nitrate above the acceptable levels (Paramasivam and Nanoti, 1997; Susheela, 1988; Chakravarty, 1990) simultaneous occurrence of these contaminants is not a rare case. Pal (1983) reported nitrate and fluoride concentrations as high as 178.6 mg/L and 21 mg/L respectively in Agra region. Gupta (1992) reported nitrate and fluoride concentrations of 251 mg/L and 3.2 mg/L respectively in Nagaur district of Central Rajasthan. Elsewhere, in the Rift

Valley region of Ethiopia nitrate and fluoride concentrations in groundwaters as high as 224 mg/L and 26 mg/L respectively were also reported (Ashley and Burley, 1994). Although, the synergistic adverse effects of these contaminants on human health particularly children are not known, yet they are suspected to be of great concern. In many cases, while the fluoride content could be same, nitrate occurrence could be ever increasing with continuing pollution through seepage in many years. However, there is no pertinent literature available to treat groundwaters containing fluoride and nitrate simultaneously.

2.5 CONCLUDING REMARKS

The literature review presented herein has highlighted the need of formulating technically sound scheme for treatment of groundwaters containing fluoride and nitrate contents occurring simultaneously. A prudent method of treatment in such a situation calls for designing an integrated treatment based upon SBR concept of treatment units design. Further, the appropriate scheme should be based upon the principle of physicochemical treatment for fluoride removal and biological treatment for nitrate removal. The present research has been planned based upon these conclusions.

Chapter 3

MATERIALS AND METHODS

CHAPTER-3

MATERIALS AND METHODS

3.1 BACKGROUND

In India, where Nalgonda technique is technoeconomically well established for raw water fluoride concentrations up to 5 mg/L, it is necessary to search its potential at higher fluoride concentrations (6 to 20 mg/L, found globally). The problems associated with the use of this technique for removal of relatively higher fluoride concentrations have resulted from high alum dose requirement. There is a need to explore possible reduction of the alum dose. The present work has studied the removal of fluorides in the range of 6 to 20 mg/L using a combination of alum and powdered activated carbon (PAC) as alum-PAC slurry instead of alum only.

Of the denitrification methods so far studied, only ion exchange and biological denitrification are widely used for drinking water treatment. Ion exchange requires regeneration which results in problems such as handling of chemicals (alkalis and acids) and regenerant disposal especially at community water supply level. In addition, the total cost of nitrate removal by ion exchange is higher than biological denitrification. Thus, to cope up with the ever increasing higher nitrate concentrations in water resources, biological denitrification seems to be a better alternative. Most of the studies conducted so far either on ion exchange or biological denitrification of drinking water were at relatively low nitrate concentrations (less than 50 mg/L as N). The present research has been planned to include higher nitrate concentrations in the range of 40 to 250 mg/L (as N) to cater for reported higher values, its ever increasing trend, and occurrence of nitrate along with fluoride.

The main objective of this research work was to study the feasibility of an integrated nitrate and fluoride removal processes for relatively higher concentrations with appropriate selection of the treatment techniques for denitrification as well as defluoridation forming a sequencing reactor system. The reactor system proposed and studied in this research involves two sequencing batch reactors (SBRs) for biological denitrification and for defluoridation by alum-PAC slurry. Defluoridation by alum-PAC slurry needs sufficient alkalinity to ensure alum precipitation, which will require addition of chemicals like lime in case of its insufficiency in water. On the other hand, biological denitrification process produces alkalinity. The present work has investigated utilization of sufficient alkalinity produced in the denitrified water, thus, avoiding the need of lime for the same purpose. Besides, increase of turbidity and contamination of treated water by microorganisms and residual organics was expected which would necessitate further treatment. Further, it was expected that alum and activated carbon in addition to fluoride could also remove color, odor, turbidity, bacteria, and organic contaminants. Some of these additional works of sequencing batch treatment employed have also been probed in the present research.

3.2 GENERAL APPROACH

Experimental studies were conducted in three phases as given below to work out the efficiency of removal of fluoride and nitrate from water by using sequencing batch reactors (SBRs).

Phase-1 study: Defluoridation (Experiments using jar test apparatus): Studies were conducted to optimize the pH and operational procedure for coagulation and adsorption, to evaluate the optimum alum and powdered activated carbon (PAC) doses required for defluoridation of water having initial fluoride concentrations in the range of 6 to 20 mg/L, and to determine the effect of selected water quality parameters on the treatment process. Experimental data were also obtained to analyze the kinetics of the treatment process.

Phase-2 study: Denitrification (Experiments using bench-scale SBR): Studies were conducted to determine the optimum ethanol (as COD) to nitrate-nitrogen ratio (COD/NO_3^--N) required for denitrification, to evaluate the denitrification efficiency of the reactor for nitrate concentrations in the range of 40 to 250 mg/L (as N), to estimate the kinetic coefficients of denitrification, and to investigate the effect of length of idle time and various fluoride concentrations on denitrification.

Phase-3 study: Denitrification-Defluoridation (Experiments using bench-scale SBRs): Finally, studies on denitrification-defluoridation treatment train were planned to evaluate the overall efficiency of the integrated treatment process for nitrate (40 to 250 mg/L as N) and fluoride (6 to 20 mg/L) removal at the operational conditions optimized earlier using the jar test and denitrifying SBR.

3.3 MATERIALS

Test water: Since there was no source of water supply containing either one or both i.e. fluoride and nitrate in and around the University, the test water with the required concentrations was prepared by adding stock solutions of sodium fluoride and/or potassium nitrate to tap water. The tap water supplied in University of Roorkee campus is drawn from underground source and is supplied without any specific treatment except chlorination. Its average characteristics are reported in Table 3.1. The pH of the water was adjusted by lime, sodium hydroxide, or hydrochloric acid as required.

To study the effect of some water quality parameters on the treatment efficiency, the tap water quality was additionally adjusted by stock solutions prepared using potassium dihydrogen phosphate (for phosphate), sodium meta silicate (for silica), sulfuric acid (for sulfate), sodium chloride (for chloride), potassium nitrate (for nitrate), and sodium bicarbonate (for alkalinity). Ethanol was used to adjust the organic content (as COD) of tap water.

Powdered activated carbon (PAC): PAC supplied by E. Merck (India) was used without any pretreatment. Its physicochemical characteristics are shown in Table 3.2.

Alum: Alum contained sixteen water molecules $[Al_2(SO_4)_3.16H_2O]$.

Quality of chemicals: All chemicals used in the study were of reagent grade supplied either by Ranbaxy Fine Chemicals Limited (India) or Merck (Germany).

3.4 PREPARATION OF SYNTHETIC TEST WATER

Synthetic test water with the required concentrations of fluoride, nitrate, and other possible constituents explored in the work plan was prepared daily by adjusting tap water with stock solutions prepared as per the following:

(i) Fluoride solution was prepared by dissolving 2.21g anhydrous sodium fluoride in one liter distilled water (1g F^-/L).

(ii) Nitrate solution was prepared by dissolving 72.18g potassium nitrate in one liter distilled water after drying it in an oven at 105°C for 24 h (10 g/L as N).

(iii) Phosphate solution was prepared by dissolving 4.39g potassium dihydrogen phosphate in one liter distilled water (1 g PO_4^{3-}-P/L).

(iv) Silica solution was prepared by dissolving 23.65 g sodium meta silicate in one liter distilled water (5 g SiO_2/L).

(v) Sulfate solution was prepared by diluting 260 mL 2 N sulfuric acid to one liter with distilled water (25 g SO_4^{2-}/L).

(vi) Chloride solution was prepared by dissolving 41.2 g sodium chloride in one liter distilled water (25 g Cl^-/L).

Table 3.1 Average Tap Water Characteristics

Characteristics	Value*
pH	7.35
Alkalinity (as $CaCO_3$)	310
Total hardness (as $CaCO_3$)	200
Total dissolved solids	350
Chloride (as Cl^-)	26
Sulfate (as SO_4^{2-})	20
Fluoride	0.1
Nitrate (as N)	2.5

* All values are in mg/L except for pH

Table 3.2 Physicochemical Characteristics of Powdered Activated Carbon (PAC)

Characteristics	Value
Particle size (80% less than, mm)	0.02
Surface area (BET, m^2/g)	1050-1250
Substance soluble in water (%)	1
Substance soluble in HCl (%)	3
Chloride (Cl^-) (%)	0.2
Sulfate (SO_4^{2-}) (%)	0.2
Iron (%)	0.1
Methylene blue adsorption	12 mL/0.1g
Losses on drying (120°C) (%)	10
Residue on ignition (600°C) (%)	5

Alkalinity of tap water was adjusted by 1% sodium bicarbonate solution (10 g of $NaHCO_3$ in one liter distilled water) or by dilution of tap water with distilled water as required, while organic content (as COD) was adjusted by adding the required quantity of ethanol to tap water.

3.5 PREPARATION OF FEED SOLUTIONS

Alum-solution: Alum solution of 2% strength was prepared by dissolving 20g of alum in one liter of distilled water (1.72 g Al (III)/L). Unless otherwise indicated, through out this work alum doses are expressed in mg/L as alum.

Alum-PAC slurry: Individual stock alum-PAC solutions were prepared to give 400 mg/L of alum and specified doses of PAC when added to the test waters. This is because 400 mg/L of alum when added at the beginning of rapid mixing reduced the pH of the test water to the optimum range. The slurries and the alum solution were prepared in small portions as required in order to avoid the aging effect (Stumm and Morgan, 1962).

Lime solution: Lime solution of 1% strength was prepared by dissolving 10g of lime in one liter distilled water (4.59 g OH^-/L) for pH adjustment.

3.6 WATER QUALITY ANALYSIS

During the defluoridation experiments, samples for analysis were either withdrawn periodically by pippetting at 3-cm below the surface of the water or taken from the supernatant at the end of settling as required. Mainly, pH and residual fluoride concentrations were measured whereas in some specific experiments, alkalinity and COD were also estimated. Since the variation in the pH of the test water during the whole mixing period was insignificant, its final values were measured within 3 minutes of completion of mixing.

During the denitrification experiments, samples for analysis were withdrawn through sampling port periodically or at the end of settling from the supernatant as required. Alkalinity, pH, nitrate, and COD of the influent and effluent were measured on a daily basis for routine performance monitoring. MLSS and MLVSS were also monitored intermittently. At steady-state nitrate, nitrite, and COD were analyzed in all cases while in addition to these pH was also measured with time intervals for one specific experiment.

During denitrification-defluoridation experiments, samples for analysis were withdrawn from the respective supernatants as discussed above. The test water (influent), denitrified and denitrified-defluoridated effluents were analyzed for fluoride, nitrate, nitrite, COD, sulfate, sulfide, aluminum, alkalinity, pH, turbidity, and MPN.

Prior to analysis, samples for fluoride, nitrate, nitrite, sulfate, sulfide, and COD (except in the final experiment) estimation were filtered through 0.45 μm membrane filters. All parameters were analyzed in accordance with the procedures outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 1995) as detailed in Table 3.3.

3.7 JAR TEST EXPERIMENTS FOR DEFLUORIDATION

3.7.1 General

Experiments were carried out in six one liter cylindrical unbaffled plastic reactors filled with 750 mL test water using the jar test apparatus equipped with multiple stirring devices having flat rectangular rotating paddles. The stirrers were used to ensure velocity gradients (G) of 260 s^{-1} (100 rpm) for rapid mixing, 100 s^{-1} (50 rpm) for intermediate mixing (between rapid and slow mixing), and 45 s^{-1} (30 rpm) for slow mixing (flocculation). The studies were conducted at room temperature (28 ± 2° C).

Table 3.3 Summary of Water Quality Analysis

Parameters	**Principle**	**Instrument/ Technique used**
Turbidity	Nephelometric	Turbidimeter, Hach model 2100 A (Loveland Co., USA)
Mixed liquor suspended solids (MLSS)	Gravimetric	Filtration and evaporation in an oven at 103-105°C (24 hours).
Mixed liquor volatile suspended solids (MLVSS)	Gravimetric	Ignition of the residue from No. 2 at 550°C.
Total dissolved solids (TDS)	Gravimetric	Evaporation of filtrate in an oven at 103-105°C (24 hours)
pH	Electrometric	Digital pH meter, Model Global DPH 500 (Global Electronics, India)
Alkalinity	Volumetric	Acid-Base titration Titrant-N/50 H_2SO_4 Indicator-Bromo Cresol Green Solution
Total hardness	Volumetric	Complexometric titration Titrant- 0.01N EDTA Indicator-Eriochrome black-T using ammonia buffer
Fluoride	SPADNS Colorimetric	UV-VIS Spectrophotometer, Model SL 159 (Elico, India). Reading was taken at 570 nm. Samples were diluted with distilled water to measure high fluoride and avoid interference from aluminum and sulfate. Sodium arsenite was used to avoid interference from residual chlorine and reading was taken after 2 hours of color development to avoid aluminum interference (APHA, 1995).

Parameters	**Principle**	**Instrument/Technique used**
Nitrate	UV Spectrophotometric screening	UV-VIS Spectrophotometer, Model Digispec-200 GL (Afeedback, India). Reading was taken at 220 and 275 nm. Samples were diluted with distilled water to measure high nitrate and avoid interference from organic matter.
Nitrite	Colorimetric	UV-VIS spectrophotometer, Model Digispec-200 GL (Afeedback, India). Reading was taken at 543 nm. Samples were diluted with distilled water to measure high nitrite concentrations.
COD	Volumetric	Titration-after digestion Titrant-Ferrous Ammonium Sulfate Indicator- Ferroin
Chloride	Volumetric	Argenometric titration Titrant-N/35.5 Silver nitrate Indicator-Potassium chromate
Sulfate	Turbidimetric	Turbidimeter, Hach model 2100 A (Loveland Co., USA). Precipitation by $BaCl_2$ as $BaSO_4$ in acidic medium
Sulfide	Iodometric	Titrant-N/40 Sodium thiosulfate Indicator-Starch solution
Aluminum	Emission Spectroscopy	Inductively Coupled Plasma Emission Spectroscopy (ICP-OE Spectrophotometer Model Plasmalab-8440, GBC, Australia)
MPN	Total Coliform Multiple Tube Test	For each sample, ten test tubes with 10 mL sample

Note: Gas was not measured due to its leakage from the denitrifying reactor through the annular space around the stirring rod of the mixer.

After preliminary trials, overall 422 jar tests were run in several series to: (i) optimize the pH, (ii) choose the best operational procedure, (iii) select the most appropriate alum and PAC doses for initial fluoride concentrations in the range of 6 to 20 mg/L, (iv) study the kinetics of the treatment process, and (v) investigate the effect of water quality parameters i.e. phosphate, silica, sulfate, nitrate, chloride, alkalinity, and organic matter (ethanol) on fluoride removal. Alum and PAC were studied in the ranges of 300 to 900 mg/L, and 0 (control) to 220 mg/L respectively.

3.7.2 Optimization of pH

The effect of pH on fluoride removal was studied in the pH range of 3 to 7.5. pH values of the test water samples were adjusted to predetermined values by 0.1N HCl or 0.1N NaOH to get the required pH of 3, 4, 5, 5.8, 6, 6.5, 7, and 7.5 during mixing. For this purpose several preliminary runs were conducted to get an idea about the adjustment of initial pH values in order to get final values of 3, 4, 5, 5.8. 6, 6.5, 7, and 7.5 after addition of (i) 400 mg/L of alum alone, (ii) 100 mg/L of PAC alone, or (iii) alum-PAC slurry (400 and 100 mg/L respectively). Thereafter, effect of pH (3 to 7.5) on removal of 15 mg/L of initial fluoride concentration was studied alternately by adding (i) 400 mg/L of alum, (ii) 100 mg/L of PAC, and (iii) alum-PAC slurry (400 and 100 mg/L respectively). Twenty four jar tests were run for 40 minutes of rapid mixing.

3.7.3 Optimization of Operational Procedure

Fluoride removal simultaneously by coagulation (using alum) and adsorption (using PAC) is influenced by operation parameters such as mixing rates and their duration, total contact time, order of addition of coagulant, lime, and adsorbent etc. Aim of this part of the study was to optimize these parameters. As a preliminary step, based on literature survey, several experimental runs were carried out to assess fluoride removal at various combinations of these parameters. Thereafter, three operational procedures as discussed below (a-c) were selected for detailed study (Fig. 3.1). Eighteen jar tests were conducted at an initial fluoride concentration of 15 mg/L maintaining the optimum pH range (5.8 to 6. 5) as found in the previous study (Section 3.7.2) using lime. PAC doses of 20, 60, 100, 140, 160, and 180 mg/L along with 700 mg/L of alum were used for defluoridation.

(a) Initially, lime (365 mg/L) was added to the reactor (jar) containing the test water and then the whole dose of alum (700 mg/L) was fed along with specific PAC dose (varying in the range of 20 to180 mg/L) as alum-PAC slurry. It was then rapidly mixed at 100 rpm for 3 minutes and flocculated at 30 rpm for 35 minutes.

(b) The same as (a) but it was rapidly mixed for 40 minutes and flocculated for 20 minutes.

(c) Initially the required PAC dose (varying in the range of 20 to 180 mg/L) was fed to the reactor (jar) containing the test water along with one portion of the alum dose (i.e. 400 mg/L) as alum-PAC slurry and rapidly mixed at 100 rpm for 40 minutes. Then after reducing the rpm to 50 for about a minute (intermediate mixing), lime (365 mg/L) and the remaining alum dose (300 mg/L) were fed simultaneously and flocculated at 30 rpm for 20 minutes.

At the end of mixing, the treated water was settled for two hours and the supernatant was analyzed.

3.7.4 Optimization of Alum and PAC Doses

Studies on optimization of alum and PAC doses for initial fluoride concentrations of 6, 10, 15, and 20 mg/L were conducted according to the optimum

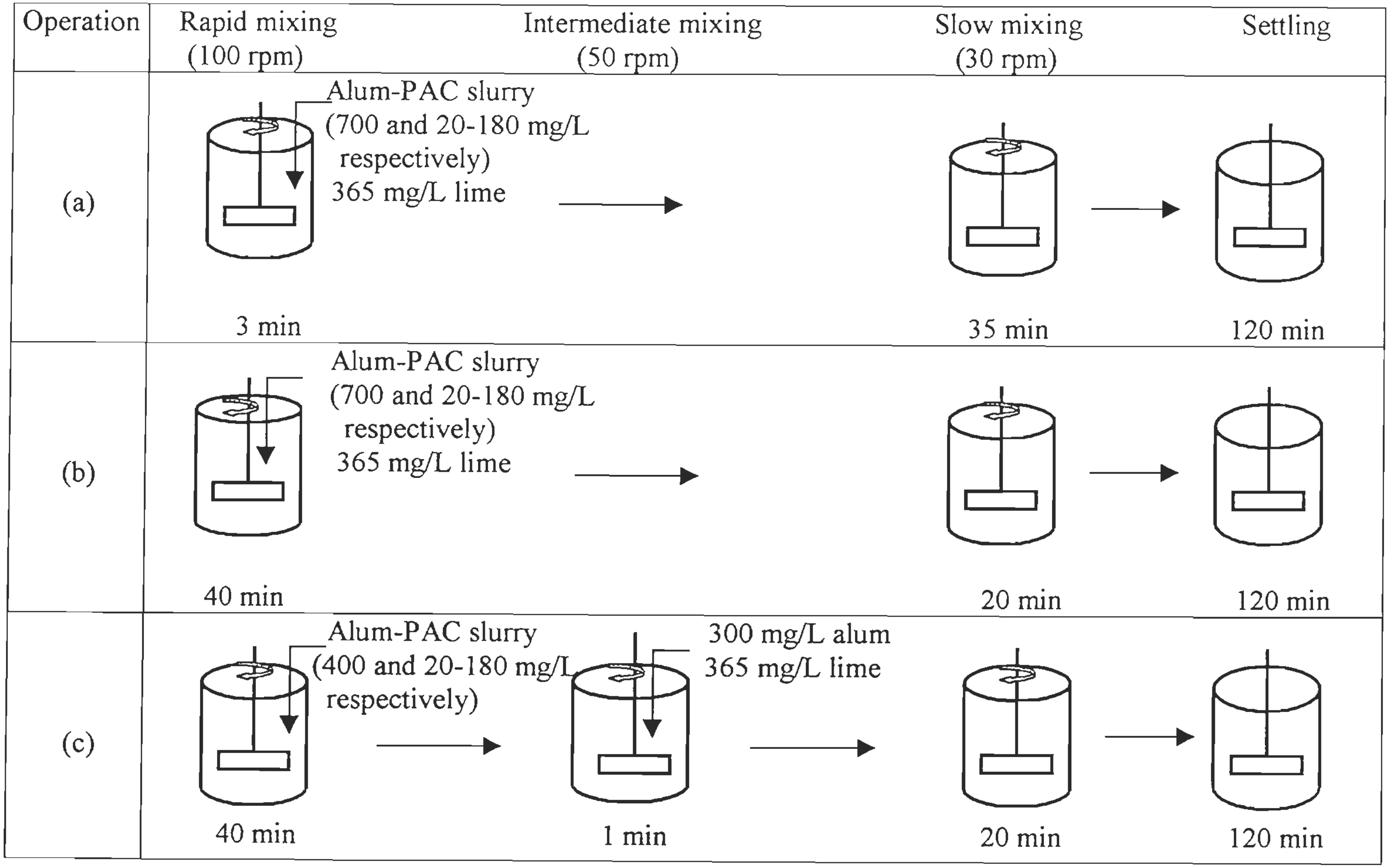


Fig. 3.1 Schematic Illustration of Defluoridation Operation Procedures.

operation procedure (c) as determined by the previous study (Section 3.7.3). For initial fluoride concentrations of (i) 6 mg/L, (ii) 10 and 15 mg/L, and (iii) 20 mg/L, alum doses in the range of (i) 300 to 800 mg/L, (ii) 500 to 800 mg/L, and (iii) 500 to 900 mg/L respectively, were investigated. Overall 190 jar tests were run. Each alum dose was tried along with 10 PAC doses in the range of 0 (control) to 220 mg/L as alum-PAC slurry (Table 3.4). The total alum dose was added to the test water in two stages: first, 400 mg/L of alum (except 300 mg/L of total alum) incorporated with PAC doses in the range of 0 to 220 mg/L was added to the test water as alum-PAC slurry at the beginning of rapid mixing. Second, the remaining alum dose in excess of 400 mg/L and lime were added simultaneously at the end of rapid (100 rpm) and before the beginning of slow mixing (30 rpm) by reducing the speed of the stirrer to 50 rpm for about a minute (intermediate mixing). Initial pH of the test water was slightly more than pH of tap water due to addition of sodium fluoride. However, during the first stage, the initial pH of the test water was reduced to the optimum pH range (5.8 to 6.5) due to addition of 400 mg/L of alum, whereas, at the second stage, the pH was maintained in the same range by different doses of lime. Details of the doses of alum, PAC, and lime for each initial fluoride concentration are given in Table 3.4. Additional 28 jar tests were run at an initial fluoride concentration of 15 mg/L using alum doses of 500, 600, 700, and 800 mg/L, each incorporated with 7 PAC doses in the range of 0 (control) to 200 mg/L. The experiments were performed similarly as discussed above with the only difference that in this case residual fluorides were estimated both at the end of rapid and slow mixing periods.

Table 3.4 Doses of Alum, PAC, and Lime Used in the Experiments

Initial fluoride concent. in test water, mg/L (1)	Total alum dose used, mg/L (2)	Various PAC doses used for each alum dose, mg/L (3)	Total lime dose used to maintain pH in the range of 5.8 to 6.5 (4)	Quantity added during			
				Rapid mixing		Intermediate mixing	
				Alum mg/L (5)	PAC mg/L (6)	Alum mg/L (7)	Lime mg/L (8)
6	300	0, 20, 60, 100, 120, 140, 160, 180, 200, 220	0	300	0, 20, 60, 100, 120, 140, 160, 180, 200, 220 (for each alum dose)	0	0
	400		0	400		0	0
	500		53	400		100	53
	600		300	400		200	300
	700		365	400		300	365
	800		560	400		400	560
10	500	0, 20, 60, 100, 120, 140, 160, 180, 200, 220	53	400	0, 20, 60, 100, 120, 140,160, 180, 200, 220(for each alum dose)	100	53
	600		300	400		200	300
	700		365	400		300	365
	800		560	400		400	560
15	500	0, 20, 60, 100, 120, 140, 160, 180, 200, 220	53	400	0, 20, 60, 100, 120, 140, 160, 180, 200, 220(for each alum dose)	100	53
	600		300	400		200	300
	700		365	400		300	365
	800		560	400		400	560
20	500	0, 20,60, 100,120, 140,160, 180, 200, 220	53	400	0, 20, 60, 100, 120, 140, 160, 180, 200, 220(for each alum dose)	100	53
	600		300	400		200	300
	700		365	400		300	365
	800		560	400		400	560
	900		630	400		500	630

3.7.5 Studies on the Role of Lime in Fluoride Removal

Two sets of experiments consisting of 12 jar tests were conducted to evaluate the role of lime in fluoride removal. The experiments were carried out on water sample having an initial fluoride concentration of 15 mg/L maintaining pH of 6, 8, and 9 during mixing. The initial pH of the test water was adjusted to predetermined values by 0.1 N HCl or 0.1 N NaOH as required to get pH of 6, 8, and 9 during mixing after addition of the chemical(s) under investigation i.e. alum, lime, and PAC. In the first batch of experiment, PAC alone (100 mg/L) and a combination of lime and PAC (560 mg/L and 100 mg/L respectively) were used for defluoridation, whereas in the second batch along with lime and PAC, alum (500 mg/L) was also used. In first and second batches, experiments were conducted at slow mixing for contact times of 30 and 60 minutes respectively. At the end of mixing, the treated water was settled for two hours and the supernatant was analyzed.

3.7.6 Studies on Process Kinetics at Various Alum and PAC Doses

These studies were conducted according to the optimum operational procedure (c) (Section 3.7.3) with the only difference that rapid and slow mixing periods were extended to 120 and 60 minutes respectively. Studies in this section could be subdivided into the following three parts:

(1) Investigations on variation of fluoride removal by alum-PAC slurry and its components with time: These experiments (12 jar tests) were carried out on water samples having initial fluoride concentrations of 6, 10, 15, and 20 mg/L using alternately (i) alum-PAC slurry of 800 and 100 mg/L respectively, (ii) 800 mg/L of alum alone, and (iii) 100 mg/L of PAC alone. As discussed previously in Sections 3.7.3 and 3.7.4, in case of alum-PAC slurry, 400 mg/L of alum and 100 mg/L of PAC were added to the test water as alum-PAC slurry at the beginning of rapid mixing and stirred at 100 rpm for 120 minutes. Thereafter, 400 mg/L of alum and 560 mg/L of lime were added simultaneously during intermediate mixing. In case of alum alone, the procedure was the same but without addition of PAC. In case of PAC alone, initially 100 mg/L of PAC (as slurry with distilled water) was added to the test water. Thereafter, maintaining the pH of the test water in the range of the optimum value (5.8 to 6.5) using 0.1 N HCl, it was stirred at 100 rpm for120 minutes and at 30 rpm for 60 minutes.

(2) Studies on variation of fluoride removal with time at different alum doses: These experiments (18 jar tests) were conducted at initial fluoride concentrations of 10, 15, and 20 mg/L using alum-PAC slurries with alum doses of 400, 500, 600, 700, 800, and 900 mg/L combined with fixed dose of PAC i.e.100 mg/L. 400 mg/L of alum and 100 mg/L of PAC (as alum-PAC slurry) were added to the test water at the beginning of rapid mixing and stirred at 100 rpm for 120 minutes. Thereafter, the excess alum above 400 mg/L and lime (Table 3.4) were added simultaneously during intermediate mixing.

(3) Investigations on variation of fluoride removal with time at different PAC doses: These experiments (18 jar tests) were carried out at initial fluoride concentrations of 10, 15, and 20 mg/L using alum-PAC slurries with PAC doses of 20, 60, 100, 120, 140, and 160 mg/L combined with fixed dose of alum i.e. 800 mg/L. 400 mg/L of alum incorporated with 20, 60, 100, 120, 140, or 160 mg/L of PAC were added to the various test water samples as alum-PAC slurry at the beginning of rapid mixing and stirred at 100 rpm for120 minutes. Thereafter, 400 mg/L of alum and 560 mg/L of lime were added simultaneously during intermediate mixing.

In all cases, at the end of mixing, the treated water was settled for two hours and the supernatant was analyzed.

3.7.7 Studies on Effects of Water Quality Parameters on Fluoride Removal

These experiments were performed to investigate the effect of such constituents, which may be present either naturally in water or added during the treatment process (including the denitrification process), on fluoride removal by alum-PAC slurry. Effects of phosphate, silica, sulfate, chloride, nitrate, alkalinity, and organic matter (ethanol) were investigated at 6 various concentrations in each case. The fate of organic matter (ethanol) in the defluoridation process was also assessed.

The experiments were conducted on test water having initial fluoride concentration of 15 mg/L along with the required values of water quality parameter under investigation according to the optimum operational procedure (Section 3.7.3). Overall 96 jar tests were conducted. Alum-PAC slurry having 800 and 100 mg/L doses respectively along with 560 mg/L of lime was used for defluoridation. The pH was maintained in the optimum range (except the alkalinity test) and at 4, 4.5, 5, 5.5, 6, 6.5, 7.5, 8, and 9.5 (pH during mixing) as required. In case of study on effect of alkalinity on defluoridation, the pH was not adjusted in order to maintain the alkalinity under investigation. During the studies on effects of phosphate, silica, nitrate, and chloride at the optimum pH (5.8 to 6.5), the pH and alkalinity were adjusted using lime, whereas in case of sulfate (the test water was acidic due to H_2SO_4 used for sulfate adjustment) it was initially adjusted to the pH of the feed water using sodium hydroxide and then to the optimum pH (5.8 to 6.5) using lime during mixing. To study the effect of water quality parameters on fluoride removal in the pH range of 4 to 9.5, the pH of the test water samples were initially adjusted to predetermined values using either 0.1N HCl or

0.1N NaOH in order to obtain pH of 4, 4.5, 5, 5.5, 6, 6.5, 7.5, 8, and 9.5 during mixing. This study was conducted only for phosphate, silica, sulfate, nitrate, and chloride along with control (water samples without additives). Additional 6 jar tests were run at the optimum pH range (5.8 to 6.5) to evaluate the contribution of lime, alum, and PAC to the removal of organic matter (ethanol) separately and in combinations. The tests were conducted according to the optimum operational procedure (Section 3.7.3) on test water having 130 mg/L of COD using 560, 800, and 100 mg/L doses of lime, alum, and PAC respectively.

3.8 EXPERIMENTAL SETUP AND TEST PROCEDURES FOR DENITRIFICATION

3.8.1 Experimental Setup

The bench-scale denitrifying SBR system consisted of a 6-L (5-L working volume) cylindrical plastic container having 16 cm internal diameter and 30 cm height (Fig 3.2). It had one entry port for influent and nitrogen, and four exit ports for removal of clarified water, sample collection, sludge discharge, and release of nitrogen. It was sealed and connected to a water displacement gas collector, equipped with a variable speed stirrer, and operated in a temperature controlled chamber which was maintained at 25 ± 2°C throughout the experimentation. Feed water was supplied to the reactor from a plastic overhead container having 5-L volume.

3.8.2 Experimental Procedures

The sludge for seeding was collected from a nearby 20 million liter per day conventional activated sludge plant, and a 37.35 L per day bench-scale continuous flow upflow anaerobic sludge blanket reactor. Sludge was mixed (1:1), filtered, and then

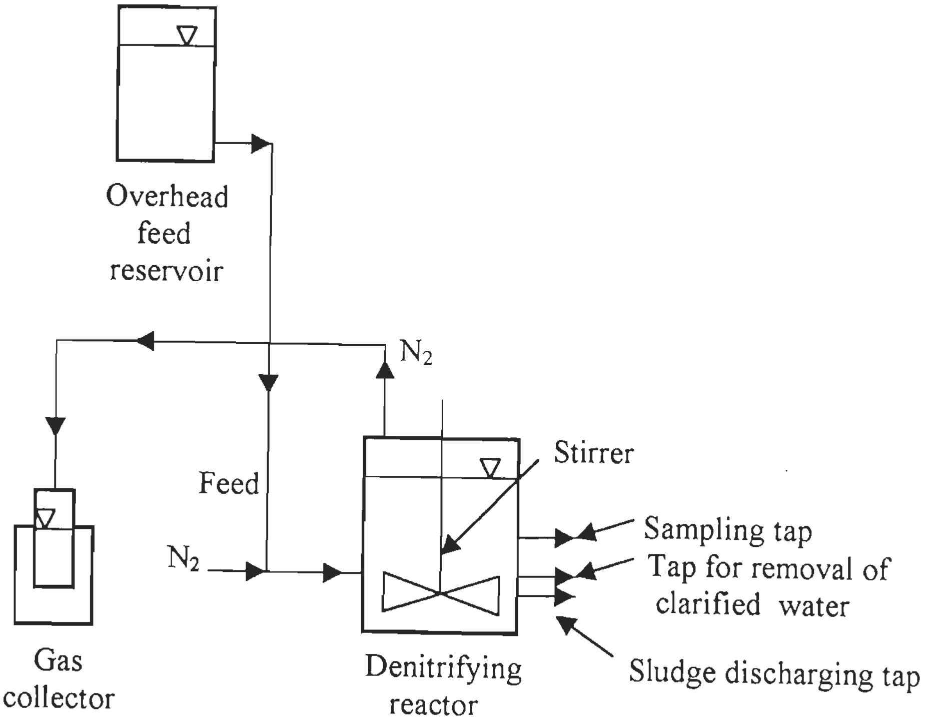


Fig. 3.2 Flow Schematic for Bench-Scale Denitrification Treatment

washed with distilled water and stored for 24 hours. Initially, 1 L of the seed and 4 L of test water having a nitrate concentration of 80 mg/L (as N), ethanol equivalent to 240 mg/L of COD, and macro and micronutrients as per Table 3.5 were fed into the reactor. The contents were gently agitated by a mixer for 9 hours per day to keep the biomass in suspension. After the contents were allowed to settle, supernatant was decanted, and reactor was refilled. The operation continued until the reactor attained steady-state. Biomass was acclimatized to develop (select) denitrifying microorganisms and to stabilize the microbial activity. It was considered to have reached a steady-state when the difference in nitrate concentration in the decanted effluent, measured during two successive days, was less than 10%. The reactor was acclimatized to attain steady-state every time operating parameters were changed and the reported observation data were collected at steady-state.

Table 3.5 Nutrients Fed Into the Reactor (Hoek, 1985)

No.	Nutrient	Concentration (mg/L)
1	Na_2HPO4	1.203
2	$FeCl_3.6H_2O$	0.271
3	$CuSO_4.5H_2O$	0.031
4	$(NH_4)6Mo_7O_{24}.6H_2O$	0.022
5	$ZnSO_4.7H_2O$	0.043
6	$CaCl_2.2H_2O$	0.146
7	NH_4Cl	2.129

Experiments were conducted in five phases having a total of 24 sets of steady-state studies (Table 3.6). During phase 1, optimum requirement of ethanol (measured as COD) was evaluated. Studies were carried out in 5 sets on water samples with nitrate concentration of 80 mg/L (as N) while COD was varied from 100 to 288 mg/L (COD/NO_3^--N ranging from 1.25 to 3.60) by adding ethanol. In phase 2, for optimum COD/NO_3^--N of 2.00 (as determined in phase 1), denitrification efficiency of the reactor was studied in 6 sets at various initial nitrate concentrations in the range of 40 to 250 mg/L (as N). In phase 3, kinetics of the denitrification process (without excess solid recycle) was studied in 5 sets at an initial nitrate concentration of 120 mg/L (as N) maintaining steady state at various HRTs in the range of 1.5 to 2.5 days. In phase 4, effect of length of the idle phase (1, 3, 6, and 14 hours) of the cycle on denitrification was investigated in 4 sets at an initial nitrate concentration of 80 mg/L (as N) maintaining steady-state at the optimum anoxic reaction time (ART) of 3 hours (as determined in phase 2). In phase 5, effect of fluoride (6 to 20 mg/L) on denitrification was studied in 4 sets at an initial nitrate concentration of 160 mg/L (as N) maintaining steady-state at the optimum ART of 3 hours (as determined in phase 2).

The analyses for various parameters were carried out after the reactor reached steady-state. The operation cycle is schematically shown in Fig. 3.3 and ranges of variation of various parameters investigated are tabulated in Table 3.6. The experiment for each set was started by filling the reactor with test water of the desired nitrate concentration. It was followed by nitrogen sparging for 5 minutes to maintain anoxic conditions. Thereafter, the required amount of nutrients and ethanol (equivalent to desired COD) were added as per Tables 3.5 and 3.6. Mixing was immediately started to keep the biomass in suspension. ART was maintained at 3 or 9 hours as required and it

Table 3.6 Test Parameters Used in the Investigation

Phase No. (1)	Experiment (2)	Set No. (3)	Nitrate conc., (mg/L as N) (4)	COD (mg/L) (5)	Fluoride concent., (mg/L) (6)	HRT d (7)	ART h (d) (8)	Settling time, (h) (9)	Idle time, (h) (10)
1	Optimum requirement of ethanol	1	80	100 (1.25)	---	1.00	9.00 (0.375)	1.00	13.45
		2		160 (2.00)					
		3		184 (2.30)					
		4		216 (2.70)					
		5		288 (3.60)					
2	Efficiency of denitrification and determination of optimum ARTs at various initial nitrate concentrations	1	40	80 (2)	---	1.00	9.00 (0.375)	1.00	13.45
		2	80	160					
		3	120	240					
		4	160	320					
		5	200	400					
		6	250	500					
3	Kinetics of the denitrification process	1	120	240 (2)	---	1.50	(1.41)	1.00	1.00
		2				1.75	(1.66)		
		3				2.00	(1.91)		
		4				2.25	(2.16)		
		5				2.50	(2.41)		
4	Effect of length of idle phase of the cycle on denitrification	1	80	160 (2)	---	0.22	3.00 (0.125)	1.00	1.00
		2				0.30			3.00
		3				0.43			6.00
		4				0.76			14.00
5	Effect of fluoride on denitrification	1	160	320 (2)	6	1.00	9.00 (0.375)	1.00	13.45
		2			10				
		3			15				
		4			20				

HRT= Hydraulic retention time ART = Anoxic reaction time

Values in parenthesis in column 5 and 8 indicate COD/NO_3^--N and ART in days respectively

HRT = One cycle operation i.e. filling, ART, settling, decanting, and idle times

Period	Fill 1	N_2 sparging	Fill 2	React (Anoxic)	Settle	Decant	Idle	Sludge wastage
Operation	Filling of water having desired nitrate concentration as per Tables 3.6 and 3.7	N_2 sparging	Feeding of desired nutrients and ethanol as per Tables 3.5, 3.6 and 3.7	Mixing Sample, and N_2 collection	Clarification	Supernatant removal	Idle	Excess sludge wastage
Time	3 min	5 min	2 min	As per Tables 3.6 and 3.7	60 min	3 min	As per Tables 3.6 and 3.7	2 min

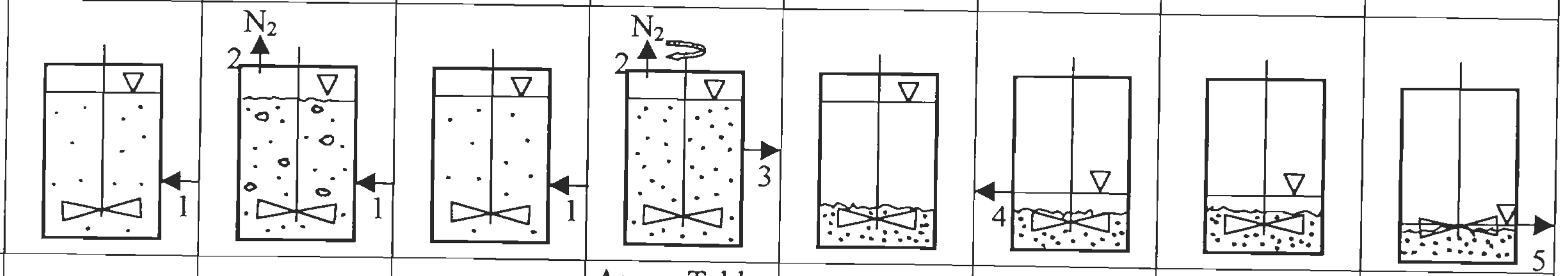


Fig. 3.3 Denitrifying SBR Operation Cycle (1-Entry of Influent or N_2, 2-Exit for N_2, 3-For Sample Collection, 4-For Removal of Clarified Water, and 5-For Sludge Wastage)

was followed by quiescent settling for one hour, decanting, and idle phase (Table 3.6). In most cases, the reactor was run only one-cycle per day. The mixed liquor volatile suspended solids (MLVSS) concentration in the reactor at the beginning of reaction was controlled by discharging sludge to maintain a predetermined sludge height after settling, which resulted in MLVSS concentration in the reactor in the range of 3.0 to 3.2 g/L at high water level.

3.9 DENITRIFICATION-DEFLUORIDATION TREATMENT PROCESS

Integrated denitrification-defluoridation treatment experiments were conducted on bench-scale cylindrical denitrifying (Section 3.8.1) and defluoridating sequencing batch reactors incorporated into a treatment train (Fig. 3.4). The batch reactor used for defluoridation was a one liter (working volume) unbaffled cylindrical plastic reactor having 10 cm internal diameter and 18 cm height provided with a variable speed stirrer.

In these experiments (Table 3.7), the overall efficiency of the integrated denitrification-defluoridation treatment process was evaluated using 24 water samples having different combinations of nitrate concentrations of 40, 80, 120, 160, 200, and 250 mg/L, and fluoride concentrations of 6, 10, 15, and 20 mg/L. For each initial nitrate concentration, steady-state was first attained at the optimum ARTs as determined in phase 2 (Table 3.6) of Section 3.8.2. The experiment for each set was started by filling the denitrifying reactor with test water of the desired nitrate and fluoride concentrations. The denitrification stage of the treatment was conducted according to the procedure discussed in Section 3.8.2 (Fig. 3.3) using the parameters tabulated in Table 3.7. After settling, one liter of the denitrified supernatant was transferred to the defluoridating reactor.

The test water in the defluoridating SBR was first rapidly (100 rpm) mixed for 3 minutes to discharge the residual nitrogen gas (if any). Thereafter, the optimum alum

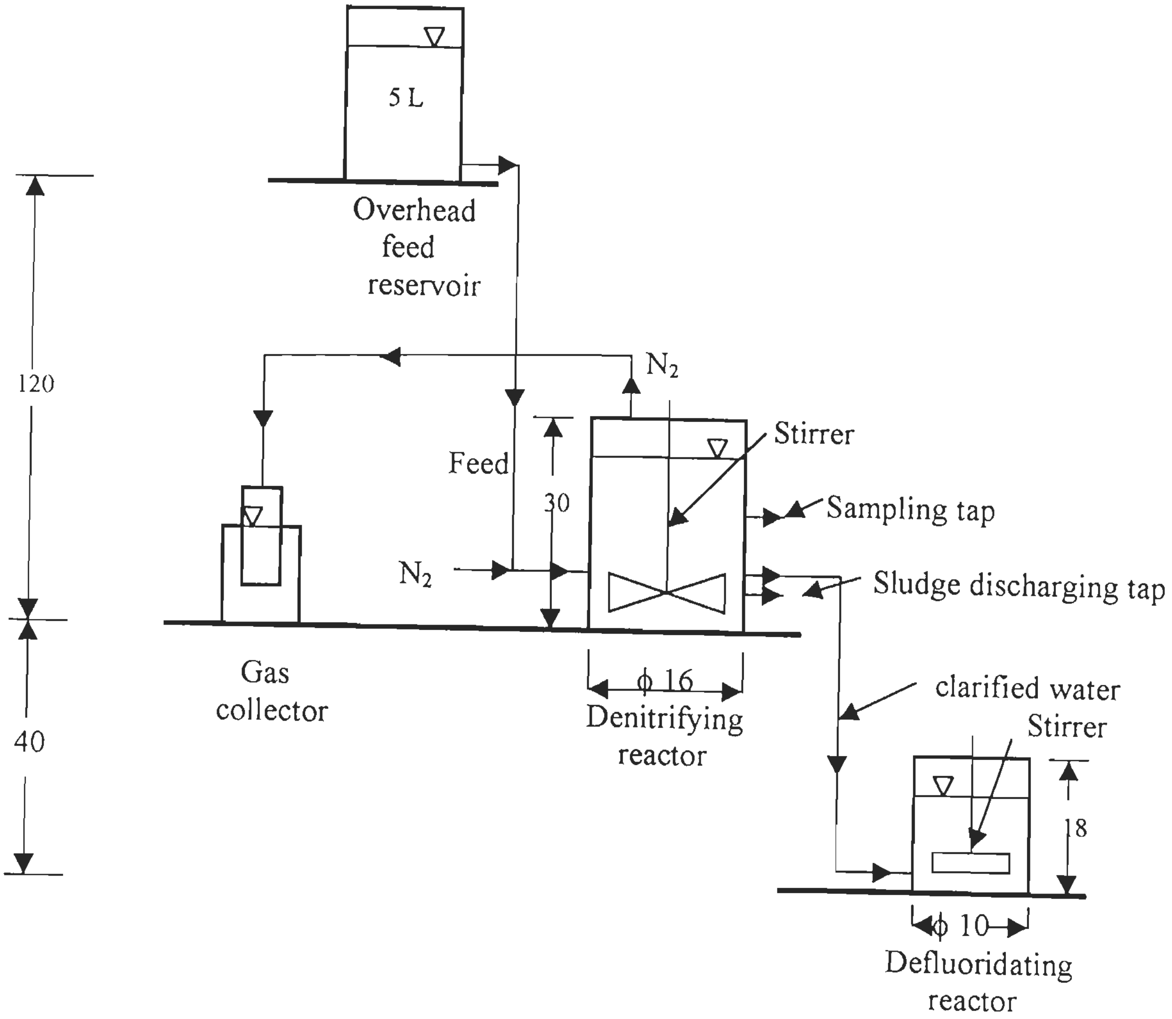


Fig. 3.4 Flow Schematic for Bench-Scale Denitrification-Defluoridation Treatment Process (All Dimensions are in cm)

doses previously found on jar test experiments for water samples of natural alkalinity of 310 mg/L (as $CaCO_3$) i.e. 500, 600, 800, and 900 mg/L of alum doses along with 100 mg/L of PAC as alum-PAC slurry were supplied to the reactor for all the 24 water samples having initial fluoride concentrations of 6, 10, 15, and 20 mg/L respectively, according to the operation procedure (c) discussed in Section 3.7.3 (Fig.3.1). The alum doses were increased to 600, 800, and 850 mg/L for the three water samples having 80 mg/L nitrate-N and initial fluoride concentrations of 6, 10, and 15 mg/L respectively, to reduce initial fluoride concentration to 1.5 mg/L. It was also increased to 700 and 900 mg/L for two other water samples having 120 mg/L nitrate-N and initial fluoride concentrations of 6 and 10 mg/L respectively, to reduce initial fluoride concentrations to < 2 mg/L. At the end of mixing, it was allowed to settle for 2 hours.

Table 3.7 Test Parameters Used in the Investigation of Integrated Denitrification-Defluoridation Treatment Process

Water sample numbers	Nitrate conc., (mg/L as N)	COD (mg/L) COD/NO_3^--N= 2.00	Fluoride concent., (mg/L)	HRT (d)	ART (h)	Settling time, (h)	Idle time, (h)
1 - 4	40	80	6, 10, 15, 20	1.00	3.00	1.00	19.45
5 - 8	80	160					
9 - 12	120	240					
13 - 16	160	320					
17 - 20	200	400			5.00		17.45
21 - 24	250	500			7.00		15.45

Chapter 4

RESULTS AND DISCUSSION

CHAPTER-4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter has been divided into three main sections, namely (1) defluoridation, (2) denitrification, and (3) an integrated nitrate and fluoride treatment process. Accordingly, observations during experimentation, analysis, interpretation, and discussion of results are presented under these subheadings.

4.2 DEFLUORIDATION

4.2.1 Effect of pH on Fluoride Removal by Alum-PAC Slurry and Its Components

For any physicochemical process an operation at optimum pH range is recommended. The objective of these experiments was to ascertain the most favorable pH range for defluoridation. Preliminary investigation indicated that the trend in relationship of pH to removal efficiency by alum-PAC slurry is independent of initial fluoride concentrations, and alum and PAC doses. Thus, for this study initial fluoride concentration (C_o) of only15 mg/L was selected. The pH of test waters were adjusted to predetermined values using 0.1N HCl or 0.1 N NaOH in order to get pH of 3, 4, 5, 5.8, 6, 6.5, 7, and 7.5 after addition of either (i) 400 mg/L of alum, (ii) 100 mg/L of powdered activated carbon (PAC), or (iii) alum-PAC slurry (400 mg/L of alum and 100 mg/L of PAC) as per experimental procedures outlined in Section 3.7.2. The data obtained from jar tests are compiled in Table 4.1 and plotted in Fig. 4.1.

In case of PAC, fluoride removal increased with decrease in pH while in case of alum, it increased with increase in pH in the range studied i.e. 3 to 7.5. Sigworth and Smith (1972), and Culp and Stoltenberg (1958) have reported optimum pH value of 3 for removal of fluoride by carbon and 6.5 to 7.5 for defluoridation by alum respectively. The optimum pH range for the alum-PAC slurry was found to be from 5.8 to 6.5. The combination of alum and PAC resulted in improvement of fluoride removal compared to the removal by alum or PAC alone.

Table 4.1 Effect of pH on Fluoride Removal by Alum-PAC Slurry and Separately by Its Components C_o=15 mg/L, Alum-400 mg/L, and PAC-100 mg/L

pH	Residual fluoride, mg/L		
	Alum-PAC slurry	Alum alone	PAC
3.00	11.00	11.50	11.00
4.00	11.05	11.30	11.40
5.00	8.35	10.20	12.00
5.80	6.50	10.00	12.00
6.00	6.50	9.75	12.00
6.50	6.60	8.90	12.25
7.00	7.20	8.50	12.40
7.50	7.40	8.30	13.00

pH affects fluoride removal since both the surface characteristics of PAC and aluminum species available in the water appear to significantly depend on pH. Surfaces of PAC particles bear negative charge (Weber, 1972) at neutral pH, therefore, its affinity to fluoride ion (which also has negative charge) is relatively less at this pH. However, with decrease in pH (increase of H^+-ion concentration) adsorption of hydrogen ion on the surface of the PAC neutralizes its negative charge (Weber, 1972) and thus enhances adsorption of fluoride. In case of alum, over much of the pH range

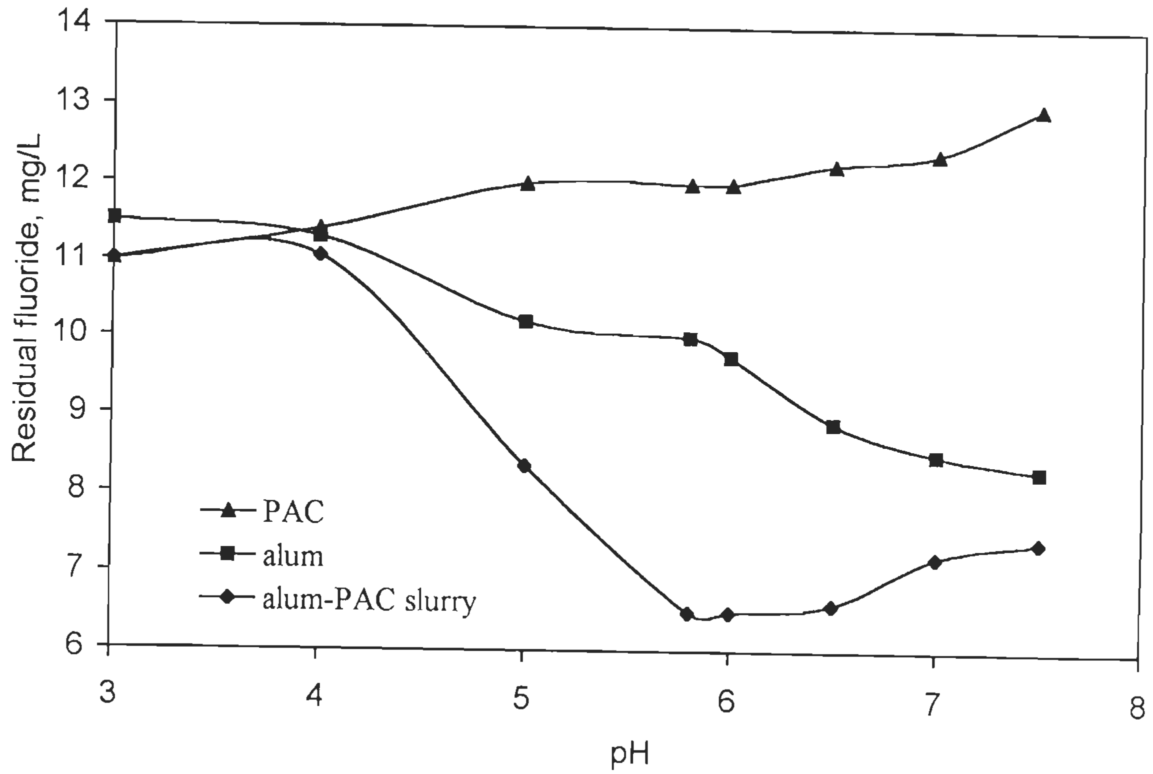


Fig. 4.1 Effect of pH on Fluoride Removal by Alum-PAC Slurry and Separately by Its Components. C_o=15 mg/L, Alum-400 mgL, and PAC-100 mg/L

(5.5 to 7.5), which is relatively favorable for fluoride removal, the principal species of aluminum present in the water during treatment is $Al(OH)_3$ (Mc Cormic et al., 1993). It is formed within 1 to 7 seconds after addition of alum to water (Amirtharajah and Mills, 1982). Therefore, fluoride could be removed predominantly by adsorption on the aluminum hydroxide floc or precipitate with it by formation of fluoaluminum complexes (Zabban and Helwick, 1975). When alum-PAC slurry is used, fluoride is possibly removed (i) by adsorption on or complexation with aluminum hydroxide floc available in the bulk solution, and floc available on the surface of the PAC (Letterman et al., 1970), (ii) by adsorption directly on the surface of the PAC, and (iii) carbon particles could also be utilized as nuclei (seeding effect) for fluroaluminum complex precipitate formation (Faust and Aly, 1983) which indirectly could enhance fluoride removal by alum. The increase in fluoride removal when PAC was added along with alum (Fig. 4.1) suggests that both of the proposed mechanisms of fluoride removal operated simultaneously. Subsequent experiments revealed that the operation procedure used in this experiment was not optimal. However, this was not supposed to make an error in assessment of optimum pH. It was confirmed by further experiments in Sections 4.2.6.1 and 4.2.6.2. Henceforth, unless otherwise stated, in all the experiments, pH of 5.8 to 6.5 was maintained during defluoridation for best removal by using lime.

4.2.2 Assessment of Optimum Operation Procedure

Fluoride removal simultaneously by coagulation (using alum) and adsorption (using PAC) is influenced by operation parameters such as mixing rates and their duration, total contact time, order of addition of coagulant, lime, and adsorbent etc. Thus, to optimize the operation procedure, several preliminary experimental runs were carried out at various combinations of these parameters. Studies were conducted at an initial fluoride concentration of 15 mg/L maintaining the optimum pH range of 5.8 to 6.5 with lime. Of these, the following three operational procedures were selected for detailed study:

(a) Initially lime (365 mg/L), and then alum (700 mg/L) were added to the jar along with specific PAC dose as alum-PAC slurry. It was then rapidly mixed for 3 minutes and flocculated for 35 minutes at G values of 260 s^{-1} (100 rpm) and 45 s^{-1} (30 rpm) respectively.

(b) The same as (a) but it was rapidly mixed for 40 minutes and flocculated for 20 minutes.

(c) Initially the required PAC dose was added along with one portion of the alum dose (i.e. 400 mg/L) as alum-PAC slurry, and rapidly mixed at G value of 260 s^{-1} (100 rpm) for 40 minutes (rapid mixing). After reducing the stirring speed to 50 rpm for about a minute (intermediate mixing), lime (365 mg/L) and the remaining alum dose (i.e. 300 mg/L as alum solution) were fed simultaneously and flocculated at G value of 45 s^{-1} (30 rpm) for 20 minutes (slow mixing).

Complete details of the operational procedures and experiments are given in Section 3.7.3. The results are presented in Table 4.2 and plotted in Fig. 4.2.

Table 4.2 Effect of Operational Procedure on Fluoride Removal

C_o=15 mg/L, pH=5.8 to 6.5

Chemicals and PAC doses, mg/L			Residual fluoride concent., mg/L		
Alum	Lime	PAC	Operation procedure (a)	Operation procedure (b)	Operation procedure (c)
700	365	20	4.60	4.75	4.10
700	365	60	4.30	4.40	3.55
700	365	100	3.95	4.10	3.10
700	365	140	4.15	4.20	3.35
700	365	160	4.20	4.15	3.70
700	365	180	4.35	4.25	3.65

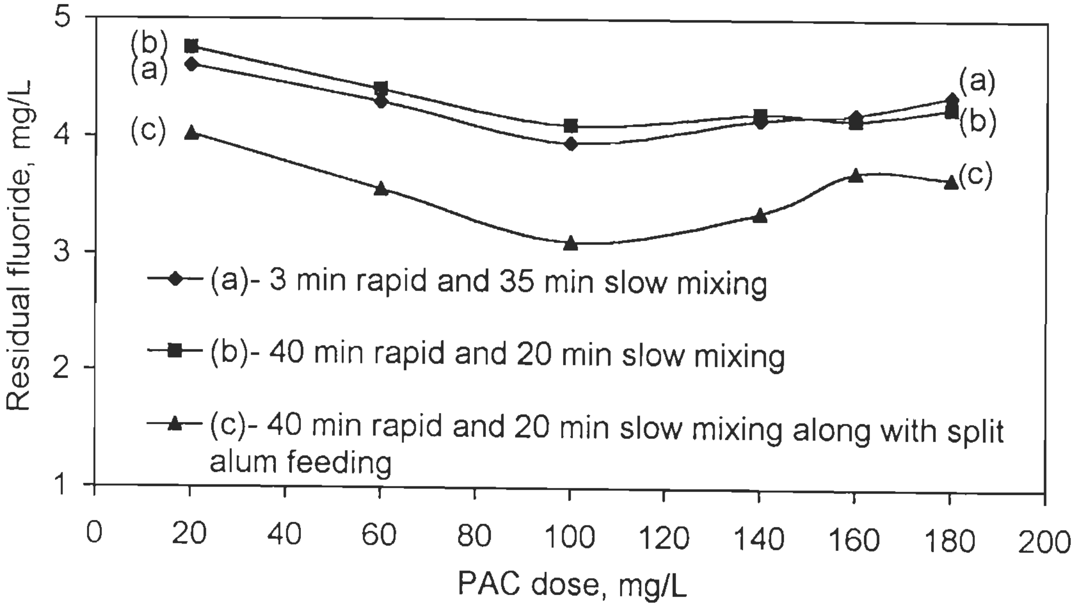


Fig. 4.2 Effect of Operational Procedure on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, Alum-700 mg/L, and pH=5.8 to 6.5

In case of operational procedure (a), insufficient contact time (3 minutes only) during rapid mixing was perhaps responsible for lower fluoride removal. In case of procedure (b), although there was sufficient mixing (100 rpm) with adequate contact time (40 minutes) favorable for adsorption of fluoride on PAC, it appears that lime interference (Najm et al., 1991) hindered the process. Little difference in fluoride removal when procedures (a) and (b) were used also suggests that adsorption of fluoride on the PAC in the presence of lime was insignificant in procedure (b). Best removal of fluoride by procedure (c) was attained because the optimum conditions for its removal by the PAC and alum were promoted by: (i) providing sufficient contact time and mixing, (ii) avoiding the interference of lime in fluoride removal by the PAC during rapid mixing as lime was added only during slow mixing, (iii) enhancing the adsorption of fluoride on or complexation with freshly added alum during intermediate mixing, and (iv) utilization of existing aluminum/fluoroaluminum hydroxide precipitates (from alum added at the beginning of rapid mixing) and PAC particles (aggregates) found in suspension as nuclei for the formation of fluoroaluminum precipitate during slow mixing. Thus, for best removal of fluoride by alum-PAC slurry, the process requires a total of one-hour contact time with 40 minutes of rapid and 20 minutes of slow mixing at G values of 260 s^{-1} (100 rpm) and 45 s^{-1} (30 rpm) respectively along with split feeding of alum.

Hence, unless otherwise mentioned, the experiments in this study were carried out following procedure (c) only. In most applications of PAC alone, in treatment of water/wastewater contact time in the range of 15 to 30 minutes is maintained (Perrich, 1981; AWWA, 1990). However, in case of its combination with alum as alum-PAC slurry, possibly coating of PAC surface by aluminum hydroxide precipitate influenced the adsorption of fluoride on the PAC which resulted in relatively longer contact time.

4.2.3 Optimization of Alum and PAC Doses

These sets of experiments were carried out to assess the optimum combination of alum and PAC for defluoridation of waters with different initial fluoride concentrations in the range of 6 to 20 mg/L at the optimum pH range of 5.8 to 6.5. Alum and PAC doses in the range of 300 to 900 mg/L, and 20 to 220 mg/L were studied respectively. The alkalinity and pH were adjusted using lime as described in Section 3.7.4. The data are compiled in Tables 4.3 - 4.6 and plotted in Figs. 4.3 - 4.10. It was noted that for a specified initial fluoride concentration, the removal of fluoride increased with increase of alum dose. This fact is also evident from Fig. 4.11 which is plotted only for PAC dose of 100 mg/L as best fluoride removal was obtained at this PAC dose for all initial fluoride concentrations and alum doses. It was more pronounced relatively at higher initial fluoride concentrations (≥10 mg/L). With increase of alum dose (i.e. Al^{3+}), aluminum hydroxide precipitate and other hydroxoaluminum species on which fluoride could be adsorbed or complexed (Zabban and Helwick, 1975) also increases thus increasing the fluoride removal. This phenomenon was more pronounced at higher fluoride concentrations because of availability of more fluoride for adsorption/complexation (i) on the $Al(OH)_3(s)$ and other hydroxoaluminum species, and (ii) on the PAC. Zabban and Helwick (1975) also noted reduction of fluoride removal efficiency of alum at low fluoride concentrations. As shown in Fig. 4.12 (typical curve for PAC dose of 100 mg/L), for a specific alum dose, in most cases, the percentage of fluoride removal decreased with increasing initial fluoride concentrations (≥ 10 mg/L). At a fixed alum and PAC (100 mg/L) dose, adsorption sites on the PAC, flocs of $Al(OH)_3(s)$ and other hydroxoaluminum species available for fluoride adsorption/complexation remain almost of the same order. Thus chances of fluoride being adsorbed or complexed decreases with increasing initial fluoride concentrations reducing the fluoride uptake rate and the percentage of removal.

It is also evident from Figs. 4.3 - 4.10 that fluoride removal increased gradually with increasing PAC dose up to 100 mg/L for all the initial fluoride concentrations studied. Further increase of PAC dose above 100 mg/L resulted in decrease of fluoride removal in case of its incorporation with alum doses up to 600 mg/L. For alum doses more than 600 mg/L, this decreasing trend was observed only up to PAC dose of 160 mg/L (except for C_o=20 mg/L) and further increase of PAC dose again resulted in increase of fluoride removal. However, increase of PAC doses > 100 mg/L did not provide further improvement in fluoride removal compared to the removal at PAC dose of 100 mg/L. Thus, for all alum doses studied, maximum fluoride removal was achieved at PAC dose of 100 mg/L. This PAC dose along with 500, 600, and 800 mg/L of alum (optimum doses) reduced initial fluoride concentrations of 6, 10, and 15 mg/L to ≤ 1.5 mg/L with removal efficiencies of 75, 85, and 90% respectively. However, in case of an initial fluoride concentration of 20 mg/L, it was reduced only to 3.15 mg/L with alum and PAC doses of 900 and 100 mg/L respectively. Preliminary study also indicated reduction of an initial fluoride concentration of 16 mg/L to 1.7 mg/L using same doses of alum and PAC referred to above. Alum doses of more than 900 mg/L were not used, as it would have resulted in unacceptable levels of aluminum and sulfate in treated water. One of the alternatives for reduction of fluoride of this water (C_o=20 mg/L) to 1.5 mg/L could be two-stage treatment using alum-PAC slurry and lime at the first stage and aluminum chloride at the second stage. At the first stage, fluoride could be reduced from 20 mg/L to 3.15 mg/L using alum-PAC slurry having 900 mg/L of alum and 100 mg/L of PAC doses. At the second stage, it could be further reduced to

1.5 mg/L or below using around 85 mg/L of aluminum chloride alone (Bulusu, 1984) since use of alum-PAC slurry had no significant advantage at relatively low initial fluoride concentrations (≤ 6 mg/L). Hence in this case, overall, 900 mg/L of alum, around 85 mg/L of aluminum chloride, and 100 mg/L of PAC along with lime for pH adjustment would be required to reduce the fluoride concentration to the permissible limit (1.5 mg/L). Compared to defluoridation by alum and lime (Bulusu et al., 1979; Bulusu, 1984), defluoridation by alum-PAC slurry and lime resulted in reduction of alum dose by 40 and 43% (Fig. 4.13) for initial fluoride concentrations of 10 and 15 mg/L respectively. However, alum-PAC slurry had no significant advantage for an initial fluoride concentration of 6 mg/L.

To clarify the above observations regarding the effect of PAC doses on fluoride removal, additional study was conducted taking measurements of residual fluoride both at the ends of rapid and slow mixing periods at an initial fluoride concentration of 15 mg/L. The results are compiled in Table 4.7 and plotted in Figs. 4.14 (a-d). If one considers fluoride removal only during rapid mixing period, 40.3% removal was recorded in the absence of PAC dose. Relatively better fluoride removal was observed at PAC doses in the range of 20-100 mg/L and best removal of fluoride i.e. 60% was obtained at PAC dose of 60 mg/L. Irrespective of total doses of alum (i.e. 500, 600, 700, and 800 mg/L), the removals during rapid mixing were same for a particular value of PAC dose. This was due to the operation procedure (3.7.3) as only 400 mg/L of alum dose was added at the beginning of rapid mixing and rest of the alum dose was added during the intermediate mixing. Hence, in all the 28 runs (Table 4.7) initially only 400 mg/L of alum was added.

During rapid mixing, 60 mg/L of PAC was found to be enough for best removal. If one takes in to account removals only during slow mixing, it could be concluded that a much higher dose of PAC was needed than 60 mg/L. However, during slow mixing period, fluoride removal was relatively less. It was found to improve for higher PAC doses of 160 and 200 mg/L. As far as cumulative removal is concerned, the variation of fluoride removal with changing doses of PAC was in much lesser order. PAC dose of 100 mg/L in alum-PAC slurry gave best removal for studied alum doses form 500 to 800 mg/L. Role of PAC in overall removal was important and probably adsorption of fluoride on PAC (uncoated or coated with aluminum floc) and its seeding effect made a significant contribution. Letterman et al. (1970) observed significant coagulation of carbon suspensions (aggregation of particles) in water even without the addition of coagulant during mixing. Obviously, this phenomenon is expected to be enhanced in the presence of significant doses of a coagulant. Almost instantly after addition of alum to the water, mainly aluminum hydroxide precipitate is formed in the bulk solution and on the surface of the PAC (Amirtharajah and Mills, 1982; Mc Cormic et al., 1993). Letterman et al. (1970) has also described coating of carbon particles with precipitating metal hydroxide. Because of this, PAC surface may be totally or partially covered and the coated PAC surface may be considered to behave as the aluminum hydroxide precipitate as also suggested by Benjamin et al. (1982), Dentel and Gossett (1988), and Ching et al. (1994). Since aluminum hydroxide precipitate is positively charged at pH less than 7 (Amirtharajah and Mills, 1982), the PAC surface covered with $Al(OH)_3(s)$ would also be positively charged (even though the charge would be less compared to the free precipitate because of the negative charge of the PAC surface). Thus, in case of using alum-PAC slurry, fluoride is thought to be removed predominantly by adsorption on or complexation with $Al(OH)_3(s)$ in the bulk solution (mainly at lower PAC doses), on the $Al(OH)_3(s)$ which covers the PAC surface (coated PAC surface), and by adsorption directly on the PAC surface (uncoated PAC surface). Gradual diffusion of fluoride through the floc surrounding the particle to the PAC surface, particularly at higher initial fluoride concentrations (higher concentration gradient), is also possible (AWWA, 1990). The requirement of longer rapid mixing time (40 minutes) to reduce fluoride concentrations to 1.5 mg/L, and no additional benefit of the alum-PAC slurry compared to alum only at relatively lower initial fluoride concentration (≈6 mg/L), also suggest this possibility. However, fluoride removal by aluminum hydroxide precipitate in the bulk solution and on the PAC surface would be predominant since the fluoride ion which is negatively charged would have more affinity to the positively charged precipitate $[Al(OH)_3(s)]^{n+}$. At the given pH (5.8 to 6.5), the extent of PAC surface coverage by $Al(OH)_3(s)$ depends upon the alum and PAC doses. However, in this case, since alum dose during rapid mixing was constant (400 mg/L) it would have depended mainly on the PAC dose. Initially with increasing PAC dose most of the PAC surface would be coated with Al(OH)3(s) (with relatively less uncoated PAC surface) until the maximum surface area which could be coated by 400 mg/L of alum is attained. Thereafter, with increasing PAC doses uncoated PAC surface area is expected to significantly increase. Thus, availability of large PAC surface area with positive (coated PAC) and negative (uncoated PAC) charges which could easily attract to each other coupled with high probability of collision and attachment (because of relatively high PAC doses) enhances aggregation of PAC particles at relatively higher doses (> 100 mg/L). Consequently this reduces the surface area of coated and uncoated PAC which could have interacted with the fluoride in the water thus reducing fluoride removal. If there had not been aggregation of PAC particles, increase of uncoated PAC

Table 4.3 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses C_o=6 mg/L, pH=5.8 to 6.5

PAC mg/L	Alum dose, mg/L											
	300		400		500		600		700		800	
	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %
0	2.80	53.3	2.15	64.2	1.80	70.0	1.65	72.5	1.40	76.7	1.15	80.8
20	2.70	55.0	1.90	68.3	1.70	71.7	1.50	75.0	1.25	79.2	1.00	83.3
60	2.40	60.0	1.80	70.0	1.50	75.0	1.45	75.8	1.20	80.0	0.95	84.2
100	2.35	60.8	1.75	70.8	1.45	75.8	1.35	77.5	1.10	81.7	0.90	85.0
120	2.45	59.2	1.90	68.3	1.50	75.0	1.40	76.7	1.15	80.8	1.00	83.3
140	2.55	57.5	1.90	68.3	1.55	74.2	1.50	75.0	1.25	79.2	1.10	81.7
160	2.60	56.7	1.95	67.5	1.65	72.5	1.55	74.2	1.30	78.3	1.10	81.7
180	2.60	56.7	1.90	68.3	1.65	72.5	1.60	73.3	1.25	79.2	1.05	82.5
200	2.65	55.8	1.95	67.5	1.75	70.8	1.60	73.3	1.25	79.2	1.00	83.3
220	2.70	55.0	2.00	66.7	1.70	71.7	1.55	74.2	1.20	80.0	1.00	83.3

Resid. fluod. = Residual fluoride Fluod. removed = Fluoride removed

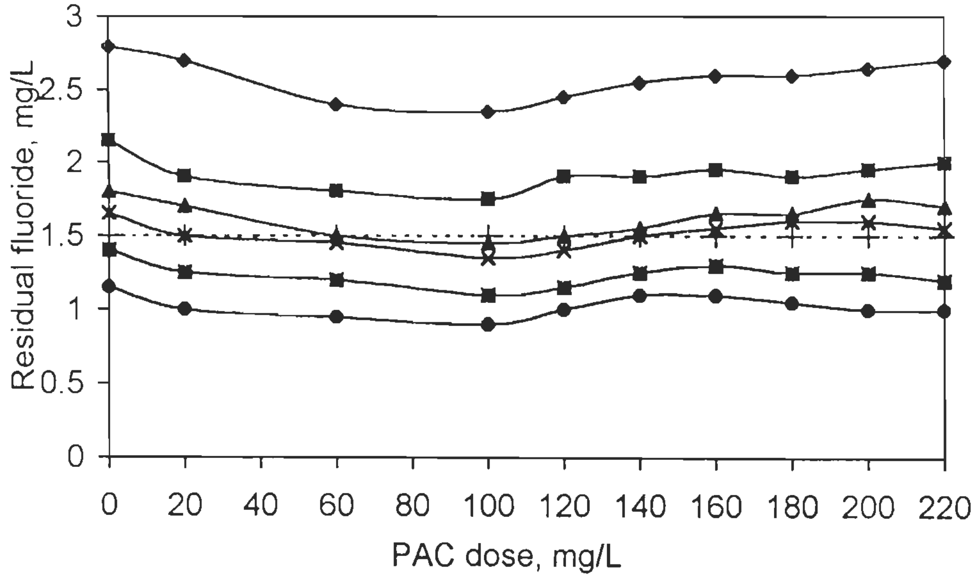


Fig. 4.3 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=6 mg/L, pH=5.8 to 6.5
(--+--+-) Accpetable Limit of Fluoride (1.5 mg/L)

Alum doses
—◆— 300 mg/L —■— 400 mg/L —▲— 500 mg/L
—×— 600 mg/L —■— 700 mg/L —●— 800 mg/L

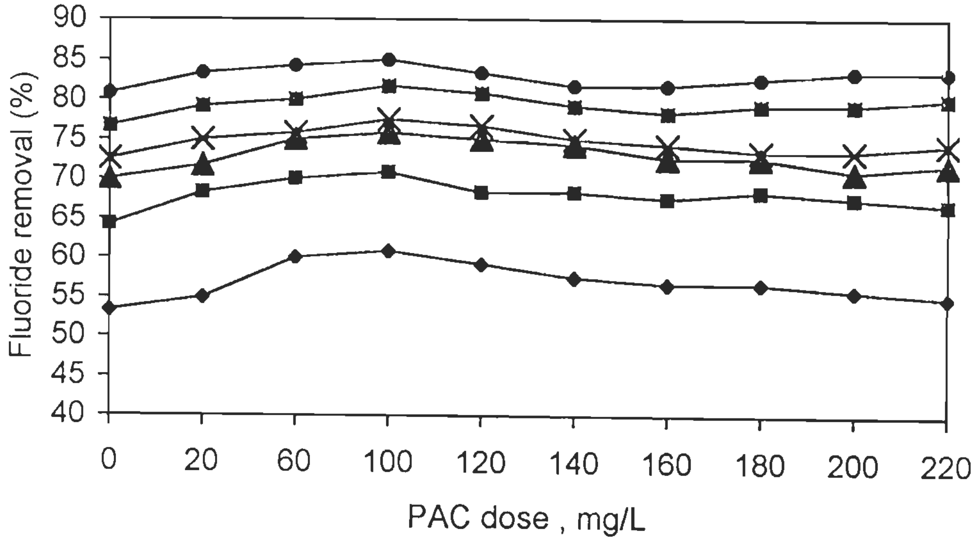


Fig. 4.4 Percentage of Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses.
C_o=6 mg/L, pH=5.8 to 6.5

Table 4.4 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses

C_o=10 mg/L, pH=5.8 to 6.5

PAC mg/L	Alum dose, mg/L							
	500		600		700		800	
	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %
0	3.60	64.0	3.15	68.5	2.90	71.0	2.30	77.0
20	3.05	69.5	2.15	78.5	2.10	79.0	2.00	80.0
60	2.55	74.5	1.80	82.0	2.00	80.0	1.45	85.5
100	1.90	81.0	1.40	86.0	1.40	86.0	1.20	88.0
120	2.00	80.0	1.60	84.0	1.30	87.0	1.10	89.0
140	2.20	78.0	1.95	80.5	1.35	86.5	1.20	88.0
160	3.15	68.5	2.25	77.5	1.80	82.0	1.75	82.5
180	3.40	66.0	2.30	77.0	1.60	84.0	1.50	85.0
200	3.65	63.5	2.40	76.0	1.45	85.5	1.25	87.5
220	3.70	63.0	2.40	76.0	1.45	85.5	1.00	90.0

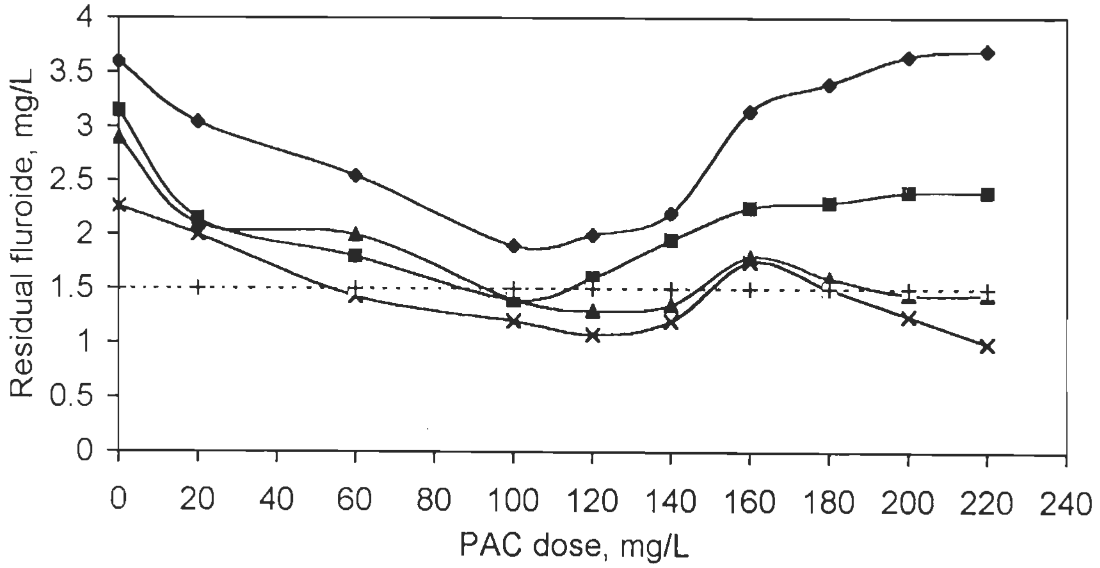


Fig. 4.5 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=10 mg/L, pH=5.8 to 6.5
(--+--+--) Acceptable Limit of Fluoride (1.5 mg/L)

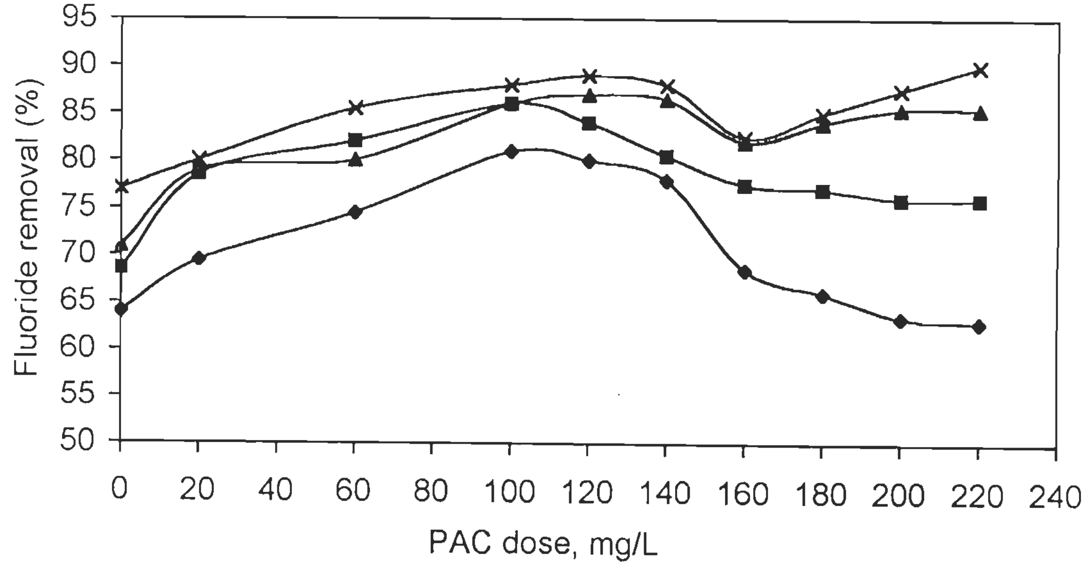


Fig.4.6 Percentage of Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=10 mg/L, pH=5.8 to 6.5

Table 4.5 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses C_o=15 mg/L, pH=5.8 to 6.5

PAC mg/L	Alum dose, mg/L							
	500		600		700		800	
	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %
0	7.50	50.0	5.55	63.0	4.50	70.0	3.65	75.7
20	5.70	62.0	4.05	73.0	3.90	74.0	3.00	80.0
60	5.40	64.0	3.45	77.0	3.40	77.3	2.00	86.0
100	5.10	66.0	3.30	78.0	3.00	80.0	1.50	90.0
120	5.45	63.7	3.55	76.3	3.40	77.3	1.60	89.3
140	5.60	62.7	3.60	76.0	3.50	76.7	1.50	90.0
160	5.75	61.7	3.75	75.0	3.60	76.0	2.15	85.6
180	5.85	61.0	3.90	74.0	3.50	76.7	2.05	86.3
200	5.90	60.6	4.10	72.7	3.30	78.0	1.90	87.3
220	6.00	60.0	4.15	72.3	3.30	78.0	1.80	88.0

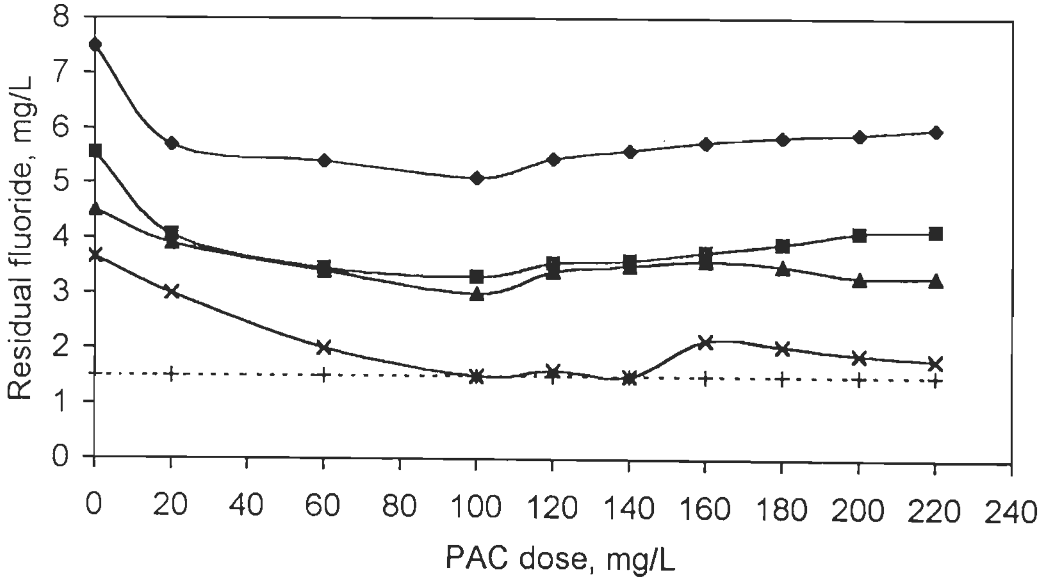


Fig. 4.7 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=15 mg/L, pH=5.8 to 6.5
(--+---+--) Acceptable Limit of Fluoride (1.5 mg/L)

Alum doses

—◆— 500 mg/L —■— 600 mg/L —▲— 700 mg/L —✕— 800 mg/L

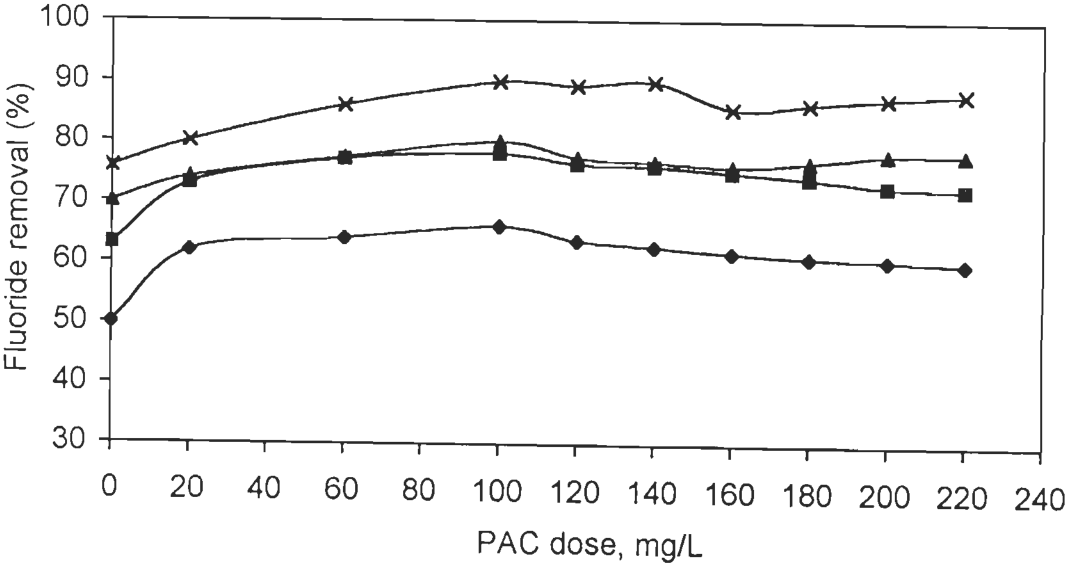


Fig.4.8 Percentage of Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=15 mg/L, pH=5.8 to 6.5

Table 4.6 **Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses** C_o=20 mg/L, pH=5.8 to 6.5

PAC mg/L	Alum dose, mg/L									
	500		600		700		800		900	
	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %	Resid. fluod. mg/L	Fluod. removed %
0	10.20	49.0	7.30	63.5	6.10	69.5	5.25	73.8	4.90	75.5
20	8.70	56.5	6.30	68.5	4.55	77.2	4.35	78.3	4.10	79.5
60	8.50	57.5	6.00	70.0	4.40	78.0	3.70	81.5	3.50	82.5
100	8.25	58.8	5.75	71.2	4.00	80.0	3.40	83.0	3.15	84.3
120	8.55	57.3	6.00	70.0	4.45	77.8	3.70	81.5	3.45	82.8
140	8.60	57.0	6.10	69.5	4.40	78.0	3.65	81.8	3.40	83.0
160	8.70	56.5	6.15	69.2	4.35	78.3	3.60	82.0	3.30	83.5
180	8.70	56.5	6.20	69.0	4.30	78.5	3.50	82.5	3.20	84.0
200	8.80	56.0	6.30	68.5	4.30	78.5	3.45	82.8	3.10	84.5
220	8.85	55.8	6.35	68.2	4.25	78.8	3.50	82.2	3.15	84.3

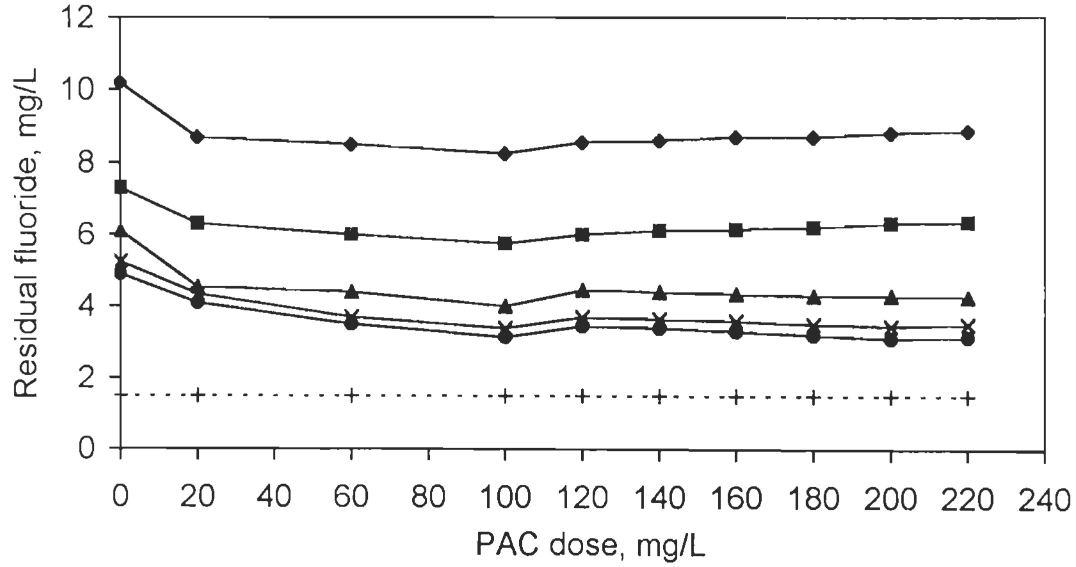


Fig. 4.9 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=20 mg/L, pH = 5.8 to 6.5
(--+---+--) Acceptable Limit of Fluoride (1.5 mg/L)

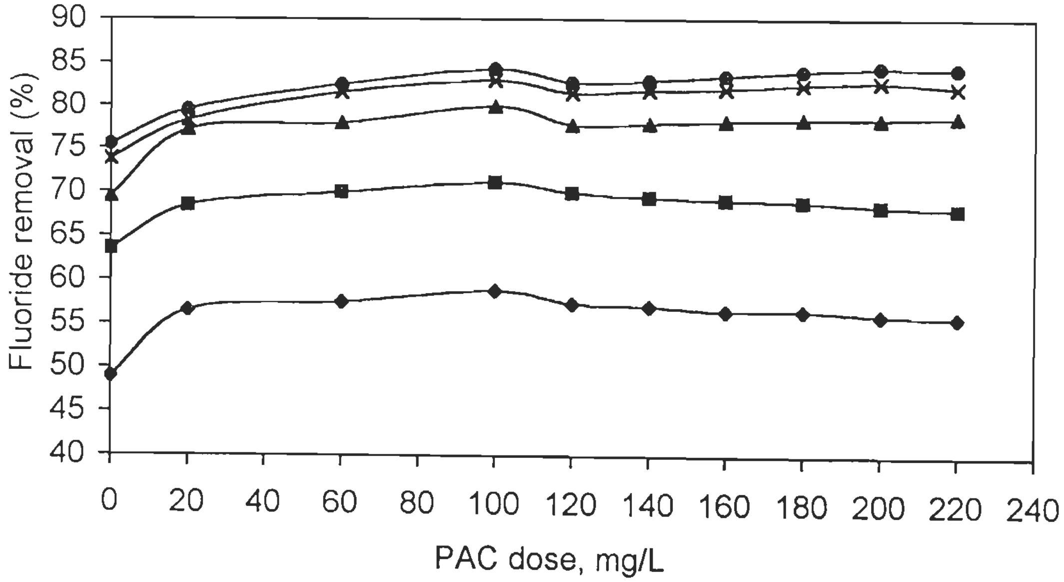


Fig. 4.10 Percentage of Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses. C_o=20 mg/L pH=5.8 to 6.5

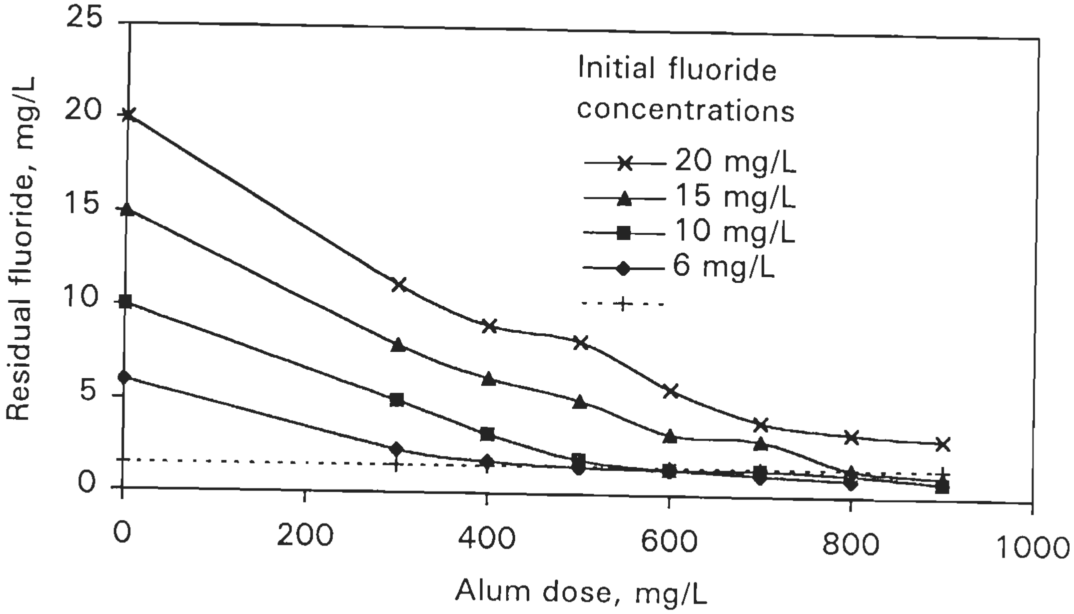


Fig. 4.11 Variation of Residual Fluoride Concentration with Alum Dose at Different Initial Fluoride Concentrations. PAC Dose-100 mg/L (No PAC at 0 mg/L Alum Dose) pH=5.8 to 6.5, (--+---+--) Accepatable Limit of Fluoride (1.5 mg/L)

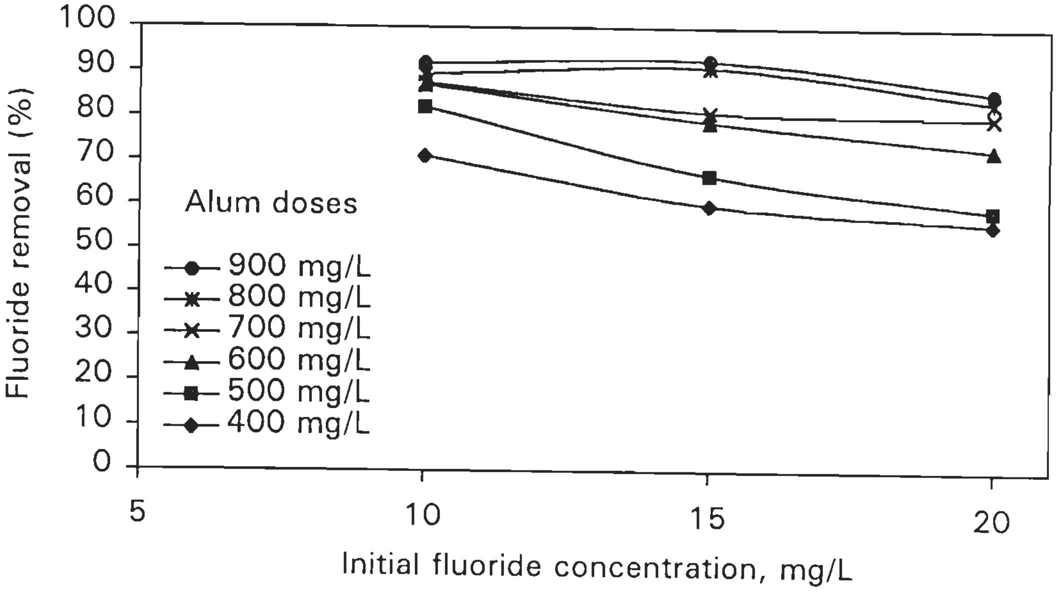


Fig.4.12 Percentage of Fluoride Removal by Alum-PAC Slurry Having Various Doses of Alum at Different Initial Fluoride Concentrations.
PAC Dose-100 mg/L, pH=5.8 to 6.5

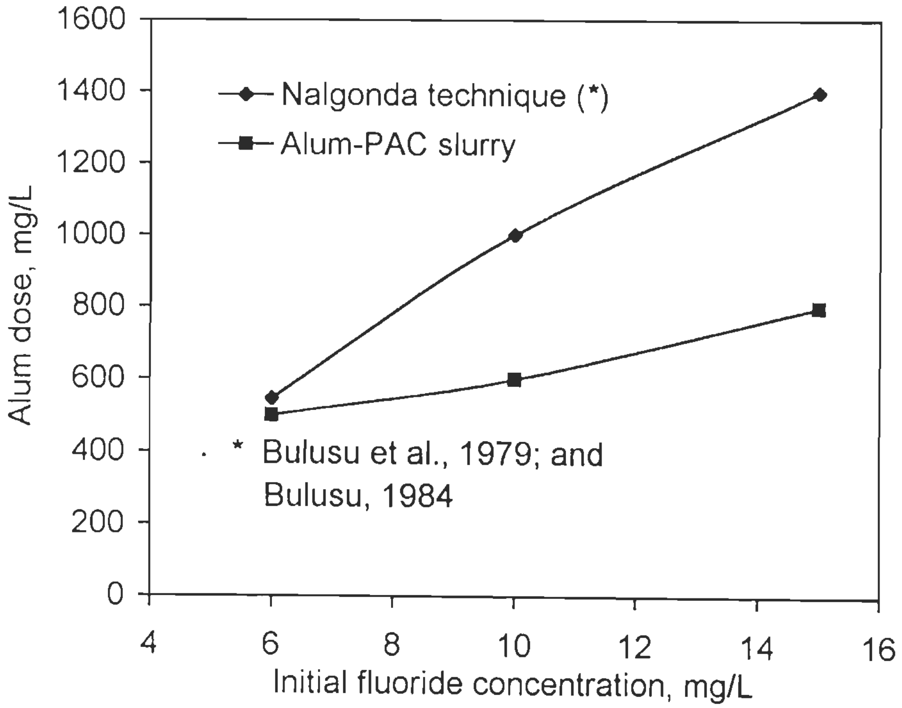


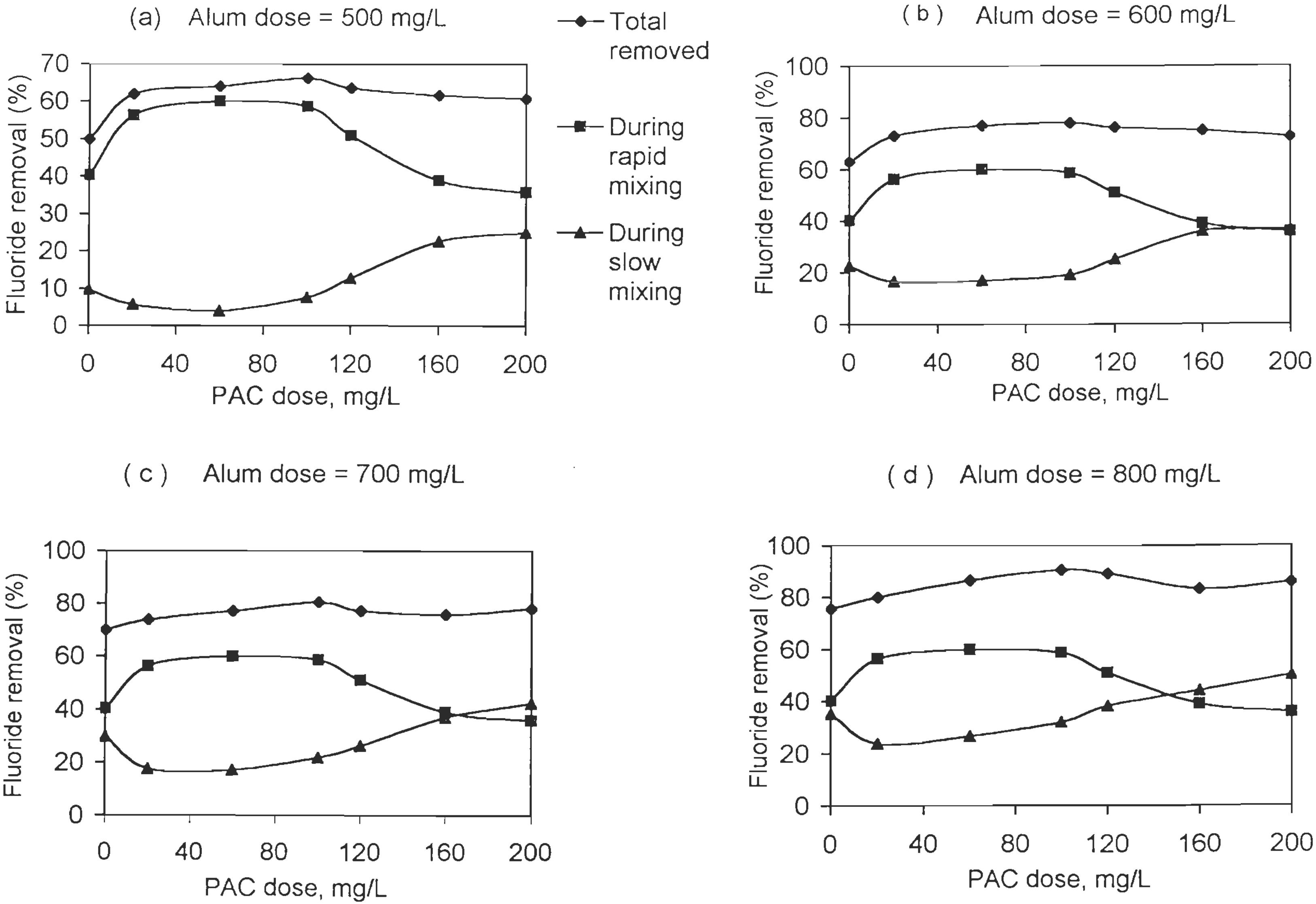
Fig. 4.13 Alum Dose Requirement to Reduce Initial Fluoride Concentrations to 1.5 mg/L by Alum-PAC Slurry, and by Alum and Lime (Nalgonda Technique).

Table 4.7 Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses During Rapid and Slow Mixing Periods

C_o=15 mg/L, pH=5.8 to 6.5

Alum mg/L	PAC mg/L	Fluoride removal					
		Total		During rapid mixing		During slow mixing	
		mg/L	%	mg/L	%	mg/L	%
500	0	7.50	50.0	6.05	40.3	1.45	9.7
500	20	9.30	62.0	8.45	56.3	0.85	5.7
500	60	9.60	64.0	9.00	60.0	0.60	4.0
500	100	9.95	66.3	8.80	58.7	1.15	7.6
500	120	9.55	63.7	7.65	51.0	1.90	12.7
500	160	9.25	61.7	5.85	39.0	3.40	22.7
500	200	9.10	60.7	5.35	35.8	3.75	25.0
600	0	9.45	63.0	6.05	40.3	3.40	22.7
600	20	10.95	73.0	8.45	56.3	2.50	16.7
600	60	11.55	77.0	9.00	60.0	2.55	17.0
600	100	11.70	78.0	8.80	58.7	2.90	19.3
600	120	11.45	76.3	7.65	51.0	3.80	25.3
600	160	11.25	75.0	5.85	39.0	5.40	36.0
600	200	10.90	72.7	5.35	35.8	5.55	36.9
700	0	10.50	70.0	6.05	40.3	4.45	29.7
700	20	11.10	74.0	8.45	56.3	2.65	17.6
700	60	11.60	77.3	9.00	60.0	2.60	17.3
700	100	12.10	80.7	8.80	58.7	3.30	22.0
700	120	11.60	77.3	7.65	51.0	3.95	26.3
700	160	11.40	76.0	5.85	39.0	5.55	37.0
700	200	11.70	78.0	5.35	35.8	6.35	42.2
800	0	11.35	75.7	6.05	40.3	5.30	35.3
800	20	12.00	80.0	8.45	56.3	3.55	23.7
800	60	13.00	86.7	9.00	60.0	4.00	26.7
800	100	13.60	90.7	8.80	58.7	4.80	32.0
800	120	13.40	89.3	7.65	51.0	5.75	38.3
800	160	12.50	83.3	5.85	39.0	6.65	44.3
800	200	12.90	86.0	5.35	35.8	7.55	50.2

Note: Amount of fluoride removed during slow mixing was calculated as a difference between the amount of fluoride removed during total and rapid mixing time.



Figs. 4.14 (a-d) Fluoride Removal by Alum-PAC Slurry at Various Alum and PAC Doses During Rapid and Slow Mixing Periods. C_o=15 mg/L, pH= 5.8 to 6.5

surface with increase of PAC dose (>100 mg/L) would have increased fluoride removal. However, during the slow mixing (30 rpm) period, relatively more PAC particles (aggregates) were found in suspension at higher PAC doses. These could be utilized as nuclei by alum freshly added during intermediate mixing for precipitation as also suggested by Faust and Aly (1983) thus enhancing fluoride removal by adsorption on the aluminum hydroxide precipitate or by formation of fluoride complex with it (Zabban and Helwick, 1975). In addition, studies conducted subsequently on fluoride removal by PAC alone (Figs. 4.16 - 4.22 and Table 4.8) showed its insignificant contribution to fluoride removal at slow mixing (30 rpm). Furthermore, a study confirmed that lime, which was added during intermediate mixing, did not remove fluoride (Table 4.8 and 4.9) during slow mixing. These observations also suggest that the only possibility of improvement of fluoride removal with increase of PAC doses during slow mixing could be due to the improvement of fluoride removal efficiency of alum which could result from the seeding effect of the PAC as discussed above. This might be responsible for reincrease of the fluoride removal at higher doses of alum (> 600 mg/L) along with PAC doses of more than 160 mg/L, since the alum dose added during the intermediate mixing period linearly increased with increase of the total alum dose.

4.2.4 The Role of Lime in Fluoride Removal

Lime was added during intermediate mixing to adjust pH and alkalinity. However, in addition to that its involvement in direct removal of fluoride in this treatment process is not known. Hence, studies were conducted to understand the role of lime in fluoride removal. Investigations were carried out on water samples having fluoride concentration of 15 mg/L maintaining pH of 6, 8, and 9 during mixing. In the first batch (Table 4.8), PAC alone (100 mg/L) and a combination of lime and PAC (560 mg/L and 100 mg/L respectively) were used for defluoridation, whereas in the second batch (Table 4.9) along with lime and PAC, alum (500 mg/L) was also used. In the first and second batches, experiments were conducted at 30 rpm (slow mixing) for contact times of 30 and 60 minutes respectively, as per experimental procedures outlined in Section 3.7.5. As shown in Table 4.8, when lime was used in combination with PAC it did not provide significant fluoride removal at pH of 6 (the optimum pH for the treatment). However, at higher pH (8 and 9) 10-18% fluoride removal was observed possibly by formation of CaF_2 precipitate (Rabosky and Miller, 1974). Nevertheless, in combination with alum (Table 4.9) lime did not provide significant fluoride removal at all pH values studied. This may be attributed to the solubility of CaF_2 in aluminum compounds (Maier, 1971). Thus, in this treatment process role of lime is restricted only to the adjustment of pH and alkalinity. It did not directly involve in fluoride removal.

4.2.5 Process Kinetics of Fluoride Removal by Alum-PAC Slurry and Its Components at Various Alum and PAC Doses

These experiments were conducted to study variation of fluoride removal by alum-PAC slurry and its components i.e. alum and PAC separately with time, the interrelationship of the slurry components on fluoride removal, effects of alum and PAC doses on fluoride removal at varying contact times and mixing conditions, and also to examine if the results could be represented by any of the adsorption models. The tests were carried out according to the optimum operation procedure (c) with the only difference that rapid and slow mixing periods were extended to 120 and 60 minutes respectively. The pH was maintained at the optimum range (5.8 to 6.5) using lime. Details of the experiments are given in Section 3.7.6. The observations are discussed by subdividing into the following three parts:

Table 4.8 Fluoride Removal by Lime with PAC at Various pH

C_o=15 mg/L, Contact time- 30 min, rpm=30

pH	Dose, mg/L		Resid. fluoride, mg/L
	Lime	PAC	
6.00	560	100	14.95
8.00	560	100	13.45
9.00	560	100	12.30
6.00	----	100	14.90
8.00	----	100	14.95
9.00	----	100	14.90

Table 4.9 Fluoride Removal by Alum-PAC Slurry with and without Lime at Various pH

C_o=15 mg/L, Contact time-60 min, rpm=30

pH	Dose, mg/L			Resid. fluoride, mg/L
	Alum	Lime	PAC	
6.00	500	560	100	5.40
8.00	500	560	100	8.75
9.00	500	560	100	10.15
6.00	500	----	100	5.50
8.00	500	----	100	8.90
9.00	500	----	100	10.05

4.2.5.1 Fluoride Removal by Alum-PAC Slurry and Its Components with Time

The variation of fluoride removal with time when treated with (i) alum-PAC slurry, (ii) alum alone, and (iii) PAC alone for initial fluoride concentrations of 6, 10, 15, and 20 mg/L are compiled in Tables 4.10 – 4.13 and plotted in Figs. 4.15 – 4.22. Same alum and PAC doses of 800 and 100 mg/L respectively were used separately and in combination irrespective of variation in initial fluoride concentration. 800 mg/L of alum was found to be the optimum dose for initial fluoride concentration of 15 mg/L, whereas 100 mg/L of PAC was the preferred best dose for all initial fluoride concentrations studied (Section 4.2.3). The removal of fluoride by alum-PAC slurry and by alum alone was found to be increasing with time for rapid and slow mixing periods until equilibrium concentrations were attained during both rapid and slow mixing periods. Contrary to this, when only PAC was used, additional fluoride removal during slow mixing was not noticed. Thus, in defluoridation by alum-PAC slurry, it appears that alum was directly involved in fluoride removal throughout the contact time whereas PAC was directly participating only during rapid mixing. Depending on the initial fluoride concentration, 53 to 65%, 38 to 52%, and 16 to 24% of the fluoride was removed during the first 10 minutes of contact time by alum-PAC slurry, alum, and PAC respectively with further approach to equilibrium at slow rate. By the end of rapid mixing, these removals increased to 55-72%, 41-64%, and 22-30% for alum-PAC slurry, alum, and PAC respectively. The removal during slow mixing both by alum-PAC slurry and by alum was found to be increasing with initial fluoride concentrations. This suggests that scarcity of fluoride in the water reduces the amount of fluoride removal. Zabban and Helwick (1975) also noted reduction of fluoride removal by alum at low fluoride concentrations. High fluoride removal by alum alone at the beginning of rapid and slow mixing periods suggests removal of fluoride mainly by adsorption on or complexation with aluminum hydroxide precipitate as it is formed within 1-7 seconds after addition of alum to water. Buffle et al. (1985) in their study on fluoride removal by hydrolyzed aluminum polymer (also could be formed during alum addition to water), analyzed the precipitate formed, and produced an empirical formula which shows adsorption/comlexation of fluoride on the hydroxoaluminum species i.e. $Al(OH)_{2.32}F_{0.68}Na_{0.01}$. The higher uptake rate by the PAC alone at the beginning of mixing could be because of availability of more fluoride in the water and more favorable free sites for adsorption at that time. Higher removal of fluoride was also observed within the first 10 minutes of contact by activated alumina (Bulusu and Nawlakhe, 1988) and by fish bone charcoal (Killedar, 1990). Assuming that the influence of PAC on fluoride removal characteristics of alum was insignificant, the share of PAC in alum-PAC slurry for fluoride removal was found by subtracting the percentage removals when alum alone was used from percentage removals when alum-PAC slurry was used. These values are also plotted in Figs. 4.16, 4.18, 4.20, and 4.22. Further analysis of these results revealed the following facts:

For initial fluoride concentration of 6 mg/L, the maximum removal (12.5%) by the PAC (in the presence of alum) was attained within 10 minutes but afterwards it decreased to 4.1% almost linearly at the end of the contact time (Fig. 4.16). In this case the PAC provided only 13% of the fluoride removal it has given without alum. At the transition from rapid to slow mixing (at this time fresh alum was added), small amount of fluorides appeared to have desorbed from the PAC surface in decreasing magnitude with increasing initial fluoride concentrations from 10 to 20 mg/L (Figs. 4.18, 4.20, and 4.22). For initial fluoride concentrations of 15 and 20 mg/L (Figs. 4.20 and 4.22) it slightly again increased within the first 10 minutes of slow mixing period. In the presence of alum, the PAC has provided 28, 59, and 41% of the fluoride removal it has given when used alone for initial fluoride concentrations of 10, 15, and 20 mg/L respectively. This suggests reduction of fluoride removal efficiency of PAC due to coating by aluminum hydroxide precipitate. Improvement of the fluoride removal at higher initial fluoride concentrations (15 and 20 mg/L) may be due to gradual diffusion of fluoride through the coating to the PAC surface because of higher concentration gradient.

Since the driving force for the mass transfer of the solute to the surface and interior of the adsorbent is the concentration gradient (Weber, 1972; Neely, 1982; Faust and Aly, 1983), any factor, which affects this gradient, may alter the adsorption process. Moreover, the rate-limiting step of adsorption at the initial stage of batch reaction and when the mixing is insufficient (such as at slow mixing period) is film diffusion (Faust and Aly, 1983). Therefore, the adsorption mainly depends on the concentration difference of the solute between the solution concentration at the outer surface of the adsorbent granule and the bulk solution. As described previously (Section 4.2.3), the negatively charged fluoride ion has more affinity to the positively charged (at pH 5.8 to 6.5) $[Al(OH)_3(s)]^{n+}$ than the PAC surface, which is negatively charged. The desorption of fluoride from PAC (for C_o=6 mg/L) after the first 10 minutes of contact seemed due to the competitive removal of fluoride by alum from the water which deplete the residual fluoride concentration increasing the concentration gradient towards the water and thus enhancing desorption. The desorption of fluoride during the transition period (from rapid to slow mixing) may be explained by the lowering of equilibrium fluoride concentration attained during the rapid mixing period

Table 4.10 Variation of Fluoride Removal by Alum-PAC Slurry and Its Components with Time C_o=6 mg/L, Alum-800 mg/L PAC-100 mg/L, pH = 5.8 to 6.5

Contact time(min)	Alum-PAC slurry		Alum alone		PAC alone		PAC in the presence of alum
	Residual fluoride concentration and percentage of removal						
	mg/L	%	mg/L	%	mg/L	%	%
0	6.00	0.0	6.00	0.0	6.00	0.0	0.0
2	2.70	55.0	3.35	44.2	5.05	15.8	10.8
10	2.10	65.0	2.85	52.5	4.75	20.8	12.5
20	1.90	68.3	2.60	56.7	4.50	25.0	11.6
40	1.80	70.0	2.40	60.0	4.25	29.2	10.0
120	1.70	71.7	2.15	64.2	4.20	30.0	7.5
122	1.20	80.0	1.60	73.3	4.15	30.8	6.7
130	0.95	84.2	1.30	78.3	4.15	30.8	5.9
150	0.90	85.0	1.20	80.0	4.10	31.6	5.0
180	0.85	85.8	1.10	81.7	4.10	31.6	4.1

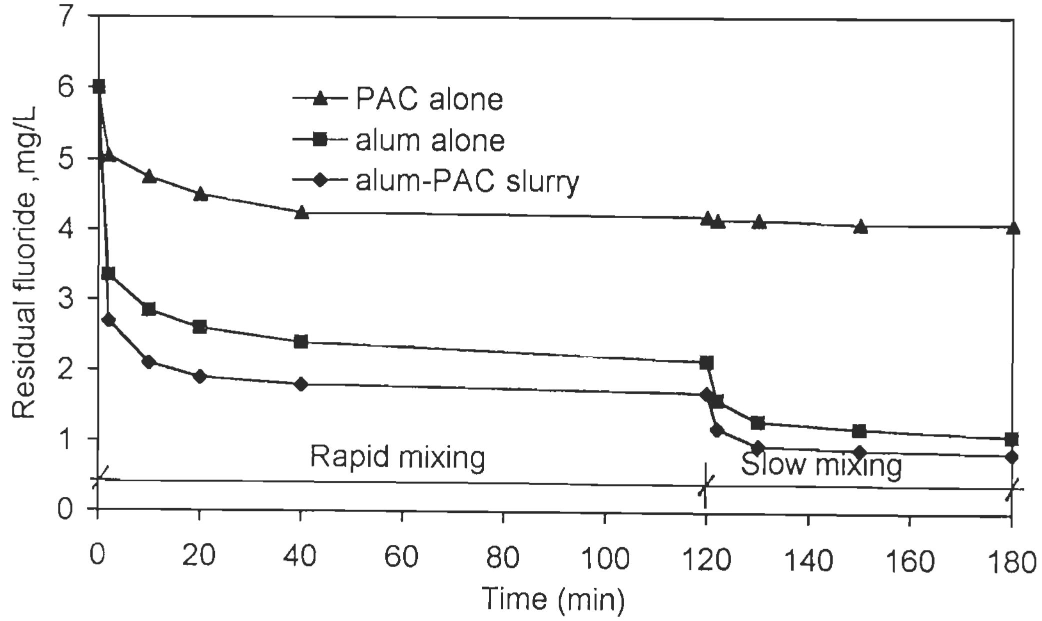


Fig. 4.15 Variation of Fluoride Removal by Alum-PAC Slurry and Its Components with Time. C_o=6 mg/L, pH=5.8 to 6.5 Alum Dose-800 mg/L , PAC Dose- 100 mg/L

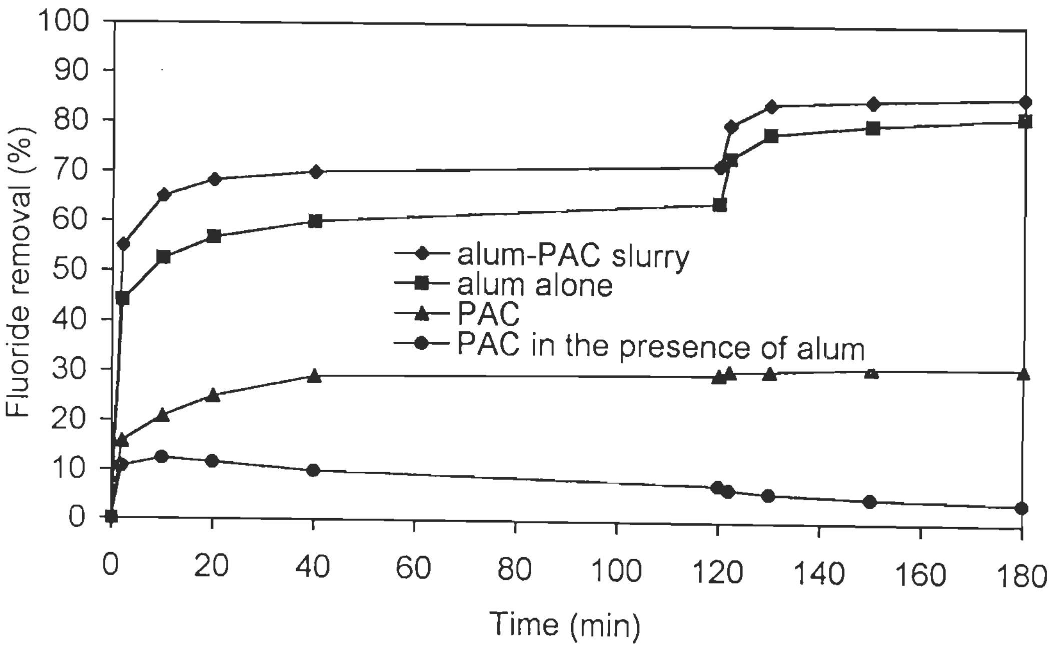


Fig. 4.16 Percentage of Fluoride Removal by Alum-PAC Slurry and Its Components with Time. C_o=6 mg/L pH=5.8 to 6.5, Alum Dose-800 mg/L, PAC Dose-100 mg/L

Table 4.11 Variation of Fluoride Removal by Alum-PAC Slurry and Its Components with Time C_o=10 mg/L, Alum-800 mg/L PAC-100 mg/L, pH=5.8 to 6.5

Contact time(min)	Alum-PAC slurry		Alum alone		PAC alone		PAC in the presence of alum
	Residual fluoride concentration and percentage of removal						
	mg/L	%	mg/L	%	mg/L	%	%
0	10.00	0.0	10.00	0.0	10.00	0.0	0.0
2	4.75	52.5	5.85	41.5	7.90	21.0	11.0
10	3.85	61.5	5.35	46.5	7.60	24.0	15.0
20	3.65	63.5	5.15	48.5	7.35	26.5	15.0
40	3.35	66.5	5.05	49.5	7.20	28.0	17.0
120	3.20	68.0	4.85	51.5	7.10	29.0	16.5
122	1.90	81.0	2.90	71.0	7.05	29.5	10.0
130	1.40	86.0	2.30	77.0	7.05	29.5	9.0
150	1.15	88.5	2.15	78.5	7.00	30.0	10.0
180	1.05	89.5	1.90	81.0	7.00	30.0	8.5

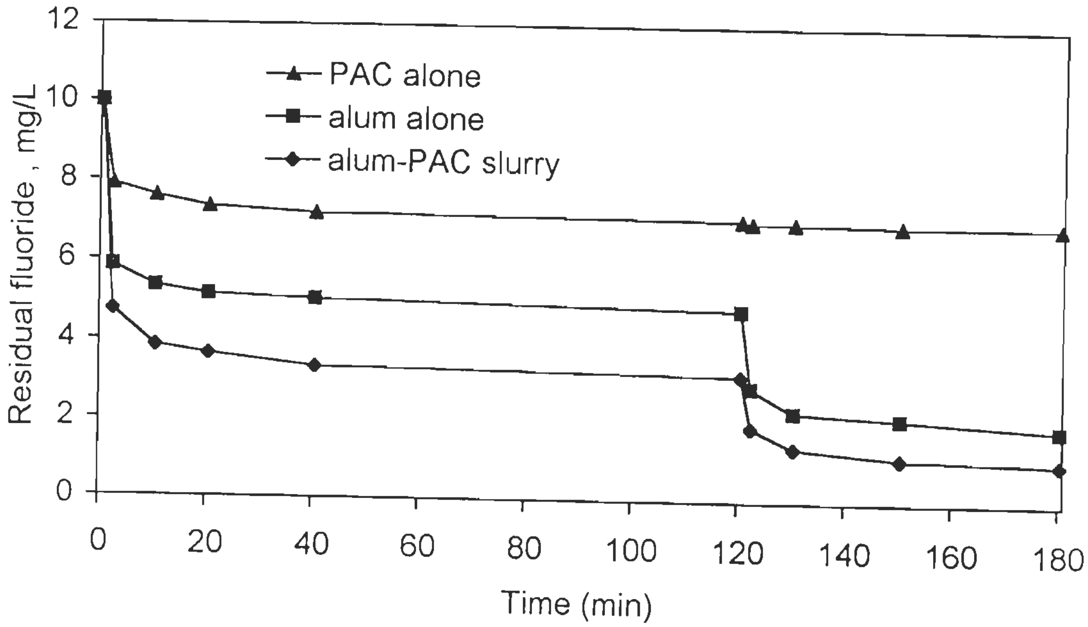


Fig. 4.17 Variation of Fluoride Removal by Alum-PAC Slurry and Its Compnents with Time. C_o=10 mg/L, pH=5.8 to 6.5 Alum Dose-800 mg/L, PAC Dose-100 mg/L

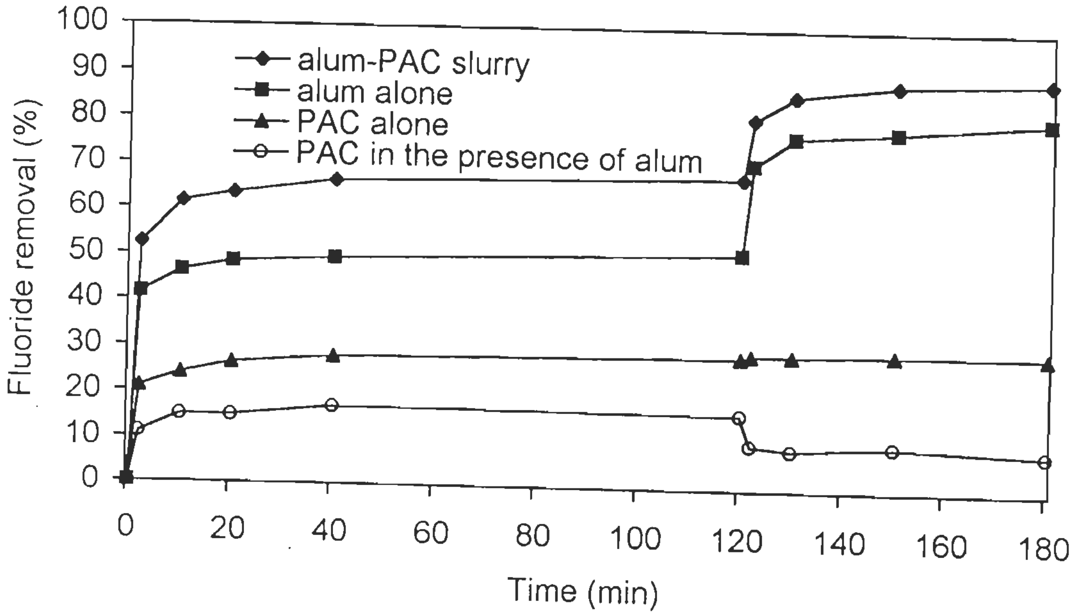


Fig. 4.18 Percentage of Fluoride Removal by Alum-PAC Slurry and Its Components with Time. C_o=10 mg/L, pH=5.8 to 6.5, Alum Dose-800 mg/L, PAC Dose-100 mg/L

Table 4.12 Variation of Fluoride Removal by Alum-PAC Slurry and Its Components with Time C_o=15 mg/L, Alum-800 mg/L PAC-100 mg/L, pH=5.8 to 6.5

Contact time(min)	Alum-PAC slurry		Alum alone		PAC alone		PAC in the presence of alum
	Residual fluoride concentration and percentage of removal						
	mg/L	%	mg/L	%	mg/L	%	%
0	15.00	0.0	15.00	0.0	15.00	0.0	0.0
2	7.75	48.3	10.20	32.0	12.40	17.3	16.3
10	6.70	55.3	9.25	38.3	12.05	19.7	17.0
20	6.50	56.7	9.05	39.7	11.80	21.3	17.0
40	6.40	57.3	8.95	40.3	11.70	22.0	17.0
120	6.25	58.3	8.80	41.3	11.60	22.7	17.0
122	2.30	84.7	3.90	74.0	11.55	23.0	10.7
130	1.65	89.0	3.60	76.0	11.55	23.0	13.0
150	1.50	90.0	3.50	76.7	11.50	23.3	13.3
180	1.40	90.7	3.45	77.0	11.50	23.3	13.7

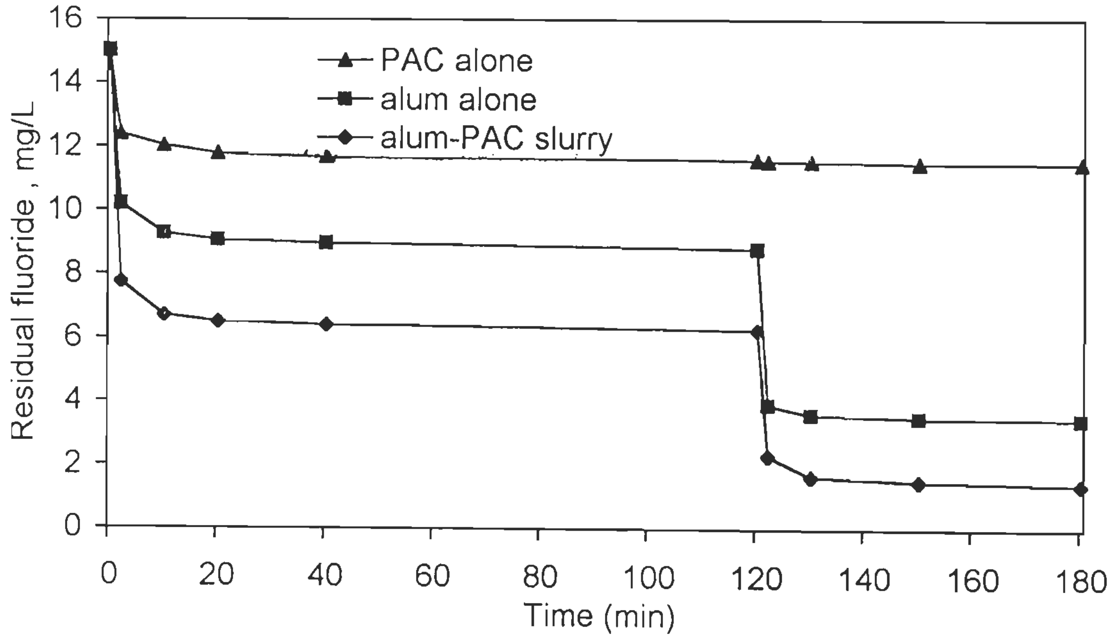


Fig. 4.19 Variation of Fluoride Removal by Alum-PAC Slurry and Its Components with Time. C_o=15 mg/L, pH=5.8 to 6.5 Alum Dose -800 mg/L, PAC Dose-100 mg/L

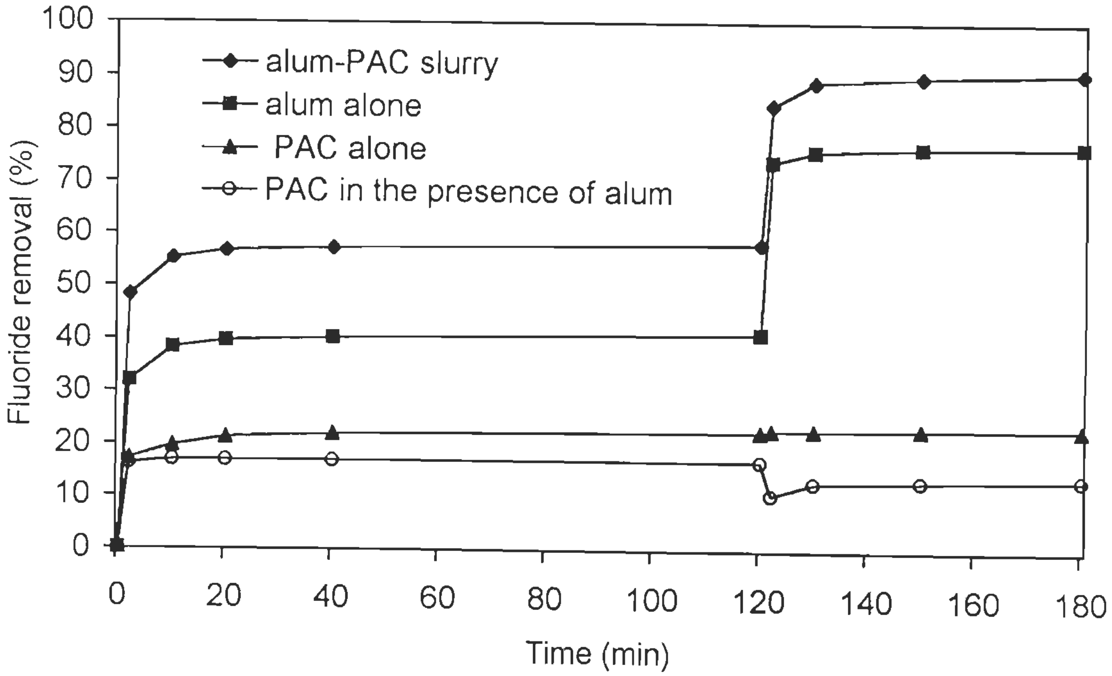


Fig. 4.20 Percentage of Fluoride Removal by Alum-PAC Slurry and Its Components with Time. C_o=15 mg/L, pH=5.8 to 6.5 Alum Dose-800 mg/L, PAC Dose-100 mg/L

Table 4.13 Variation of Fluoride Removal by Alum-PAC Slurry and Its Components with Time C_o=20 mg/L, Alum-800 mg/L PAC-100 mg/L, pH=5.8 to 6.5

Contact time(min)	Alum-PAC slurry		Alum alone		PAC alone		PAC in the presence of alum
	Residual fluoride concentration and percentage of removal						
	mg/L	%	mg/L	%	mg/L	%	%
0	20.00	0.0	20.00	0.0	20.00	0.0	0.0
2	10.05	49.8	12.40	38.0	17.60	12.0	11.8
10	9.45	52.8	11.60	42.0	16.30	18.5	10.8
20	9.20	54.0	11.45	42.8	15.90	20.5	11.2
40	9.10	54.5	11.35	43.2	15.75	21.2	11.3
120	9.05	54.8	11.20	44.0	15.60	22.0	10.8
122	3.90	80.5	5.70	71.5	15.60	22.0	9.0
130	3.45	82.8	5.40	73.0	15.55	22.2	9.8
150	3.35	83.3	5.25	73.8	15.55	22.2	9.5
180	3.30	83.5	5.15	74.2	15.50	22.5	9.3

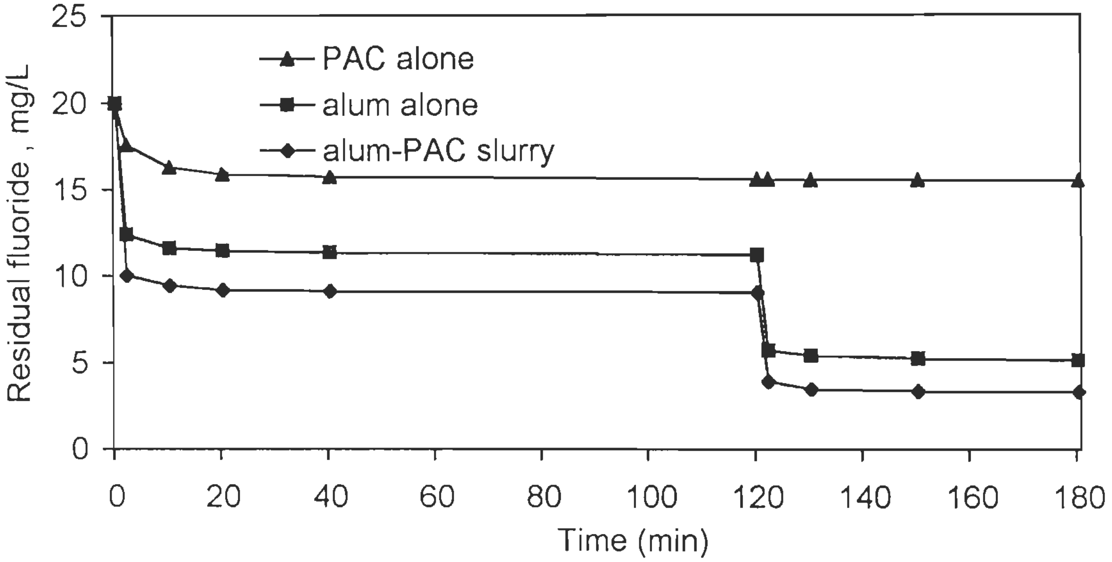


Fig. 4.21 Variation of Fluoride Removal by Alum-PAC Slurry and Its Compnents with Time. C_0=20 mg/L, pH=5.8 to 6.5
Alum Dose-800 mg/L, PAC Dose-100 mg/L

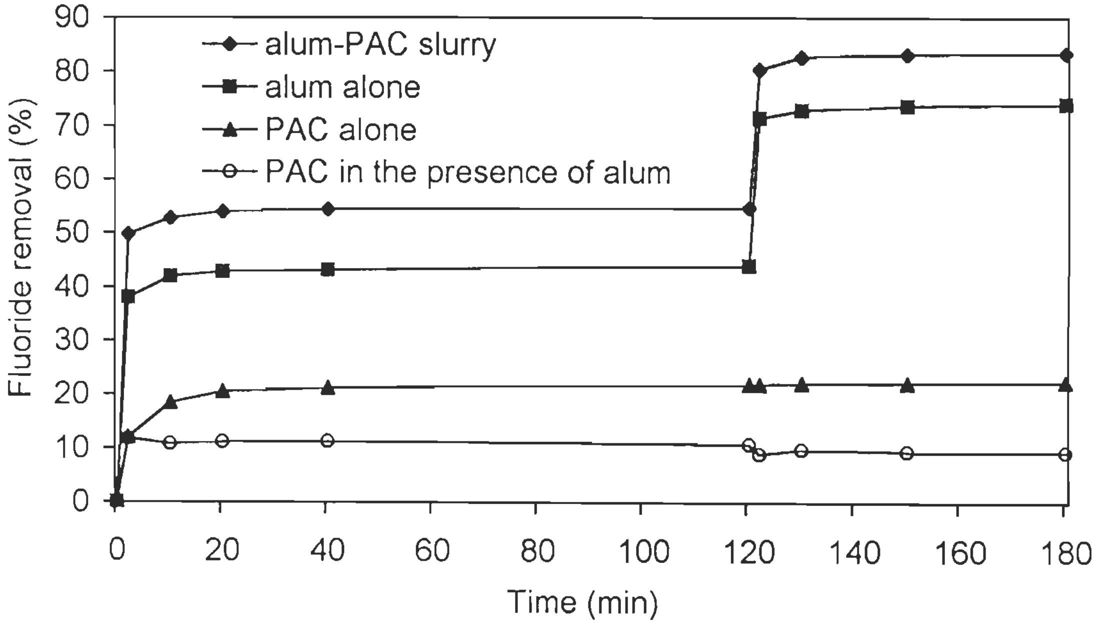


Fig. 4.22 Percentage of Fluoride Removal by Alum-PAC Slurry and Its Components with Time. C_0=20 mg/L, pH=5.8 to 6.5
Alum Dose-800 mg/L, PAC Dose-100 mg/L

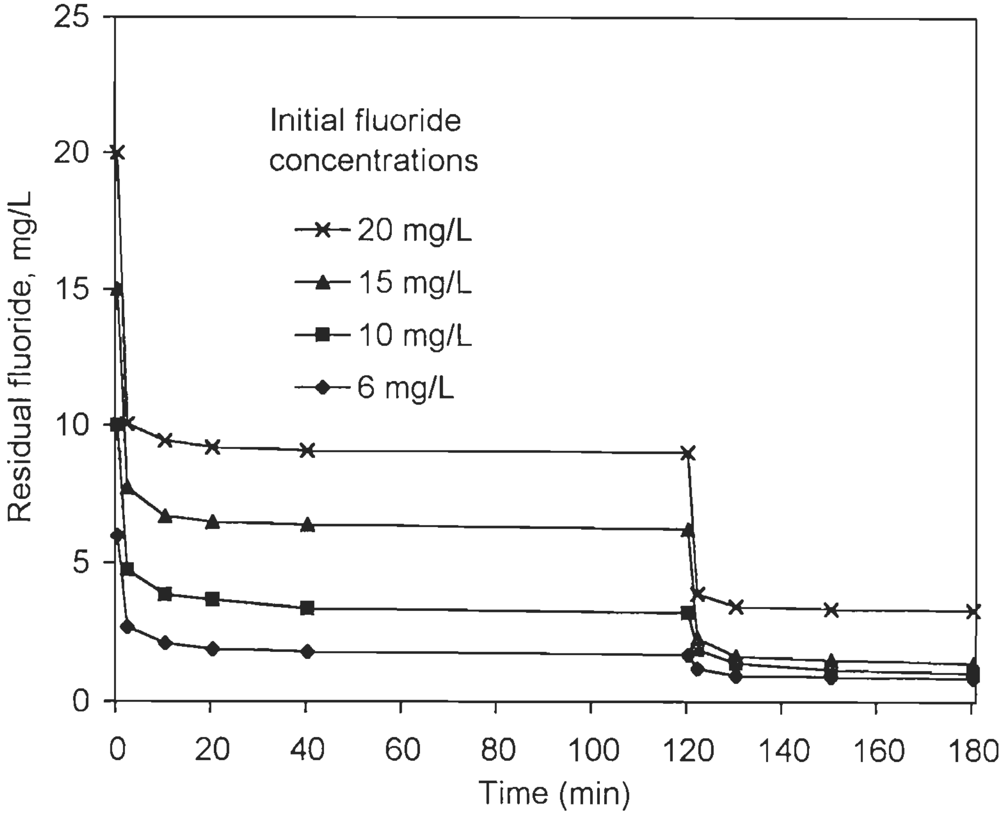


Fig. 4.23 Variation of Residual Fluoride with Time at Various Initial Fluoride Concentrations.
Alum Dose - 800 mg/L, PAC Dose -100 mg/L, pH=5.8 to 6.5

due to the addition of fresh alum which further increases the concentration gradient towards the water and consequently triggers desorption. Non-occurrence of this phenomenon in case of 400 mg/L alum dose of alum-PAC slurry (Figs. 4.24 - 4.29) where fresh alum was not added during the transition period (intermediate mixing) and in case of fluoride removal by PAC alone (Figs. 4.15 – 4.22) also support this suggestion. However, desorption decreased with increasing initial fluoride concentrations (Figs. 4.16, 4.18, 4.20, and 4.22) and PAC doses (Figs. 4.32, 4.34, and 4.36). This might be explained that the more the initial fluoride the higher is the residual equilibrium fluoride concentration available in the water at the end of rapid mixing (Fig. 4.23, 120th min) since the dose of alum added during this period was constant (400 mg/L). Hence this decreases the concentration gradient towards the water with increasing initial fluoride concentration which consequently lowers the desorption effect. Desorption of organics from GAC (granular activated carbon) bed due to reduction of its concentration in the influent was also reported (Voudrias et al., 1986; AWWA, 1990). On the other hand, PAC particles (aggregates) available in suspension during the slow mixing period (30 rpm) proportionally increases with increase of PAC doses. This enhances precipitation of aluminum hydroxide (fresh alum was added at this time) on which more fluoride would be adsorbed/complexed due to its seeding effect which compensates the desorption effect.

4.2.5.2 Fluoride Removal by Alum-PAC Slurry (Having Different Alum Doses) with Time

This investigation was carried out to study the effect of alum doses (400 to 900 mg/L) incorporated with 100 mg/L of PAC on fluoride removal in relation with the contact time and mixing condition and to verify the validity of the data for adsorption models. Experiments were conducted using water samples having initial fluoride concentrations of 10, 15, and 20 mg/L. The results are presented in Tables 4.14 – 4.16 and plotted in Figs. 4.24 – 4.29. This study once again showed that the trend of fluoride removal for rapid and slow mixing is the same as it was discussed previously in Section 4.2.5.1 for alum-PAC slurry having doses of 800 mg/L and 100 mg/L respectively. The removal of fluoride during the rapid mixing period for the given initial fluoride concentration was constant since the amount of alum and PAC in alum-PAC slurry added during this time were the same in all the cases (400 mg/L of alum and 100 mg/L of PAC). The excess amount of alum to the 400 mg/L was added during the intermediate mixing as described in Section 3.7.4 (Table 3.4). Hence, for specified initial fluoride concentrations the removal increased during slow mixing with increase of alum dose. However, at relatively higher alum doses with decreasing initial fluoride concentration the fluoride removal efficiency of alum relatively decreased with increase of dose. It is more evident from Fig. 4.11. This might be explained by the relatively low fluoride removal efficiency of alum at fluoride concentrations below 4 mg/L (Zabban and Helwick, 1975) since the equilibrium residual fluoride concentrations at the end of rapid mixing were in this order (Fig. 4.23 ,120th minutes). This is supported by the observations plotted in Fig.4.23 where residual fluoride concentrations at the end of rapid mixing period (120th min) decreased with decrease of initial fluoride concentrations (9.05, 6.25, 3.2, and 1.7 mg/L for initial fluoride concentrations of 20, 15, 10, and 6 mg/L respectively). Nevertheless, 400 mg/L of alum added during the intermediate mixing almost had the same effect in further reduction of fluoride (except for C_o=20 mg/L) irrespective of the residual fluoride concentrations at the end of rapid mixing time. Nawlakhe et al. (1974) and Culp and Stoltenberg (1958) also observed

Table 4.14 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time C$_o$=10 mg/L, PAC-100 mg/L, pH=5.8 to 6.5

Contact time(min)	Alum dose, mg/L											
	400		500		600		700		800		900	
	Residual fluoride concentration and percentage of removal											
	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%
0	10.00	0.0	10.00	0.0	10.00	0.0	10.00	0.0	10.00	0.0	10.00	0.0
2	4.80	52.0	4.80	52.0	4.80	52.0	4.80	52.0	4.80	52.0	4.80	52.0
10	3.90	61.0	3.90	61.0	3.90	61.0	3.90	61.0	3.90	61.0	3.90	61.0
20	3.60	64.0	3.60	64.0	3.60	64.0	3.60	64.0	3.60	64.0	3.60	64.0
40	3.40	66.0	3.40	66.0	3.40	66.0	3.40	66.0	3.40	66.0	3.40	66.0
120	3.15	68.5	3.15	68.5	3.15	68.5	3.15	68.5	3.15	68.5	3.15	68.5
122	3.10	69.0	2.30	77.0	1.90	81.0	1.70	83.0	1.40	86.0	1.15	88.5
130	3.05	69.5	1.95	80.5	1.50	85.0	1.40	86.0	1.15	88.5	0.90	91.0
150	3.00	70.0	1.90	81.0	1.35	86.5	1.30	87.0	1.15	88.5	0.85	91.5
180	2.90	71.0	1.80	82.0	1.30	87.0	1.25	87.5	1.05	89.5	0.80	92.0

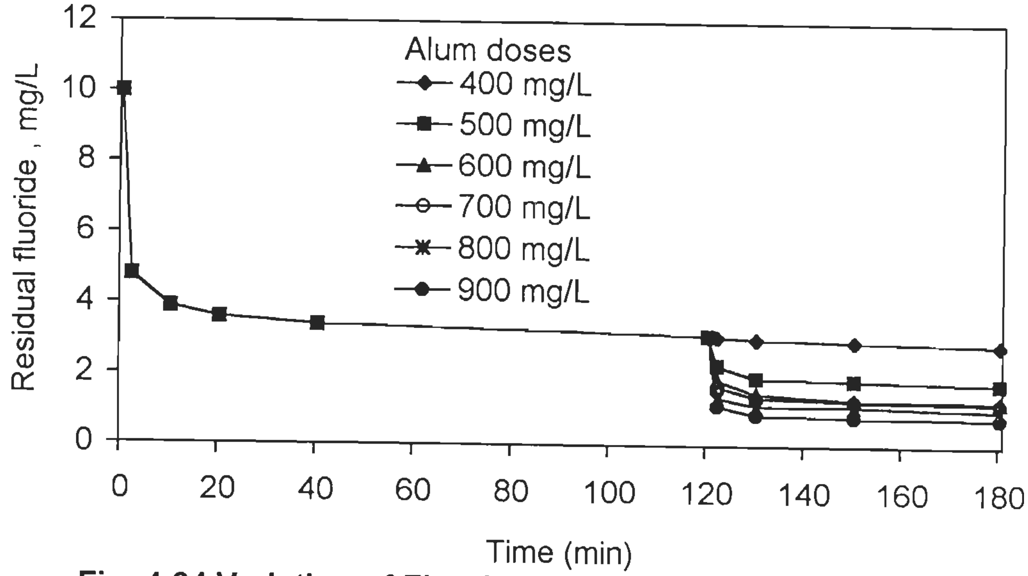


Fig. 4.24 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time.
C_o=10 mg/L, pH=5.8 to 6.5, PAC Dose-100 mg/L

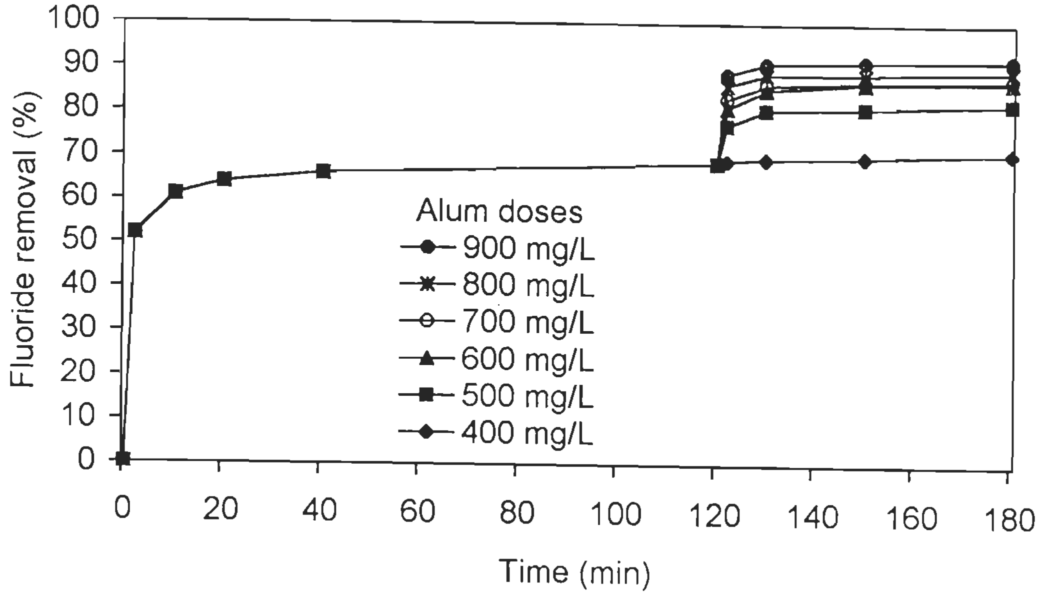


Fig. 4.25 Percentage of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time.
C_o=10 mg/L, pH=5.8 to 6.5, PAC Dose-100 mg/L

Table 4.15 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time C_o=15 mg/L, PAC-100 mg/L, pH=5.8 to 6.5

Contact time(min)	Alum dose, mg/L											
	400		500		600		700		800		900	
	Residual fluoride concentration and percentage of removal											
	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%
0	15.00	0.0	15.00	0.0	15.00	0.0	15.00	0.0	15.00	0.0	15.00	0.0
2	7.55	49.7	7.55	49.7	7.55	49.7	7.55	49.7	7.55	49.7	7.55	49.7
10	6.70	55.3	6.70	55.3	6.70	55.3	6.70	55.3	6.70	55.3	6.70	55.3
20	6.40	57.3	6.40	57.3	6.40	57.3	6.40	57.3	6.40	57.3	6.40	57.3
40	6.20	58.7	6.20	58.7	6.20	58.7	6.20	58.7	6.20	58.7	6.20	58.7
120	6.15	59.0	6.15	59.0	6.15	59.0	6.15	59.0	6.15	59.0	6.15	59.0
122	6.10	59.3	5.60	62.7	4.10	72.7	3.70	75.3	2.10	86.0	1.85	87.7
130	6.05	59.7	5.15	65.7	3.40	77.3	3.05	79.6	1.55	89.7	1.25	91.7
150	6.05	59.7	5.05	66.3	3.30	78.0	2.90	80.7	1.40	90.7	1.15	92.3
180	6.00	60.0	5.00	66.7	3.20	78.7	2.85	81.0	1.35	91.0	1.10	92.7

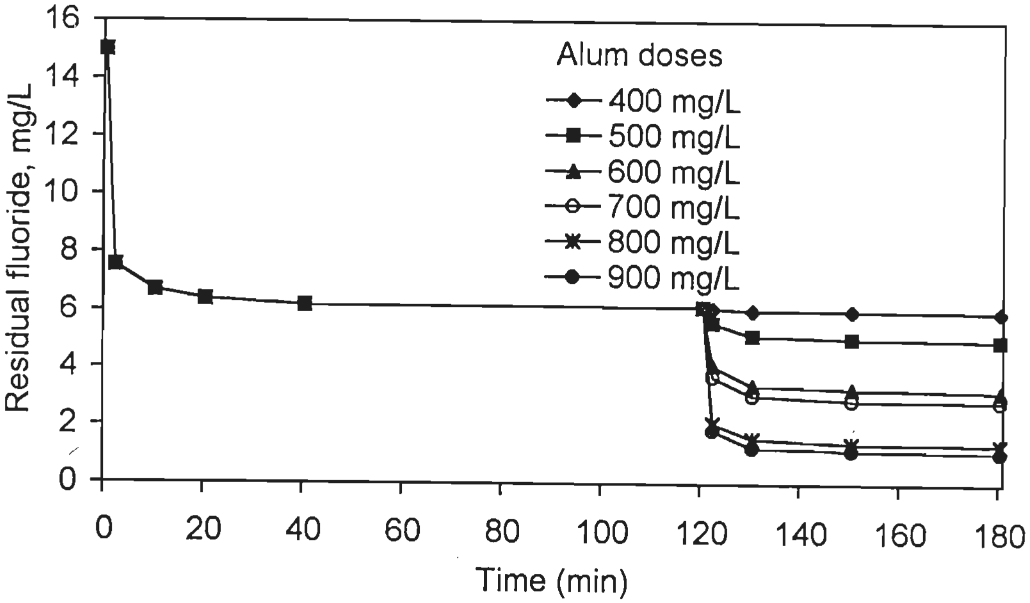


Fig. 4.26 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time.
C_o=15 mg/L, pH=5.8 to 6.5, PAC Dose-100 mg/L

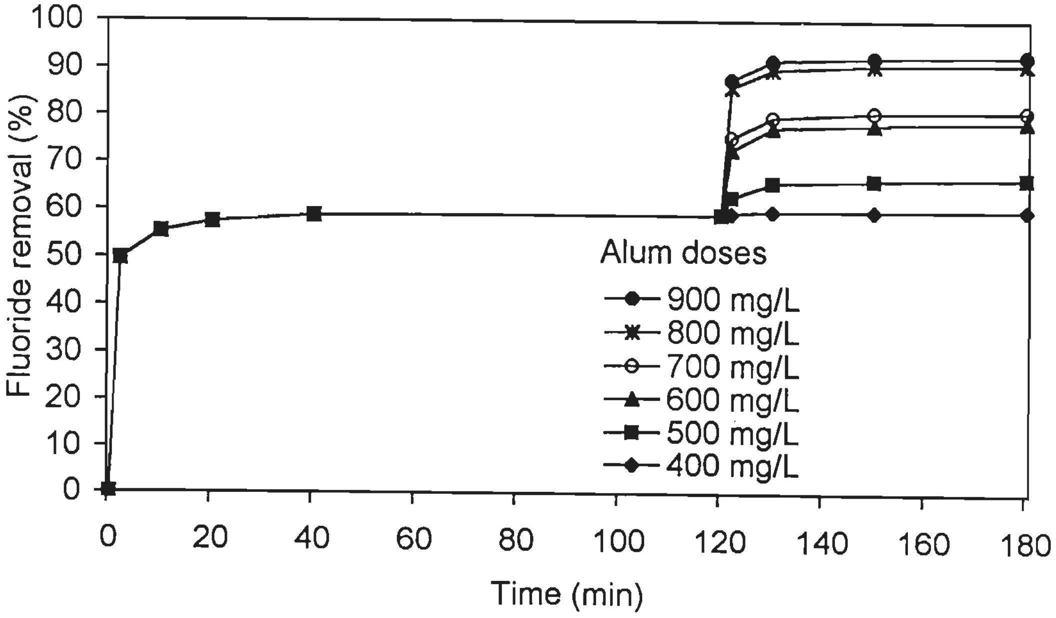


Fig. 4.27 Percentage of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time.
C_o=15 mg/L, pH=5.8 to 6.5, PAC Dose-100 mg/L

Table 4.16 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time C_o=20 mg/L, PAC-100 mg/L, pH=5.8 to 6.5

Contact time(min)	Alum dose, mg/L											
	400		500		600		700		800		900	
	Residual fluoride concentration and percentage of removal											
	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%
0	20.00	0.0	20.00	0.0	20.00	0.0	20.00	0.0	20.00	0.0	20.00	0.0
2	10.15	49.2	10.15	49.2	10.15	49.2	10.15	49.2	10.15	49.2	10.15	49.2
10	9.40	53.0	9.40	53.0	9.40	53.0	9.40	53.0	9.40	53.0	9.40	53.0
20	9.25	53.8	9.25	53.8	9.25	53.8	9.25	53.8	9.25	53.8	9.25	53.8
40	9.15	54.2	9.15	54.2	9.15	54.2	9.15	54.2	9.15	54.2	9.15	54.2
120	9.00	55.0	9.00	55.0	9.00	55.0	9.00	55.0	9.00	55.0	9.00	55.0
122	8.90	55.5	8.60	57.0	6.50	67.5	5.05	74.8	4.10	79.5	3.65	81.8
130	8.85	55.8	8.30	58.5	5.60	72.0	4.10	79.5	3.35	83.2	3.05	84.8
150	8.85	55.8	8.25	58.8	5.50	72.5	4.00	80.0	3.30	83.5	3.00	85.0
180	8.80	56.0	8.20	59.0	5.45	72.8	4.00	80.0	3.30	83.5	2.90	85.5

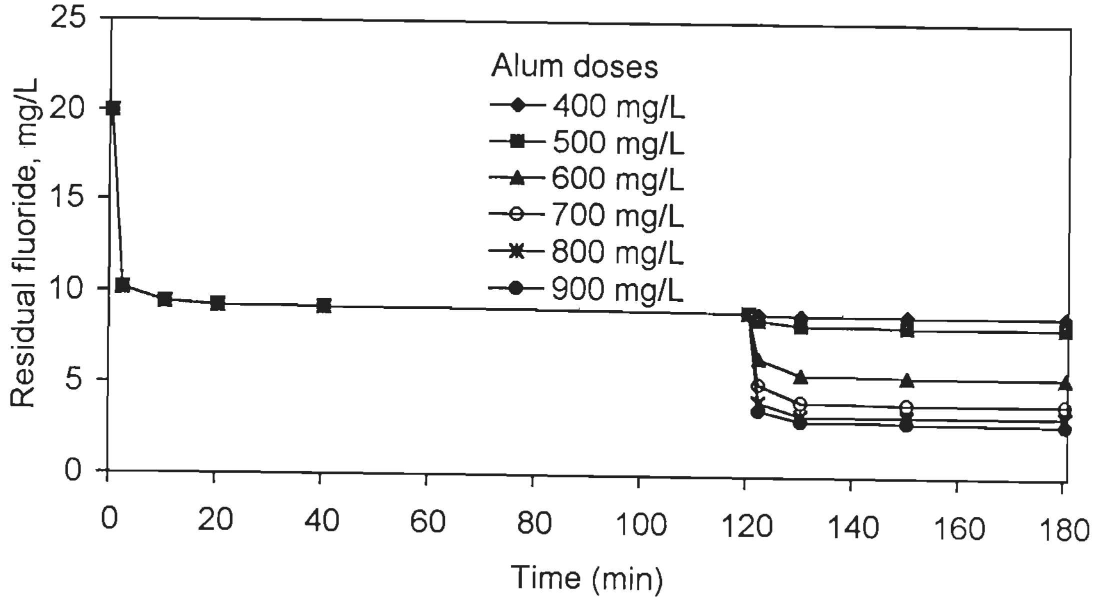


Fig. 4.28 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time.
C_o=20 mg/L, pH=5.8 to 6.5, PAC Dose-100 mg/L

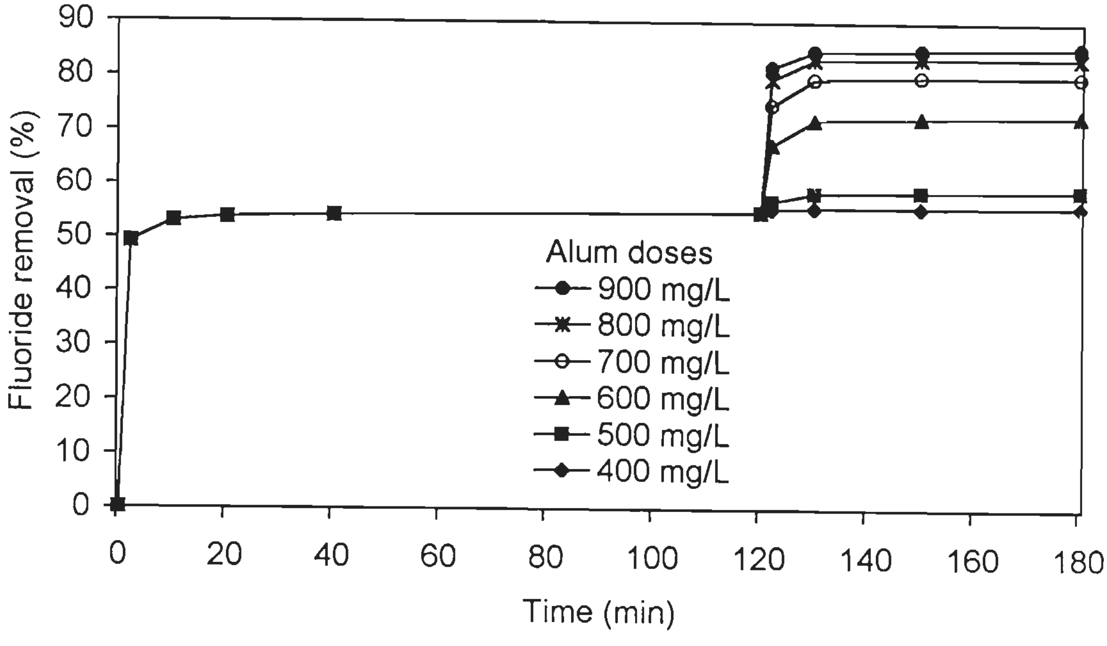


Fig. 4.29 Percentage of Fluoride Removal by Alum-PAC Slurry Having Different Doses of Alum with Time.
C_o=20 mg/L, pH=5.8 to 6.5, PAC Dose-100 mg/L

such phenomenon during defluoridation by alum alone. Depending on the initial fluoride concentration and the alum dose 8 to 80% of the fluoride remained in the water after rapid mixing was removed during the first 10 min of slow mixing.

Validity of these data to the available adsorption models (Langmuir, Freundlich, and BET) were attempted for fluoride removal by alum during slow mixing period (since alum dose was varying at this time). Alum (added during rapid mixing), lime, and PAC as discussed previously were not directly involved in fluoride removal during slow mixing period. Culp and Stoltenberg (1958) also observed that once precipitated alum floc has no further capacity in fluoride removal. Hence all fluoride removal after rapid mixing was assumed to be carried out by the alum added during intermediate mixing only. Based on this assumptions the following linearized form of adsorption equations were utilized for computation:

Langmuir equation:

$$1/q_e = 1/Q + 1/bQC \tag{4.1}$$

BET equation:

$$C/(C_s-C)q_e = 1/BQ + (B-1)C/BQC_s \tag{4.2}$$

Freundlich equation:

$$\log q_e = \log k + 1/n \log C \tag{4.3}$$

where q_e- concentration of fluoride removal per unit weight of alum as Al (III), mg F^-/mg Al(III)

C- concentration of fluoride at equilibrium in solution, mg F^-/L

Q- maximum concentration of fluoride removed per unit weight of alum [as Al(III)] in forming a complete monolayer, mg F^-/mg Al(III)

b- constant related to the enthalpy of adsorption,

Table 4.17 Langmuir Isotherm for Alum [as Al (III)]

C_o=10 mg/L

Alum dose (added during intermediate mixing) mg/L Al(III)	Residual fluoride concentration, mg/L		Fluoride removal during slow mixing mg/L	Fluoride removal per unit weight of alum mg F^-/ mg Al	b	Q
	At the end of rapid mixing	At the end of slow mixing (C_e)	(2)-(3)	(q_e)		
1	2	3	4	5	6	7
8.6	3.15	1.80	1.35	0.16	---	---
17.1	3.15	1.30	1.85	0.11	---	---
25.7	3.15	1.25	1.90	0.07	0.20	0.24
34.3	3.15	1.05	2.10	0.06	---	---
42.9	3.15	0.80	2.35	0.05	---	---

Note:

1) The data in column 1, 2 and 3 are brought from Table 3.4 (column 7) and Table 4.14 (residual fluoride at 120th and 180th minutes) respectively.
2) mg Al (III)/L =alum dose (mg/L) added during intermediate mixing (Table 3.4) for corresponding total doses divided by11.66 (concentration of alum with 16 water molecules in mg/L which contain 1 mg/L Al(III).
3) Ends of the rapid and slow mixing are 120th and 180th minutes respectively.

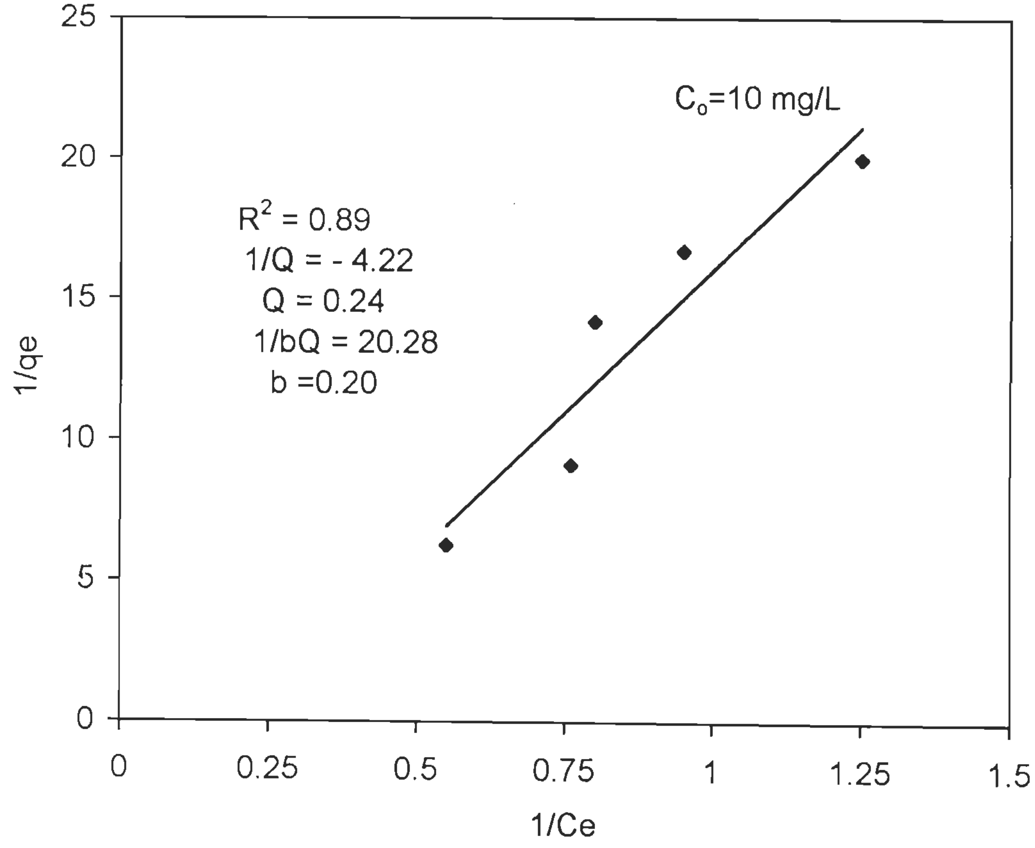


Fig. 4.30 Langmuir Adsorption Isotherm for Alum

C_s- the saturation concentration of fluoride, mg F^-/L

B- constant expressive of the energy of interaction with surface,

K, n-empirical constants.

Accordingly the data were plotted and by their conformity to a straight line the fitness of them to the given adsorption model was verified with a slope and intercept of 1/bQ and 1/Q; B-1/BQ and 1/BQ, and 1/n and log k for Langmuir, BET, and Freundlich equations respectively.

Thus, the data for initial fluoride concentration of 10 mg/L was found to conform more to Langmuir isotherm equation (Fig. 4.30) with correlation coefficient of 0.89. The values of b and Q were calculated to be 0.2 and 0.24 mg F^-/mg Al(III) respectively (Table 4.17). However, the data for initial fluoride concentrations of 15 and 20 mg/L were highly scattered and could not fit either to this or the other adsorption models. These observations indicate that fluoride removal by alum is not purely an adsorption process but in addition some other fluoride removal mechanisms (e.g. coprecipitation and/or complexation with hydroxylated aluminum) are also operating. However, more detail investigation is required to reach to conclusion. Nawlakhe et al. (1975) also reported that fluoride removal by alum is not a true case of adsorption and could not be described by adsorption models.

4.2.5.3 Fluoride Removal by Alum-PAC Slurry (Having Different PAC Doses) with Time

This investigation was carried out to study the effect of PAC doses (20 to 160 mg/L) incorporated with 800 mg/L of alum on fluoride removal in relation with the contact time and mixing condition and to verify the validity of the data for adsorption models. It was conducted at initial fluoride concentrations of 10, 15, and 20 mg/L. The results are presented in Tables 4.18 – 4.20 and plotted in Figs. 4.31 – 4.36. Assuming the PAC influence on fluoride removal characteristics of alum is insignificant, the share of each dose of PAC in the alum-PAC slurry for fluoride removal was found by subtracting the percentage removals when alum alone (Tables 4.11 – 4.13) was used from percentage removals when alum-PAC slurry with the given dose of PAC (Tables 4.18 – 4.20) was used for the same initial fluoride concentration. This contribution of PAC is also presented in the same tables and figures. Accordingly, the trend of fluoride removal remained the same (as it was discussed previously in Sections 4.2.5.1 and 4.2.5.2 for PAC dose of 100 mg/L) with more fluoride removal during the first 10 minutes of rapid and slow mixing periods. For all initial fluoride concentrations studied, fluoride removal during both periods was increasing with increase of PAC dose up to 100 mg/L, whereas the removal decreased with increase of PAC dose from 120 to 160 mg/L. This effect was particularly pronounced for rapid mixing period and initial fluoride concentrations of 10 and 15 mg/L. In most cases, small amount of fluorides appeared to have desorbed from PAC surface during the transition period. However, this phenomenon decreased with increase of initial fluoride concentrations and PAC doses. The same explanation as it was discussed in Section 4.2.5.1 could be given to these observations also.

To study the validity of the data for adsorption models, for each initial fluoride concentrations and PAC doses amount of fluoride removed during rapid mixing time by the PAC i.e. fluoride removal contribution by PAC in alum-PAC slurry (PAC removes fluoride during rapid mixing only) was found assuming the PAC influence on fluoride removal characteristics of alum is insignificant. It was found by subtracting the residual fluoride at the end of rapid mixing time (120th min) when alum alone(Tables 4.11- 4.13)

Table 4.18 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of PAC with Time

C_o=10 mg/L, Alum-800 mg/L, pH=5.8 to 6.5

Contac time (min)	PAC dose, mg/L																	
	20			60			100			120			140			160		
	Residual fluoride concentration and percentage of removal																	
	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC
0	10.00	0.0	0.0	10.00	0.0	0.0	10.00	0.0	0.0	10.00	0.0	0.0	10.00	0.0	0.0	10.00	0.0	0.0
2	4.75	53.0	11.5	4.40	56.0	14.5	4.15	58.5	17.0	4.20	58.0	16.5	4.25	57.5	16.0	4.55	54.5	13.0
10	4.15	58.5	12.0	3.90	61.0	14.5	3.70	63.0	16.5	3.85	61.5	15.0	3.95	60.5	14.0	4.30	57.0	10.5
20	4.05	59.5	11.0	3.75	62.5	14.0	3.55	64.5	16.0	3.70	63.0	14.5	3.80	62.0	13.5	4.15	58.5	10.0
40	3.95	60.5	11.0	3.65	63.5	14.0	3.40	66.0	16.5	3.60	64.0	14.5	3.75	62.5	12.0	4.05	59.5	10.0
120	3.85	61.5	10.0	3.55	64.5	13.0	3.35	66.5	15.0	3.55	64.5	13.0	3.75	62.5	11.0	3.95	60.5	9.0
122	2.60	74.0	3.0	2.30	77.0	6.0	2.15	78.5	7.5	2.25	77.5	6.5	2.35	76.5	5.5	2.45	75.5	4.5
130	2.25	77.5	3.5	1.70	83.0	6.0	1.40	86.0	9.0	1.45	85.5	8.5	1.40	86.0	9.0	1.70	83.0	6.0
150	2.10	79.0	4.0	1.50	85.0	5.5	1.25	87.5	9.0	1.20	88.0	9.5	1.25	87.5	9.0	1.55	84.5	6.0
180	1.70	83.0	2.0	1.45	85.5	4.5	1.15	88.5	7.5	1.10	89.0	8.0	1.20	88.0	7.0	1.35	86.5	5.5

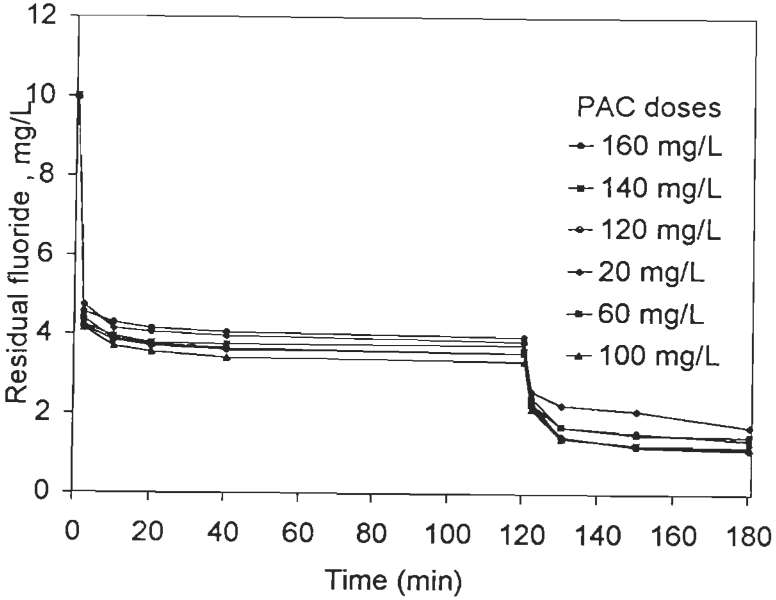


Fig. 4.31 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of PAC with Time. C_o=10 mg/L, pH=5.8 to 6.5, Alum Dose-800 mg/L

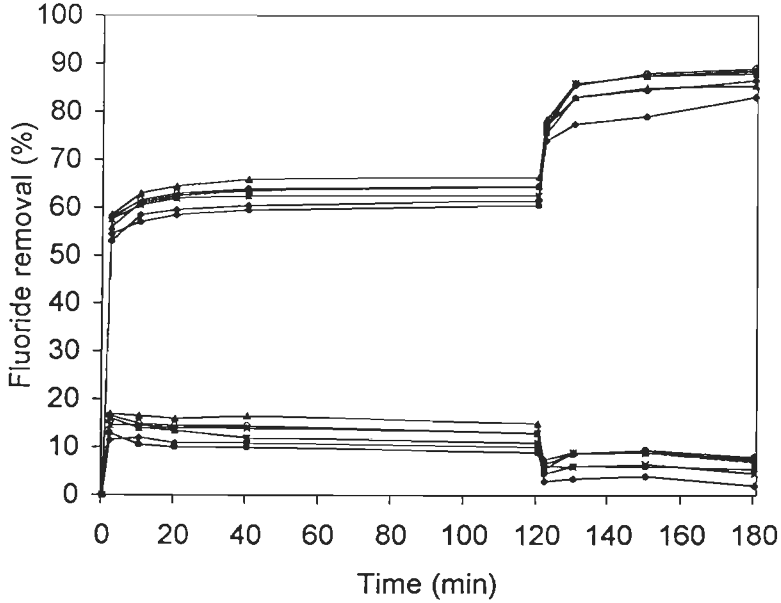


Fig. 4.32 Percentage Fluoride Removal by (i) Alum PAC Slurry Having Different Doses of PAC and 800 mg/L of Alum (Upper Set of Curves), and (ii) Different Doses of PAC in the Presence of 800 mg/L of Alum (Lower Set of Curves) with Time. C_o=10 mg/L, pH=5.8 to 6.5

Table 4.19 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of PAC with Time

C_o=15 mg/L, Alum-800 mg/L, pH=5.8 to 6.5

Contact time (min)	PAC dose, mg/L																	
	20			60			100			120			140			160		
	Residual fluoride concentration and percentage of removal																	
	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC
0	15.00	0.0	0.0	15.00	0.0	0.0	15.00	0.0	0.0	15.00	0.0	0.0	15.00	0.0	0.0	15.00	0.0	0.0
2	8.05	46.3	14.3	7.85	47.7	15.7	7.60	49.3	17.3	8.35	44.3	12.3	9.30	38.0	6.0	10.55	29.7	---
10	7.10	52.7	14.3	6.90	54.0	15.7	6.80	54.7	16.3	7.40	50.7	12.3	8.40	44.0	5.6	9.60	36.0	---
20	6.95	53.7	14.0	6.60	56.0	16.3	6.45	57.0	17.3	7.25	51.7	12.0	8.20	45.3	5.6	9.25	38.3	---
40	6.70	55.3	15.0	6.35	57.7	17.3	6.15	59.0	18.7	7.10	52.7	12.3	8.05	46.3	6.0	9.00	40.0	---
120	6.60	56.0	14.7	6.30	58.0	16.7	6.05	59.7	18.3	7.00	53.3	12.0	7.90	47.3	6.0	8.95	40.3	---
122	3.40	77.3	3.3	2.50	83.3	9.3	2.05	86.3	12.3	2.35	84.3	10.3	2.65	82.3	8.3	3.05	79.7	5.7
130	3.05	79.7	3.7	2.10	86.0	10.0	1.60	89.3	13.3	1.80	88.0	12.0	1.90	87.3	11.3	2.55	83.0	7.0
150	3.00	80.0	3.3	2.00	86.7	10.0	1.45	90.3	13.7	1.60	89.3	12.7	1.55	89.7	13.0	2.20	85.3	8.7
180	3.00	80.0	3.0	1.90	87.3	10.3	1.40	90.7	13.7	1.55	89.7	12.7	1.50	90.0	13.0	2.10	86.0	9.0

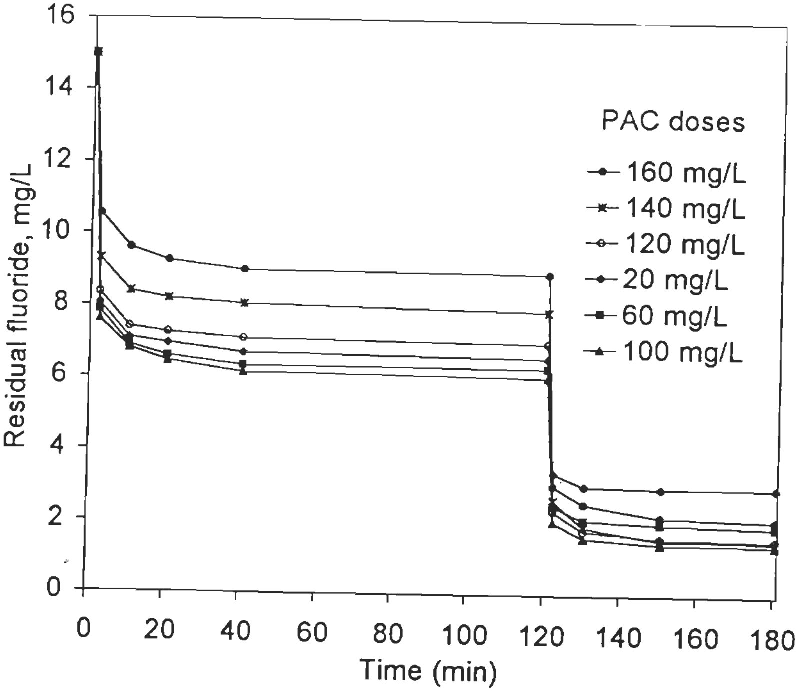


Fig. 4.33 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of PAC with Time. C_o=15 mg/L, pH=5.8 to 6.5, Alum Dose-800 mg/L

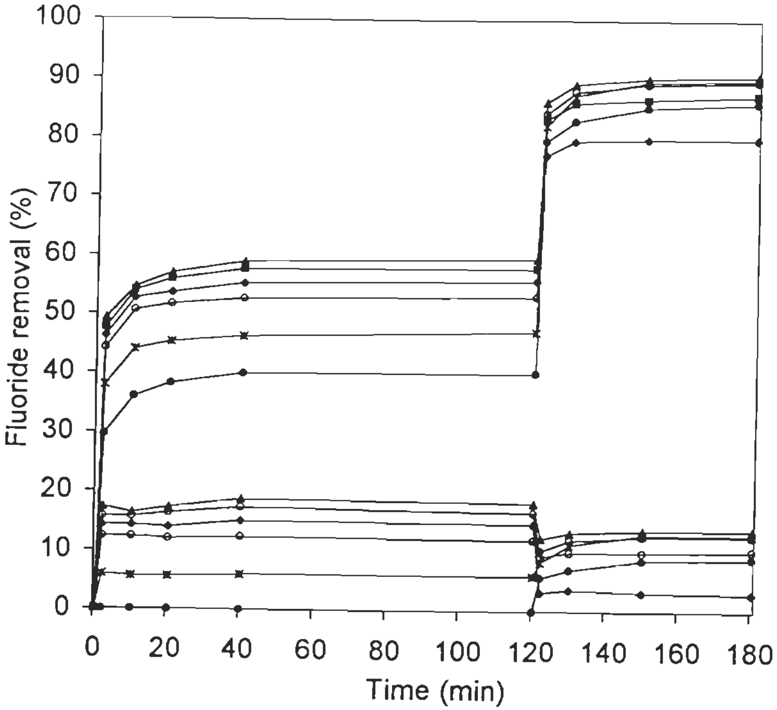


Fig. 4.34 Percentage Fluoride Removal by (i) Alum-PAC Slurry Having Different Doses of PAC and 800 mg/L of Alum (Upper Set of Curves), and (ii) Different Dose of PAC in the Presence of 800 mg/L of Alum (Lower Set of Curves) with Time. C_o=15 mg/L, pH=5.8 to 6.5

Table 4.20 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of PAC with Time

C_o=20 mg/L, Alum-800 mg/L, pH=5.8 to 6.5

Contact time (min)	PAC dose, mg/L																	
	20			60			100			120			140			160		
	Residual fluoride concentration and percentage of removal																	
	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC	mg/L	% remov. by the slurry	% removed by the PAC
0	20.00	0.0	0.0	20.00	0.0	0.0	20.00	0.0	0.0	20.00	0.0	0.0	20.00	0.0	0.0	20.00	0.0	0.0
2	12.50	37.5	------	11.30	43.5	5.5	10.65	46.8	8.8	11.05	44.7	6.8	11.20	44.0	6.0	11.15	44.2	6.2
10	11.05	44.8	2.8	10.15	49.2	7.2	9.45	52.8	10.8	9.80	51.0	9.0	9.80	51.0	9.0	10.20	49.0	9.0
20	10.65	46.8	4.0	9.80	51.0	8.2	9.15	54.2	11.5	9.55	52.2	9.5	9.65	51.8	9.0	9.85	50.8	6.5
40	10.50	47.5	4.2	9.60	52.0	8.8	9.00	55.0	11.8	9.40	53.0	9.8	9.55	52.2	9.0	9.65	51.8	5.0
120	10.50	47.5	3.5	9.55	52.2	8.2	8.90	55.5	11.5	9.30	53.5	9.5	9.50	52.5	8.5	9.60	52.0	4.0
122	5.20	74.0	2.5	4.60	77.0	5.5	4.30	78.5	7.0	4.50	77.5	6.0	4.65	76.8	5.2	4.70	76.5	5.0
130	4.40	78.0	5.0	3.70	81.5	8.5	3.40	83.0	10.0	3.60	82.0	9.0	3.55	82.2	9.2	3.45	82.8	9.8
150	4.25	78.8	5.0	3.55	82.2	8.5	3.35	83.2	9.5	3.50	82.5	8.8	3.40	83.0	9.2	3.35	83.2	9.5
180	4.20	79.0	4.8	3.50	82.5	8.2	3.35	83.2	9.0	3.40	83.0	8.8	3.40	83.0	9.2	3.30	83.5	9.2

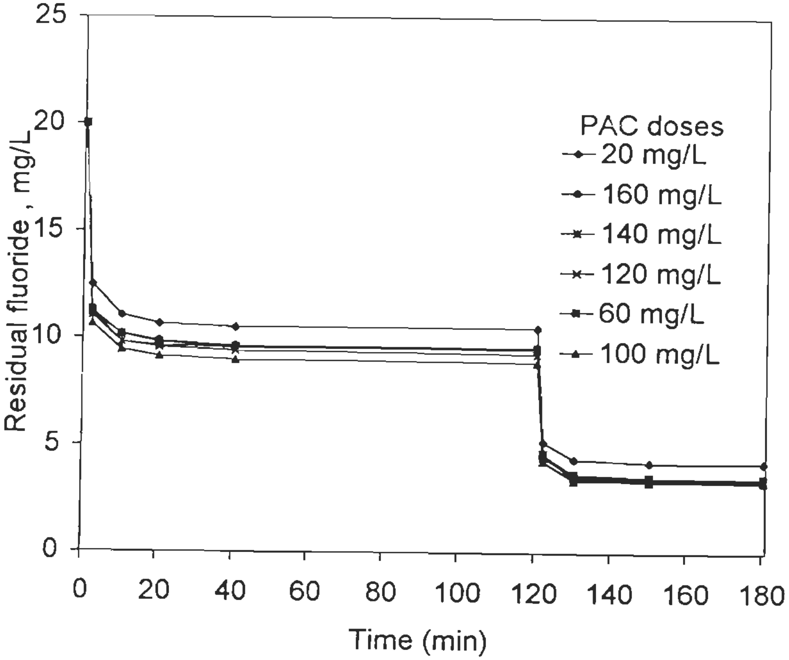


Fig. 4.35 Variation of Fluoride Removal by Alum-PAC Slurry Having Different Doses of PAC with Time. C_o=20 mg/L, pH=5.8 to 6.5, Alum Dose-800 mg/L

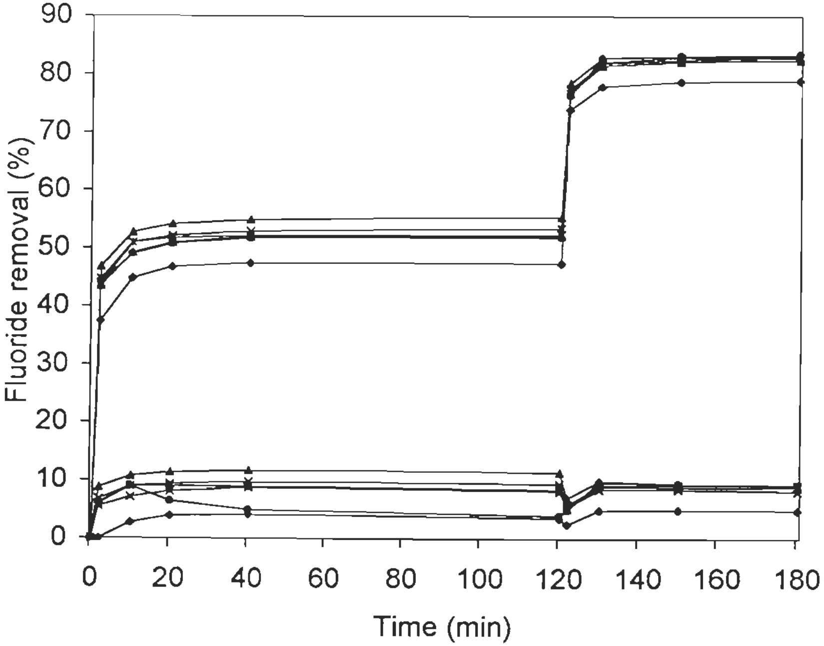


Fig. 4.36 Percentage Fluoride Removal by (i) Alum-PAC Slurry Having Different Doses of PAC and 800 mg/L of Alum (Upper Set of Curves), and (ii) Different Doses of PAC in the Presence of 800 mg/L of Alum (Lower Set of Curves) with Time. C_o=20 mg/L, pH=5.8 to 6.5

Table 4.21 Amount of Fluoride Removed by the PAC in the Presence of Alum

PAC dose mg/L	Residual fluoride concent. at the end of rapid mixing, mg/L		Fluoride removed by the PAC	Fluoride removed per mg of PAC mg F^-/mg (q_e)
	During removal by alum alone	During removal by alum-PAC slurry		
(1)	(2)	(3)	(4)	(5)
C_o=10 mg/L				
20	4.85	3.85	1.00	0.05
60	4.85	3.55	1.30	0.02
100	4.85	3.35	1.50	0.015
120	4.85	3.55	1.30	0.01
140	4.85	3.75	1.10	0.008
160	4.85	3.95	0.90	0.006
C_o=15 mg/L				
20	8.80	6.60	2.20	0.11
60	8.80	6.30	2.50	0.04
100	8.80	6.05	2.75	0.03
120	8.80	7.00	1.80	0.015
140	8.80	7.90	0.90	0.006
160	8.80	8.95	---	---
C_o=20 mg/L				
20	11.20	10.50	0.70	0.04
60	11.20	9.55	1.65	0.03
100	11.20	8.90	2.30	0.02
120	11.20	9.30	1.90	0.015
140	11.20	9.50	1.70	0.01
160	11.20	9.60	0.80	0.005

Note: 1) The data in column 2 and 3 are brought from Tables 4.11-13 and Tables 4.18-20 respectively.

2) Fluoride removed by the PAC (4) is calculated as the difference of residual fluoride during removal by alum (2) and alum-PAC slurry (3).

was used from residual fluoride for the same contact time when alum-PAC slurry with the given dose of PAC (Tables 4.18 – 4.20) was used. These data are presented in Table 4.21. Thus, as discussed previously in Section 4.2.5.2, validity of the data for the three isotherm equations were attempted. The data are highly scattered and could not fit any of the adsorption models. This might be because (i) in the presence of alum in addition to fluoride removal by direct adsorption on the surface of the PAC, adsorption/complexation of fluoride by alum coated on the surface of the PAC took place which deviated the mechanism of fluoride removal from pure adsorption, and/or (ii) as described previously (Section 4.2.3), the coagulation (aggregation) of PAC particles by alum which reduce the adsorption surface area with increase of PAC dose could scatter the data, although, the removal mechanism is adsorption.

4.2.6 Effect of Water Quality Parameters on Fluoride Removal

These experiments were performed to investigate effects of some selected constituents, which may either be naturally present in water or added/produced during the defluoridation and/or denitrification on fluoride removal by alum-PAC slurry. The parameters studied were phosphate, silica, sulfate, nitrate, chloride, alkalinity, and organic matter. Except alkalinity and organic matter, all the other parameters were studied both in the optimum pH range (5.8 to 6.5) and in the pH range of 4 to 9.5 to assess their effect at various pH, since they can affect the optimum pH of coagulation by alum (Letterman and Vanderbook, 1983). The experiments were conducted according to the optimum operation procedure using 800 mg/L of alum and 100 mg/L of PAC doses at an initial fluoride concentration of 15 mg/L. Details of the experimental procedure are given in Section 3.7.7.

4.2.6.1 Effect of Phosphate

Orthophosphate is the predominant form of phosphorous in the aquatic environment. It is also added into the water at preceding denitrification stage as a nutrient. Study was conducted to assess its effect on fluoride removal in the optimum pH range of 5.8 to 6.5 and in the pH range of 4 to 9.5. Concentrations of phosphate in the range of 0 (control) to 10 mg/L (as PO_4^{3-}-P) were studied in the optimum pH range (5.8 to 6.5), whereas the effect of phosphate in the pH range of 4 to 9.5 was studied at a phosphate concentration of 10 mg/L. The high concentration range of phosphorous was fixed taking into account the possible leakage of phosphate from the denitrifying reactor at the preceding treatment stage. The results are presented in Tables 4.22 and 4.23 and plotted in Figs. 4.37 and 4.38. For comparison the data of the control (without phosphate) is also plotted in Fig. 4.38.

Residual fluoride in the treated water increased with increase of phosphate. At 8 to 10 mg/L of phosphate, the residual fluoride increased by 24.1% compared to the control. Stumm and Morgan (1962) and Letterman Vanderbook (1983) have reported that phosphate has more affinity to aluminum than fluoride does. This competition of phosphate with fluoride for aluminum most probably resulted in formation of insoluble precipitate of $AlPO_4$ and in turn it adversely affected defluoridation. However, Nawlakhe and Bulusu (1978) did not observe this effect in their study with polyphosphates up to 5 mg/L using test water with 5.1 mg/L of fluoride in case of fluoride removal by alum alone. The study on effect of phosphate on fluoride removal in the pH range of 4 to 9.5 (Fig.4.38) showed slight increase of residual fluoride in the pH range of 5.5 to 7.5 compared to the control. This range of pH coincided with the optimum pH range for phosphate removal by alum (Hsu, 1975). This indicates that competition of phosphate for aluminum attributed to the adverse effect.

Table 4.22 Effect of Various Water Quality Parameters on Fluoride Removal by Alum-PAC Slurry

C_o=15 mg/L, Alum-800 mg/L, PAC-100 mg/L, pH=5.8 to 6.5

Phosphate		Silica		Sulfate		Nitrate		Chloride		Total alkalinity		Organic matter (ethanol)		
Concent. mg PO_4^{3-}-p/L	resid. fluoride mg/L	concent. mg SiO_2/L	resid. fluoride mg/L	concent. mgSO_4^{2-}/L	resid. fluoride mg/L	concent. mg NO_3^--N/L	resid. fluoride mg/L	concent. mg Cl^-/L	resid. fluoride mg/L	concent. mg/L as $CaCO_3$	resid. fluoride mg/L	concent. mg COD/L	resid. fluoride mg/L	resid. COD mg/L
0	1.45	0	1.40	380	1.55	0	1.50	26	1.40	150	9.30	0	1.45	0
2	1.45	10	1.50	480	1.40	25	1.45	126	1.45	300	5.40	26	1.50	0
4	1.65	20	1.65	580	1.45	50	1.45	226	1.45	400	1.45	52	1.45	15
6	1.75	30	1.85	680	1.45	100	1.55	326	1.45	500	1.50	78	1.50	46
8	1.80	40	2.10	780	1.40	150	1.40	426	1.40	600	2.70	104	1.55	66
10	1.80	60	2.45	980	1.45	250	1.50	626	1.40	850	3.10	130	1.50	92

Table 4.23 Effect of Water Quality Parameters on Fluoride Removal by Alum-PAC Slurry at Various pH

C_o=15 mg/L, Alum-800 mg/L, PAC-100 mg/L

pH	Control (without additives)	Phosphate		Silica		Sulfate		Nitrate		Chloride	
	resid. fluoride mg/L	concent. mg PO_4^{3-}-P/L	resid. fluoride mg/L	concent. mg SiO_2/L	resid. fluoride mg/L	concent. mg SO_4^{2-}/L	resid. fluoride mg/L	concent. mg NO_3^--N/L	resid. fluoride mg/L	concent. mg Cl^-/L	resid. fluoride mg/L
4.00	10.50	10	10.60	60	10.15	980	10.40	250	10.60	626	10.55
4.50	9.55	10	9.55	60	9.10	980	9.45	250	9.50	626	9.60
5.00	5.50	10	5.60	60	5.75	980	5.50	250	5.45	626	5.55
5.50	3.00	10	3.35	60	3.90	980	3.10	250	3.00	626	3.05
6.00	1.50	10	1.80	60	2.40	980	1.45	250	1.50	626	1.50
6.50	1.65	10	1.95	60	2.45	980	1.55	250	1.70	626	1.55
7.50	5.10	10	5.25	60	5.60	980	5.15	250	5.05	626	5.10
8.00	6.85	10	6.90	60	7.15	980	6.90	250	6.80	626	6.80
9.50	9.20	10	9.15	60	9.50	980	9.20	250	9.20	626	9.25

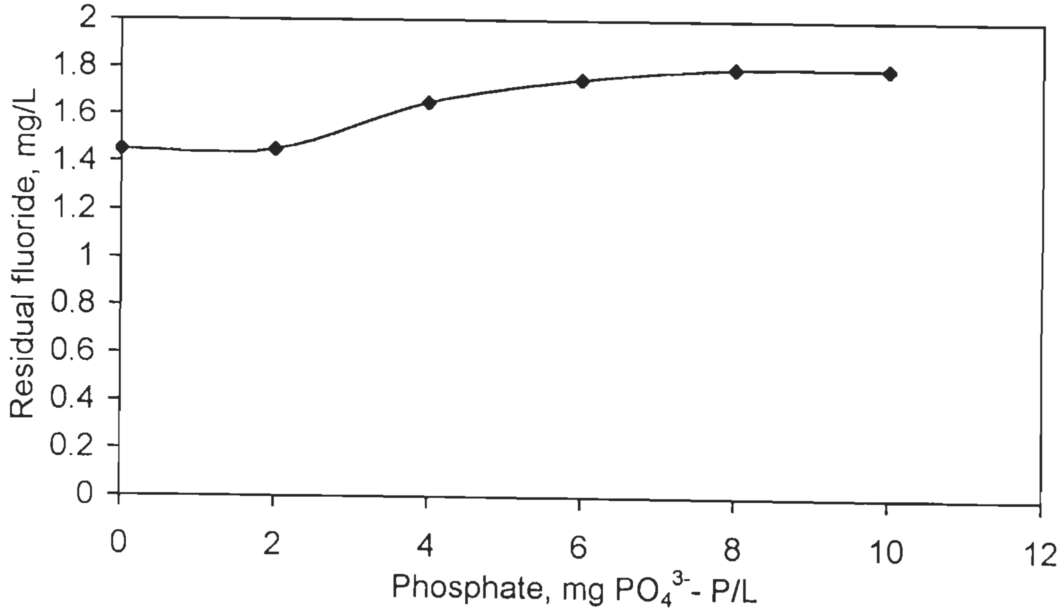


Fig. 4.37 Effect of Phosphate on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, pH=5.8 to 6.5 Alum Dose-800 mg/L, PAC Dose-100 mg/L

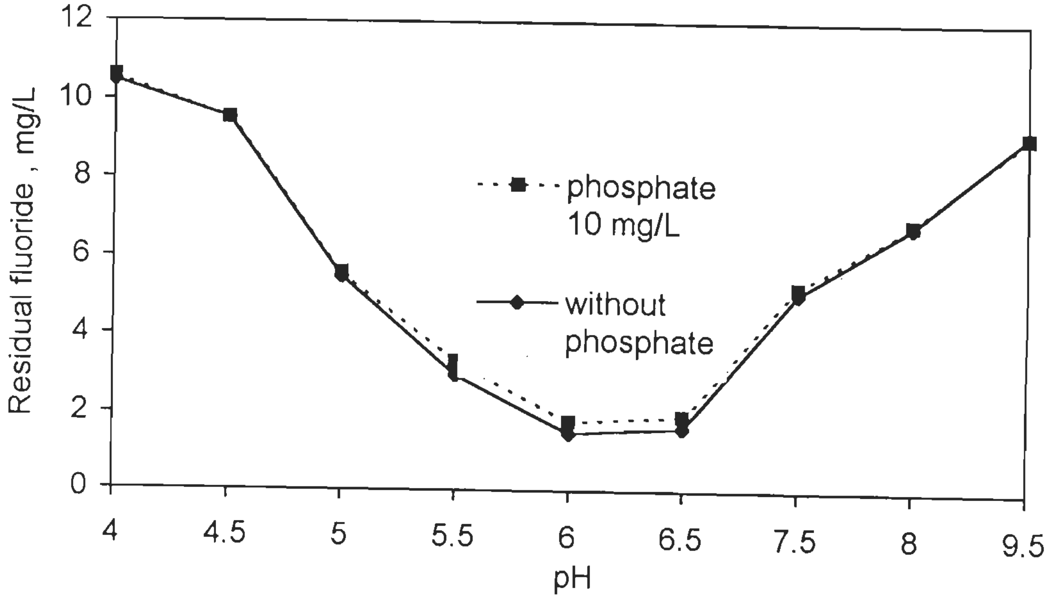


Fig. 4.38 Effect of Phosphate on Fluoride Removal by Alum-PAC Slurry at Various pH. C_o=15mg/L Alum Dose-800 mg/L, PAC Dose-100 mg/L

4.2.6.2 Effect of Silica

Concentration of silica in natural waters commonly range from 1 to 30 mg/L. However, concentrations up to 363 mg/L have been found in groundwater (Bodek, et al., 1988). To facilitate the comparison of results, silica concentrations ranging from 0 (control) to 60 mg/L were studied in the optimum pH range (5.8 to 6.5), whereas the effect of silica on fluoride removal in the pH range of 4 to 9.5 was studied only at concentration of 60 mg/L. The results are presented in Tables 4.22 and 4.23 and plotted in Figs. 4.39 and 4.40. For comparison the data of the control (without silica) is also plotted in Fig. 4.40.

Almost linear increase of residual fluoride in treated water with increase of silica was observed. At 60 mg/L of silica, the residual fluoride increased by 75% compared to the control. Adverse effect of silica on fluoride removal by alum alone was also observed by Nawlakhe and Bulusu (1978) in their study on water sample with 5.1 mg/L of fluoride and with silica concentration in the same range (0 to 60 mg/L). The study on effect of silica on fluoride removal in the pH range of 4 to 9.5 (Fig. 4.40) showed that in the presence of 60 mg/L of silica, at lower pH (4 to 4.5), fluoride removal improved by 7.8 to 8.2% compared to the control. Whereas, at pH more than 5 it decreased by 2.6 to 6.7%, the maximum being at pH 6. Zabban and Helwick (1975) suggested that removal of fluoride by alum was due to the formation of hydroxylated aluminum complex precipitate with fluoride or adsorption to the aluminum hydroxide precipitate. At pH of more than 5, the formation of aluminum hydroxide precipitate was affected by the presence of silica. Silica has been reported to enhance precipitation of aluminum as poorly crystallized mineral species: $Al_2SiO_5(OH)_4$ (Bodek et al., 1988) which had been normally fully formed as aluminum hydroxide precipitate at these pH

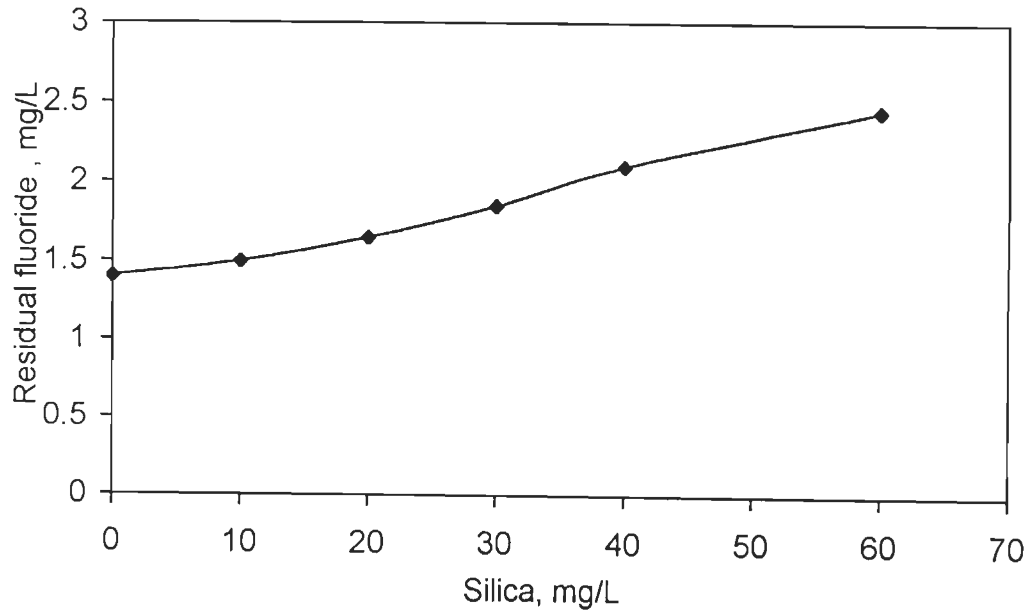


Fig. 4.39 Effect of Silica on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, pH=5.8 to 6.5 Alum Dose-800 mg/L, PAC Dose-100 mg/L

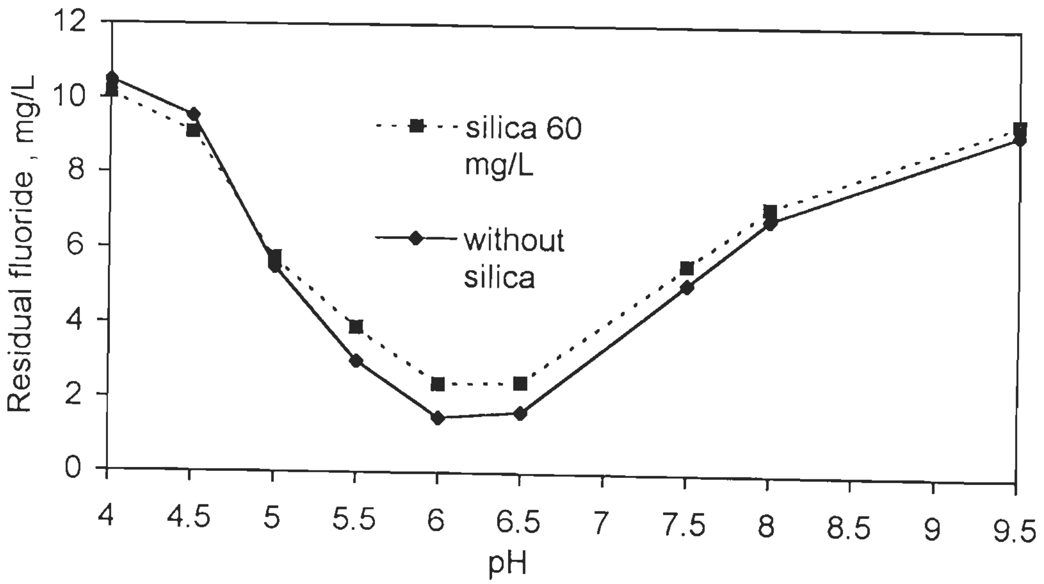


Fig. 4. 40 Effect of Silica on Fluoride Removal by Alum-PAC Slurry at Various pH. C_o=15 mg/L Alum Dose-800 mg/L, PAC Dose-100 mg/L

(more than 5) without silica (Hundt and O' melia, 1988). Moreover, like phosphate silica too has more affinity to aluminum than fluoride does (Letterman and Vanderbook, 1983). Hence, this may also retard the complexation/adsorption of fluoride on aluminum hydroxide precipitates at pH more than 5, whereas at low pH (less than 5) where normally aluminum hydroxide precipitate formation is relatively insignificant, the removal of fluoride might have been improved due to complexation of fluoride in the structure of alum-silica species [$(Al_2SiO_5(OH)_4$] by replacing hydroxide ions (Sherwin and Weston, 1966) which otherwise was left in solution.

4.2.6.3 Effects of Sulfate, Nitrate, and Chloride

Taking into account the concentrations of sulfate, nitrate, and chloride in natural water, the changes during treatment, and the available data (on fluoride removal by alum alone), these studies were conducted in the concentration ranges of 380 to 980 mg/L of sulfate (as SO_4^{2-}), 0 to 250 mg/L of nitrate (as N), and 26 to 626 mg/L of chloride (as Cl^-) in the optimum pH range of 5.8 to 6.5. The effect of sulfate, nitrate, and chloride in the pH range of 4 to 9.5 was assessed only at concentrations of 980, 250, and 626 mg/L respectively. The results are shown in Tables 4.22 and 4.23 and plotted in Figs. 4.41 - 4.43. The data on their effect in the pH range of 4 to 9.5 were not plotted since they are the same with the control curves in case of phosphate and silica (Figs. 4.38 and 4.40). It was noted that all the parameters did not have significant impact on fluoride removal neither in the optimum pH range (5.8 to 6.5) nor in the pH range of 4.0 to 9.5. The same was also observed by Nawlakhe et al. (1975) and by Nawlakhe and Bulusu (1978) in their study on water samples with 5.1 mg/L of fluoride and concentrations of sulfate, nitrate, and chloride in the ranges of 306 to 806 mg/L (as SO_4^{2-}), 0 to 11 mg/L (as N), and 178 to 890 mg/L (as Cl^-) respectively, during a study on

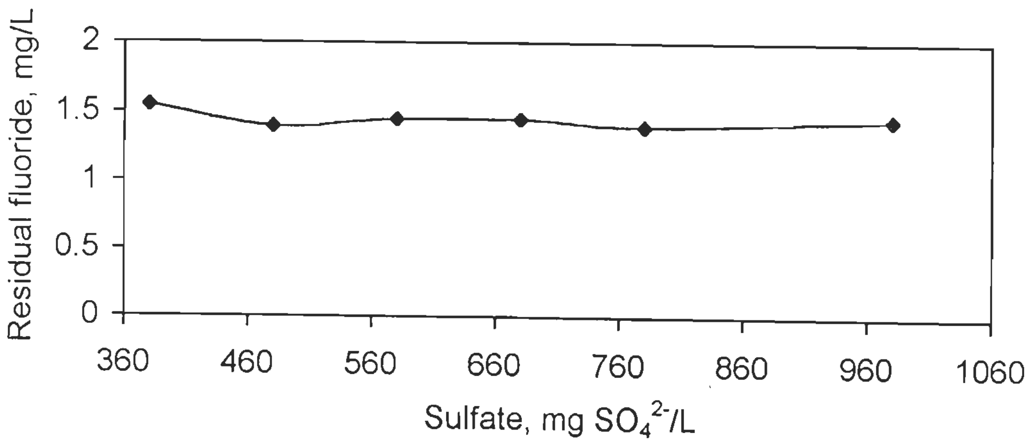


Fig. 4.41 Effect of Sulfate on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, pH=5.8 to 6.5
Alum Dose-800 mg/L, PAC Dose-100 mg/L

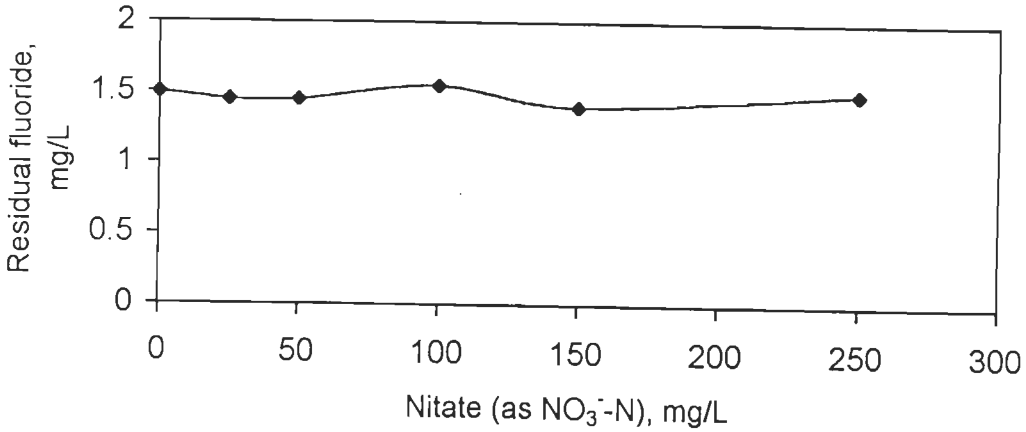


Fig. 4.42 Effect of Nitrate on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, pH=5.8 to 6.5
Alum Dose-800 mg/L, PAC Dose-100 mg/L

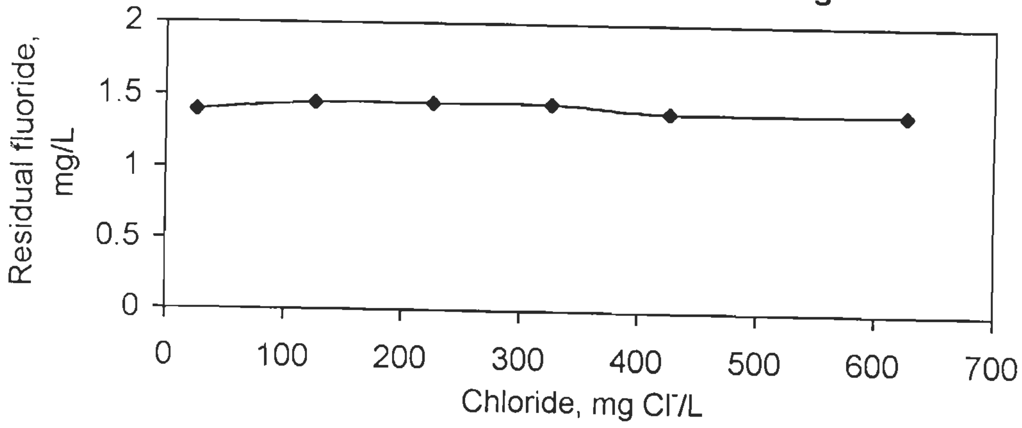


Fig. 4.43 Effect of Chloride on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, pH=5.8 to 6.5
Alum Dose-800 mg/L, PAC Dose- 100 mg/L

fluoride removal by alum alone. Nitrate and chloride do not compete for aluminum with fluoride since they have less affinity to it (Letterman and Vanderbook, 1983). However, in case of sulfate, although it has more affinity to aluminum than fluoride does, its effect in the concentration range studied may be reduced by the formation of calcium sulfate (Bodek et al., 1988) with lime (560 mg/L of lime was added for pH and alkalinity adjustment). This could result in scarcity of free sulfate ion in the water to compete with fluoride for aluminum.

4.2.6.4 Effect of Alkalinity

Nawlakhe et al. (1975) and Bulusu et al. (1979) had exhaustively studied effect of alkalinity on fluoride removal by alum alone. Hence, this study was directed only to verify the trend of the effect of alkalinity on fluoride removal by alum-PAC slurry on water sample with an initial fluoride concentration of 15 mg/L, and compare the results with the former observations. Total alkalinity in the range of 150 to 850 mg/L as $CaCO_3$ was studied by adjusting the tap water with sodium bicarbonate and by dilution with distilled water. The results are presented in Tables 4.22 and 4.23 and plotted in Fig. 4.44. Residual fluoride decreased with increase of total alkalinity in the range of 150 to 400 mg/L and leveled in the range of 400 to 500 mg/L. Above 500 mg/L the residual fluoride increased first sharply and then only marginally up to 850 mg/L. Minimum residual fluoride was observed in the alkalinity range of 400 to 500 mg/L. This indicated that 0.5 to 0.63 mg/L (as $CaCO_3$) of alkalinity is required for each mg/L of alum dose. Nawlakhe et al. (1975) also observed the necessity of optimum amount of alkalinity to achieve residual fluoride to meet the standard, on one hand, and to reduce the amount of alum, on the other hand. Zabban and Helwick (1975) suggested that adequate alkalinity is a prerequisite for the formation of aluminum hydroxide

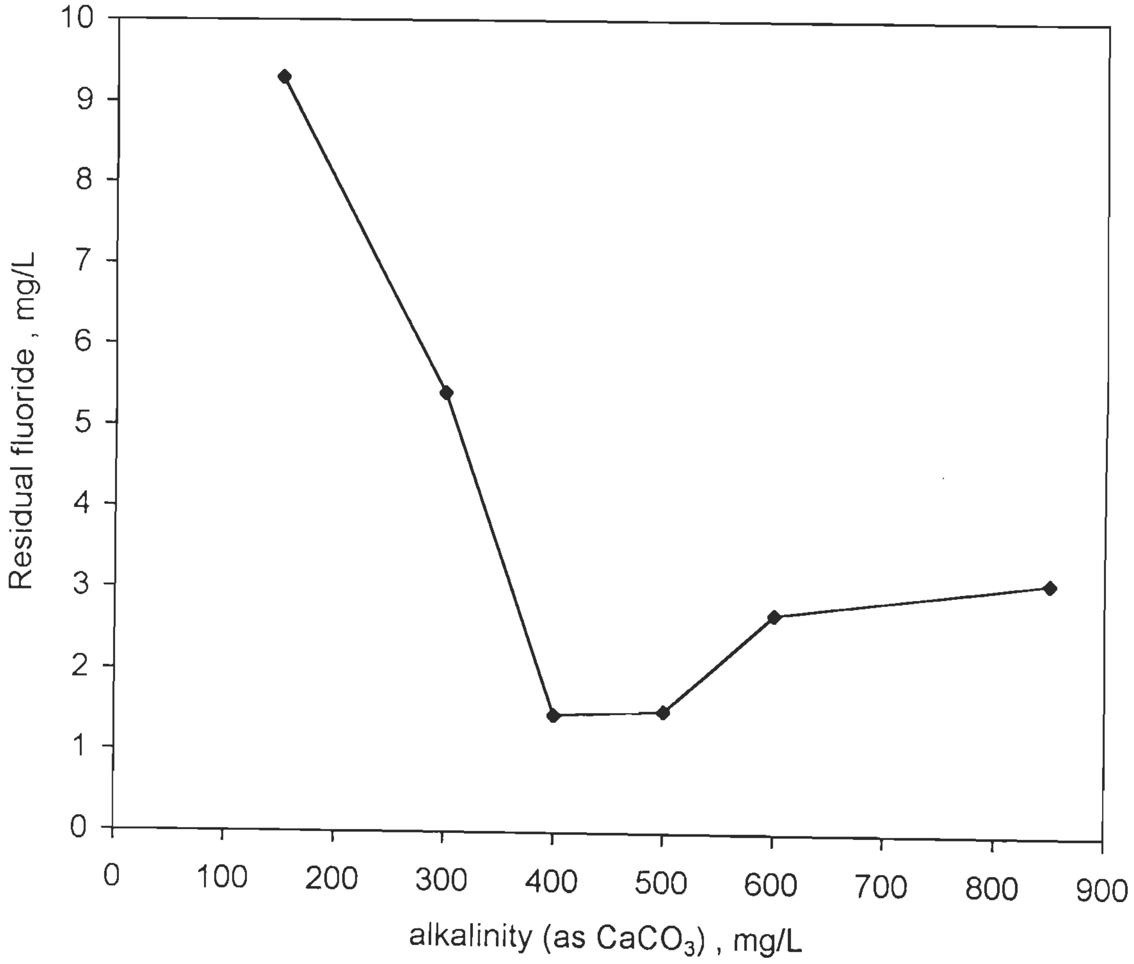


Fig. 4.44 Effect of Alkalinity on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, Alum Dose-800 mg/L, PAC Dose-100 mg/L

precipitate in which fluoride is complexed or adsorbed and consequently removed. Furthermore, in case of insufficient alkalinity, the pH would also drop significantly low beyond the optimum values for fluoride removal due to its low buffering capacity. Thus, the deterioration of fluoride removal at low alkalinity (< 400 mg/L) was because of its inadequacy, whereas at high alkalinity (> 500 mg/L) hydroxide ion has competed with fluoride for aluminum (Sherwin and Weston, 1966; Hanna and Rubin, 1970). Moreover, because of its high buffering capacity the pH was also raised beyond its optimum value (5.8 to 6.5).

4.2.6.5 Effect of Organic Matter (Ethanol)

As discussed in Section 4.3.1, since organic matter (ethanol) was used as external carbon source at the denitrification stage of the treatment, this study was conducted to assess its effect on fluoride removal and also to examine its fate during defluoridation. Hence, ethanol (measured as COD) in the concentration range of 0 (control) to 130 mg/L was studied at the optimum pH range (5.8 to 6.5). The results are presented in Table 4.22 and plotted in Fig. 4.45. In the concentration range studied, organic matter (ethanol) did not affect fluoride removal. This is consistent with observations reported earlier by Nawlakhe and Bulusu (1978). Moreover, in the treatment process, depending on the initial concentrations, 29.5 to 100% removals of COD was also noted. This could be attributed to lime (Semmen and Honkstein, 1982), alum (Randtke, 1988), PAC (Stukenberg, 1975; Haberrer and Schmidt, 1991), and by air stripping (volatilization) during mixing (Dyksen and Hess, 1981; Fiege and Ruggiero, 1983). To clarify which of the above has predominant role in the removal, additional experiments were conducted using alum (800 mg/L), lime (560 mg/L), and PAC (100 mg/L) separately and combined at the optimum pH range (5.8 to 6.5) and at

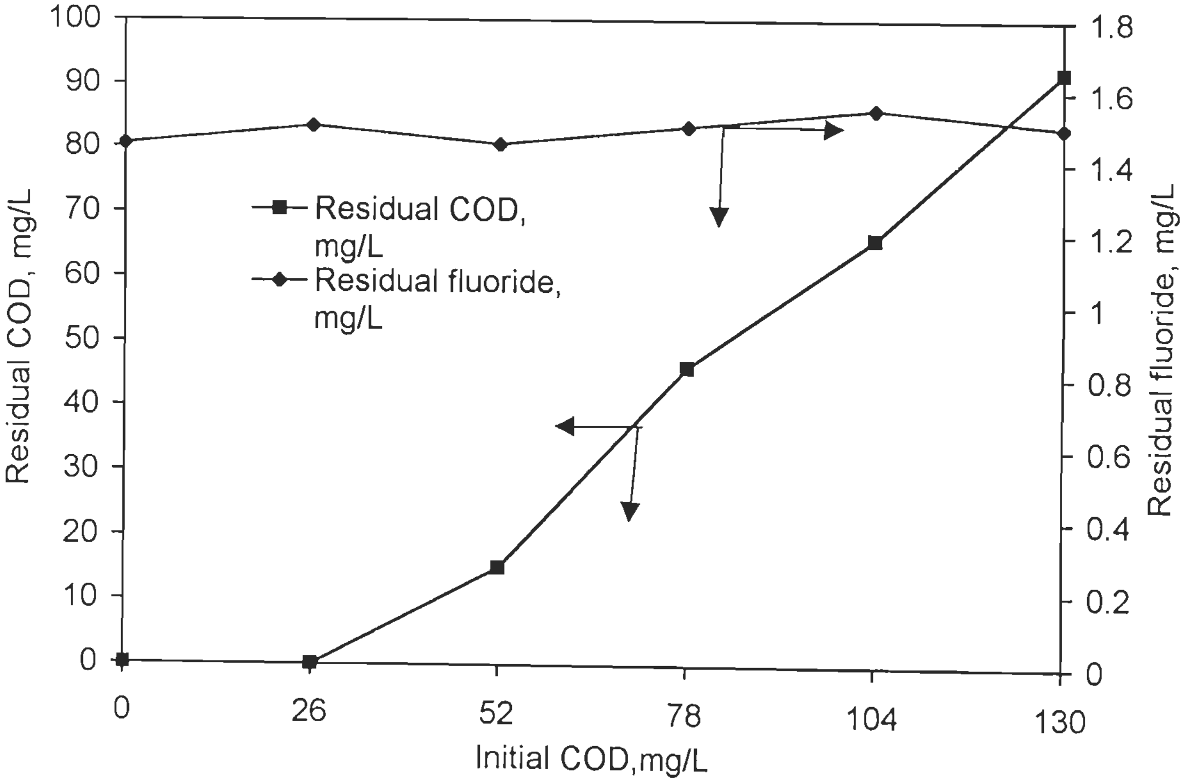


Fig. 4.45 Effect of Organic Matter (Ethanol) on Fluoride Removal by Alum-PAC Slurry. C_o=15 mg/L, pH=5.8 to 6.5 Alum Dose-800 mg/L, PAC Dose-100 mg/L

130 mg/L of initial COD. The contribution from air stripping (volatilization) during mixing was also studied by the control comparing the initial and final COD concentrations. The results are presented in Table 4.24. In the pH range studied (5.8 to 6.5), lime did not show significant COD removal, whereas alum, PAC, and aeration (volatilization) removed 16.9%, 6%, and 3.2% of the initial COD respectively. Thus predominantly it was removed by alum. When they combined (as alum-PAC slurry), 29.5% COD removal was obtained. Removal of synthetic organic chemicals (SOCs) from solution by coagulation in the pH range of 5 to 8.5 (depending on their charge) was described by Randtke (1988) and 10% removal of ethanol by activated carbon was also reported (Perrich, 1981). Liao and Randtke (1986) reported negligible (< 2%) removal of alcohol by lime softening.

Table 4.24 Removal of Organic Matter (Ethanol) by Alum-PAC Slurry and Its Components Initial COD =130 mg/L, pH=5.8 to 6.5

Alum, mg/L	Lime, mg/L	PAC mg/L	Residual COD, mg/L	% COD removal
---	---	---	125.8	3.2
800	---	---	103.9	20.1
---	---	100	118.0	9.2
800	560	100	91.6	29.5
800	560	---	102.0	21.5
---	560	---	124.4	4.3

4.3 DENITRIFICATION

4.3.1 Effect of Carbon to Nitrate-Nitrogen Ratio (as COD/NO_3^--N) on Denitrification

Although methanol is commonly used as external carbon source in wastewater denitrification, due to its possible toxicity (Mc Carty et al., 1969; Christensen and Harremoës, 1977; Clifford and Liu, 1993), it is not recommended for denitrification of drinking water. Hence, despite their relative high cost (compared with methanol), ethanol and acetic acid were being used in full-scale drinking water treatment plants (Richard et al., 1980; Clifford and Liu, 1993). Of these, ethanol is cheaper (Mc Carty et al., 1969; Gayle et al., 1989), more effective than acetic acid in terms of C/N ratio (Kapoor and Viraraghavan, 1997), and yields equal or higher denitrification rate compared to methanol (Æesøy et al., 1998). Thus, in this study ethanol was used as external carbon source.

The objective of this investigation was to assess the effect of ethanol (measured as COD) to nitrate-nitrogen ratio on denitrification and to find the optimum value for further studies. Experiments were conducted in 5 sets by varying COD/NO_3^--N ratio as 1.25, 2.00, 2.30, 2.70, and 3.60 and maintaining nitrate concentration (80 mg/L as N), duration of anoxic reaction (9 hours) and settling (1 hour) as constant. Details of the experimental setup (Fig. 3.2) and test procedures are given in Sections 3.8.1 and 3.8.2. At each COD/NO_3^--N ratio, the reactor was first acclimatized and then at steady-state nitrate, nitrite, and COD were measured for a total of 9 hours reaction time with maximum intervals of 2 hours. The results are presented in Table 4.25 and plotted in Figs. 4.46 - 4.51.

In the first one hour, significant removal of nitrate was observed at all COD/NO_3^--N ratios [Figs. 4.46(a-e)]. For COD/NO_3^--N ratio of 1.25, removal of

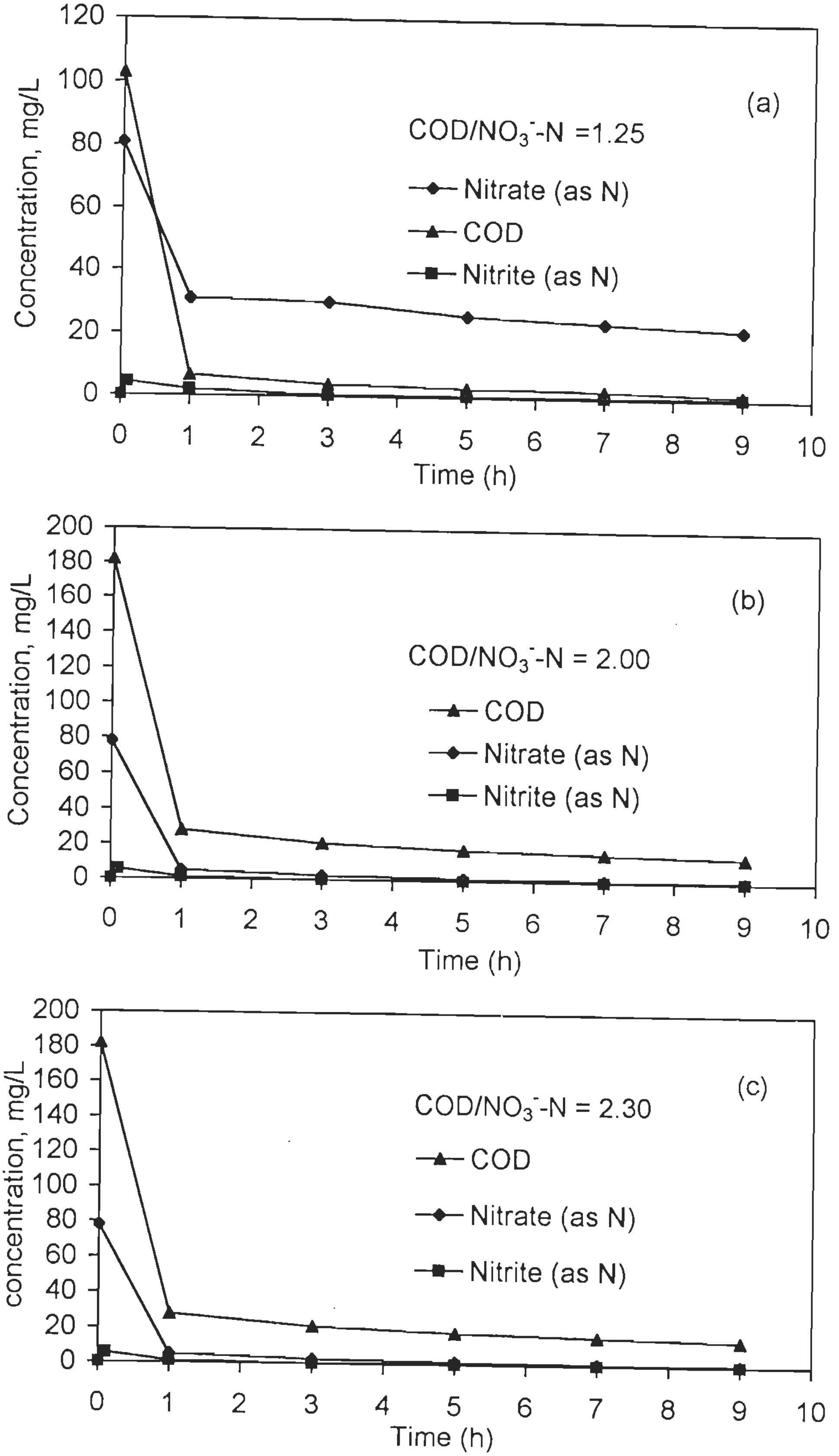
61.7 % was observed while for higher ratios it varied from 90.2 % to 96.6 % (Table 4.25). After one hour, although nitrate removal continued but at a very slow rate. Variation of percentage removal of nitrate for different COD/NO_3^--N ratios is plotted separately in Figs. 4.47(a-e) and collectively for all COD/NO_3^--N ratios in Fig. 4.48. The total nitrate removal in 9 hours reaction time was 72.8 % at COD/NO_3^--N ratio of 1.25, whereas at higher ratios it varied in very close range from 98.7 to 99.4 %. It could be concluded that for COD/NO_3^--N ≥ 2, the effect of COD/NO_3^--N ratio on denitrification was insignificant (Figs. 4.48 and 4.50).

To fix the COD/NO_3^--N ratio from 1.25 to 3.60 (since initial nitrate-nitrogen was ≈ 80 mg/L in all cases), the initial COD values were varied between 103 and 296 mg/L (Table 4.25). The removal of COD with time followed the trend similar to the nitrate removal [Figs. 4.46(a-e)]. As it is evident, significant reduction of COD also took place during initial first hour. It was reduced from initial COD of 103 mg/L to 6.5 mg/L (93.7 %) at COD/NO_3^--N ratio of 1.25, from 165 to 13 (92.1 %) at COD/NO_3^--N ratio of 2.00, 182 to 28 mg/L (84.6 %) at COD/NO_3^--N ratio of 2.30, 215 to 62 (71.2 %) at COD/NO_3^--N ratio of 2.70, and 296 to 125 (57.8 %) at COD/NO_3^--N ratio of 3.60 indicating lower removals with increasing COD/NO_3^--N ratios. COD removal rate decreased considerably after one hour but it continued until the end of reaction period i.e. 9 hours with the overall removal in the range of 70.9 % to 98.5 %. Fig. 4.49 gives variation of percentage of COD removal with time at different COD/NO_3^--N ratios, while residual COD values in effluents from different reactors operating at different COD/NO_3^--N ratios is given in Fig. 4.51. Although at COD/NO_3^--N ratio of 1.25 the residual COD obtained was lowest (1.5 mg/L), the residual nitrate was maximum (22 mg/L). Comparison of Figs. 4.50 and 4.51 indicates that COD/NO_3^--N ratio of 2.00 would yield good COD and nitrate removals simultaneously.

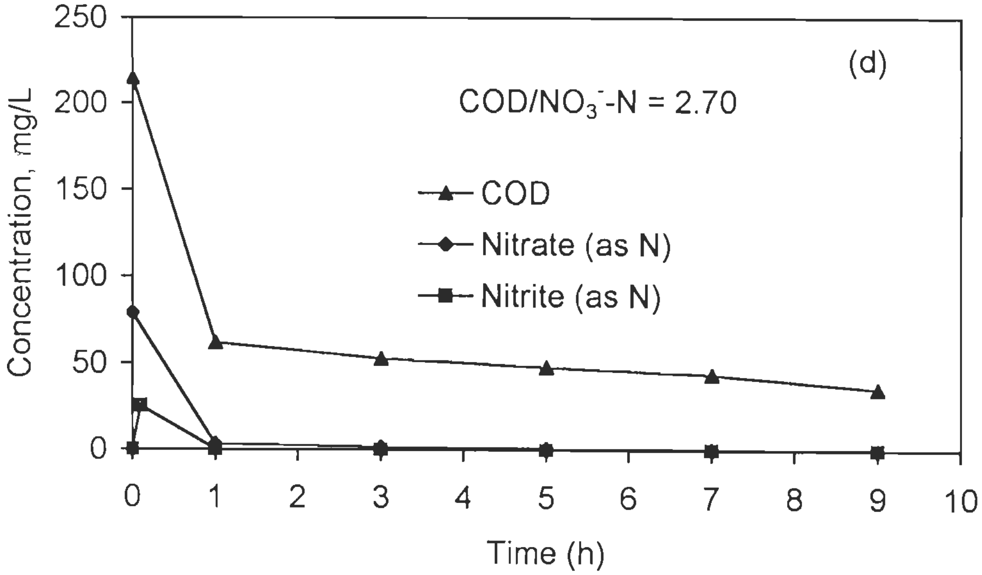
Table 4.25 Denitrification and COD Profiles at Various COD/NO_3^--N Ratio

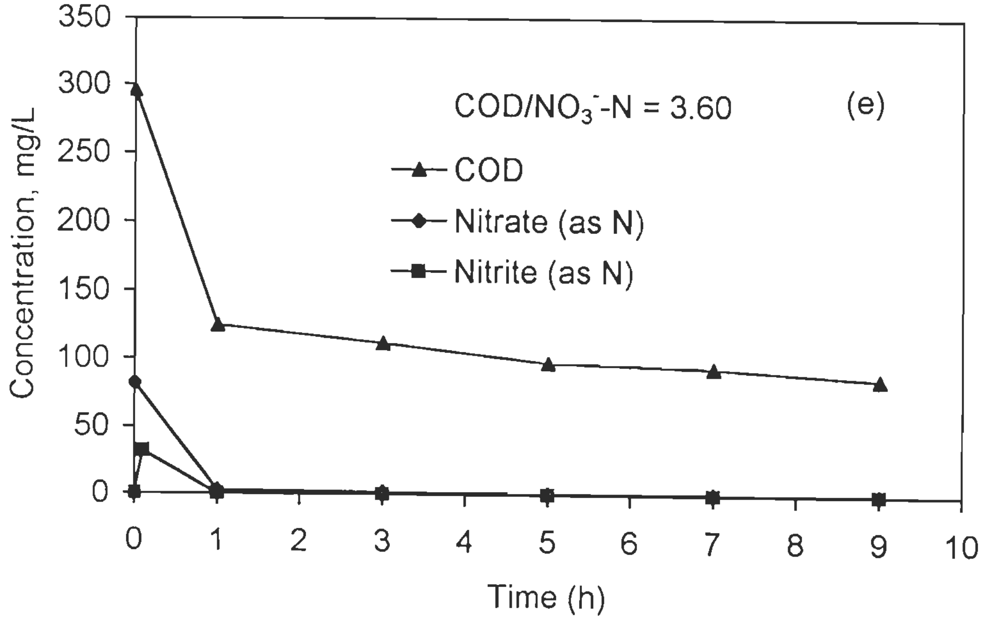
Initial Nitrate Concentration ≈ 80 mg/L (as N)

contact time (h)	COD/NO_3^--N Ratio																								
	1.25					2.00					2.30					2.70					3.60				
	Residual concent., mg/L			% removal		Residual concent., mg/L			% removal		Residual concent., mg/L			% removal		Residual concent., mg/L			% removal		Residual concent., mg/L			% removal	
	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD
0.0	81	0	103	0	0	82	0	165	0	0	78	0	182	0	0	79	0	215	0	0	82	0	296	0	0
0.1	----	4.2	---	----	----	----	2.1	---	----	----	----	5.5	----	----	---	---	25.5	----	----	----	----	32	----	----	---
1.0	31	2.0	6.5	61.7	93.7	8	0.85	13	90.2	92.1	5	1.2	28	93.6	84.6	3.5	0.5	62	95.6	71.2	2.8	0.18	125	96.6	57.8
3.0	30	0.50	4.0	62.9	96.1	3	0.04	9	96.3	94.5	2.5	0.06	21	96.8	88.5	1.8	0.08	53	97.7	75.3	2.0	0.06	112	97.6	62.2
5.0	26	0.50	3.0	67.9	97.1	2.5	0.03	8	97.0	95.1	1.5	0.02	18	98.1	90.1	1.25	0.03	48	98.4	77.7	1.0	0.03	98	98.8	66.9
7.0	24	0.45	2.5	70.3	97.6	1.6	0.02	6.5	98.0	96.1	1.0	0.02	16	98.7	91.2	0.9	0.01	44	98.9	79.5	0.8	0.01	94	99.0	68.2
9.0	22	0.45	1.5	72.8	98.5	1.0	0.02	5.0	98.7	97.0	0.6	0.01	14	99.2	92.3	0.5	0.01	36	99.4	83.2	0.5	0.01	86	99.4	70.9

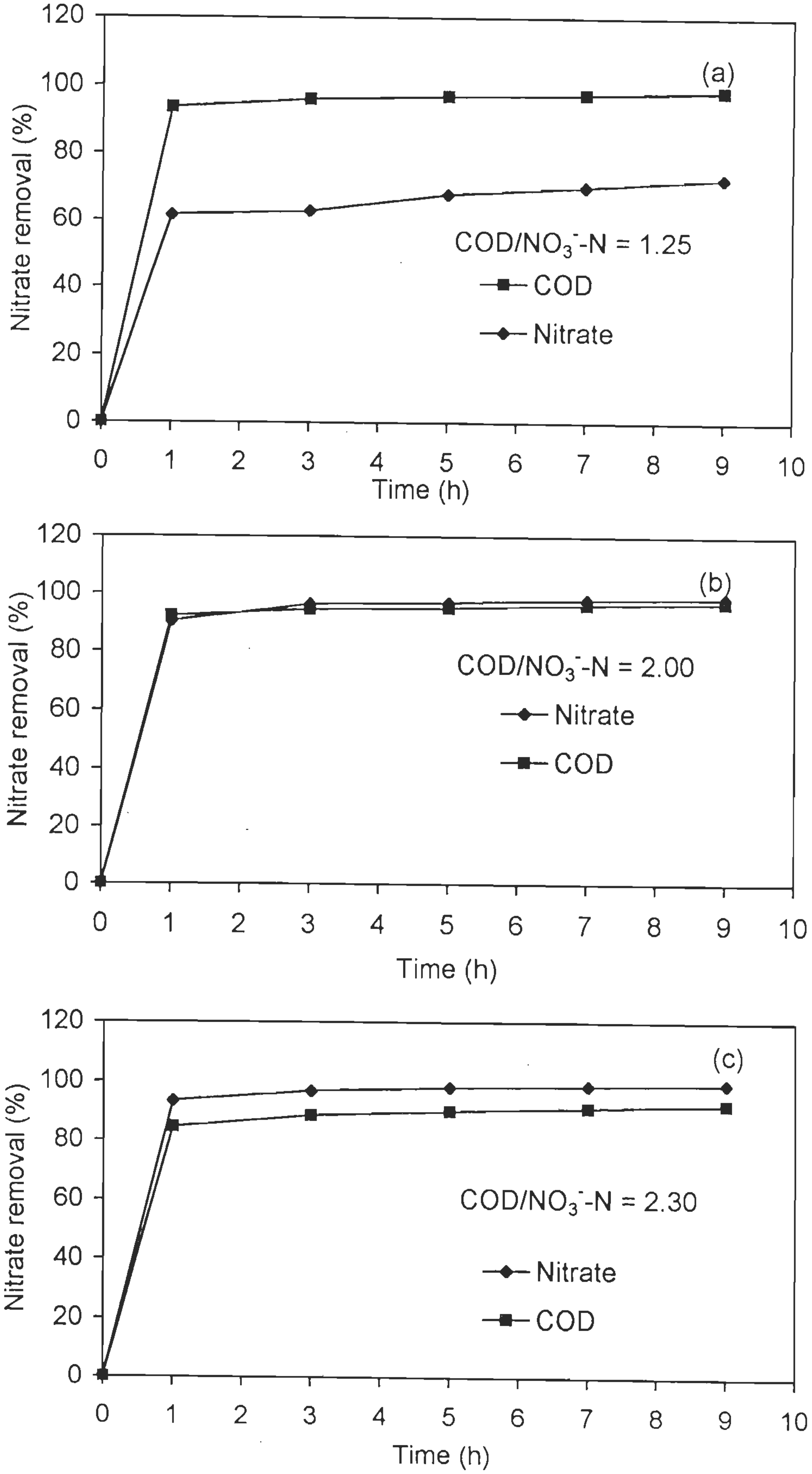


Figs. 4.46 (a-c) Denitrification and COD Profiles at Various Carbon-to-Nitrogen (as COD/NO$_3^-$-N) Ratio.

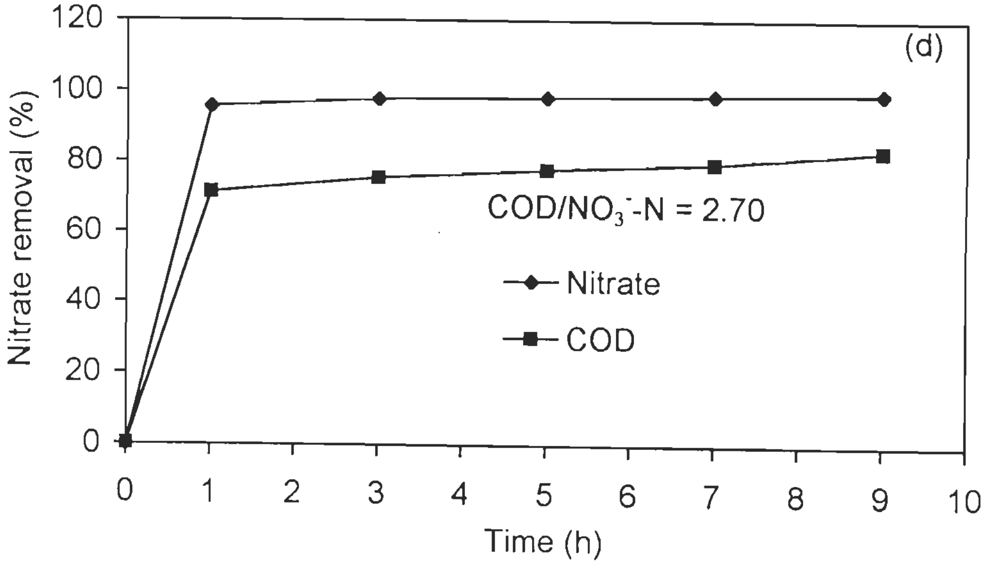


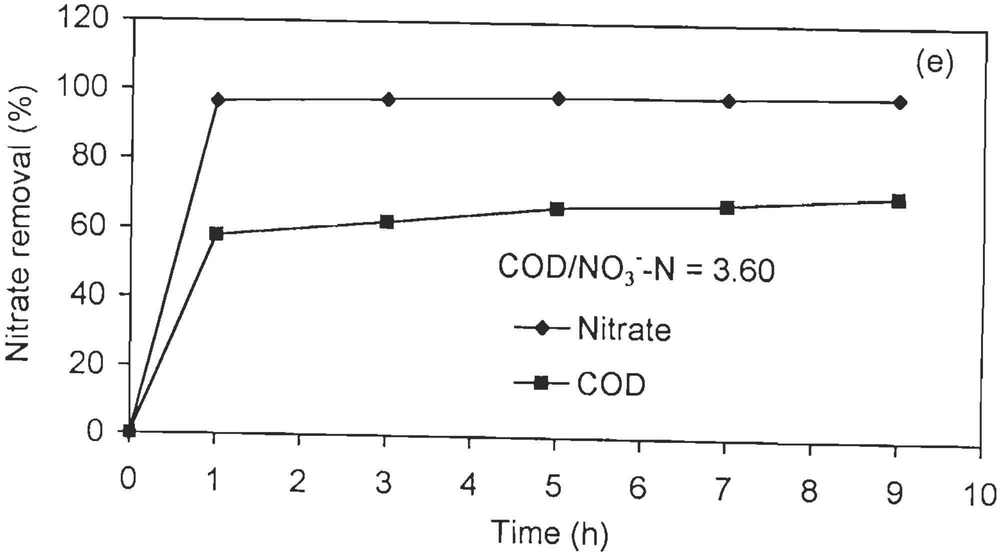


Figs. 4.46 (d-e) Denitrification and COD Profiles at Various Carbon- to- Nitrogen (as COD/NO_3^--N) Ratio.



Figs. 4.47 (a-c) Percentage Removal of Nitrate and COD at Various COD/NO$_3^-$-N Ratio.





Figs. 4.47 (d-e) Percentage Removal of Nitrate and COD at Various COD/NO$_3^-$-N Ratio.

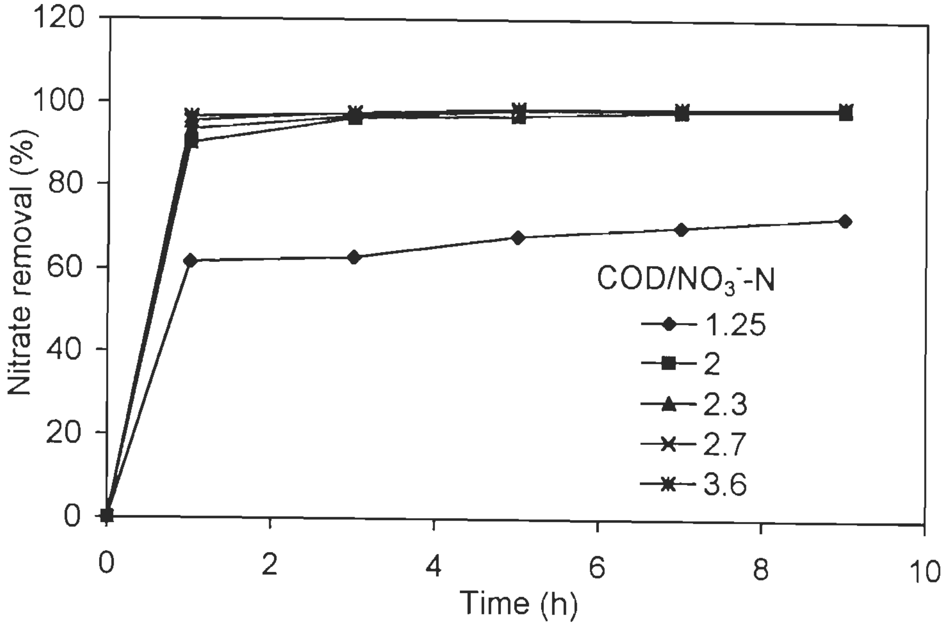


Fig. 4.48 Variation of Percentage of Nitrate Removal with Time at Different COD/NO_3^--N

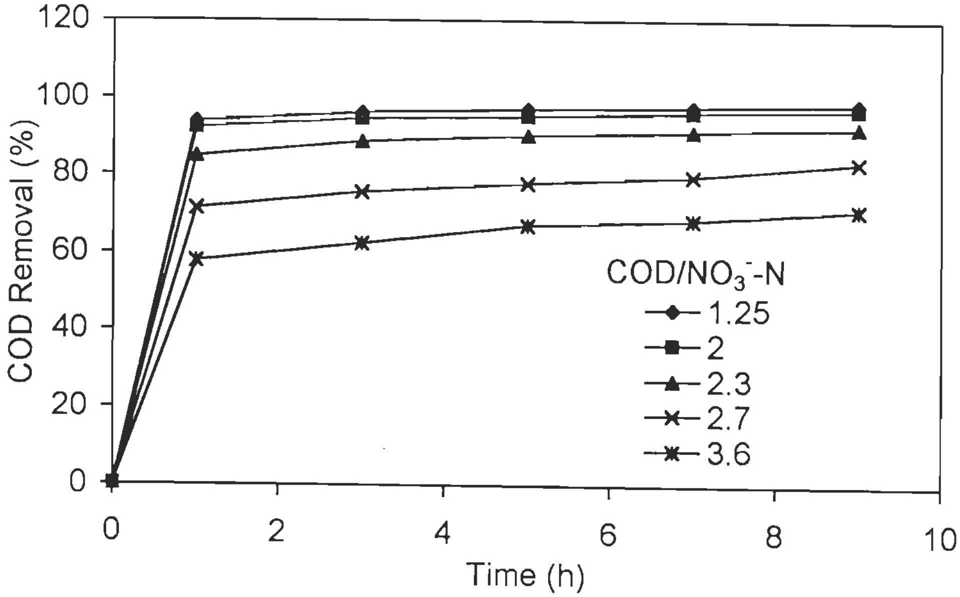


Fig. 4.49 Variation of Percentage of COD Removal with Time at Different COD/NO_3^--N Ratio.

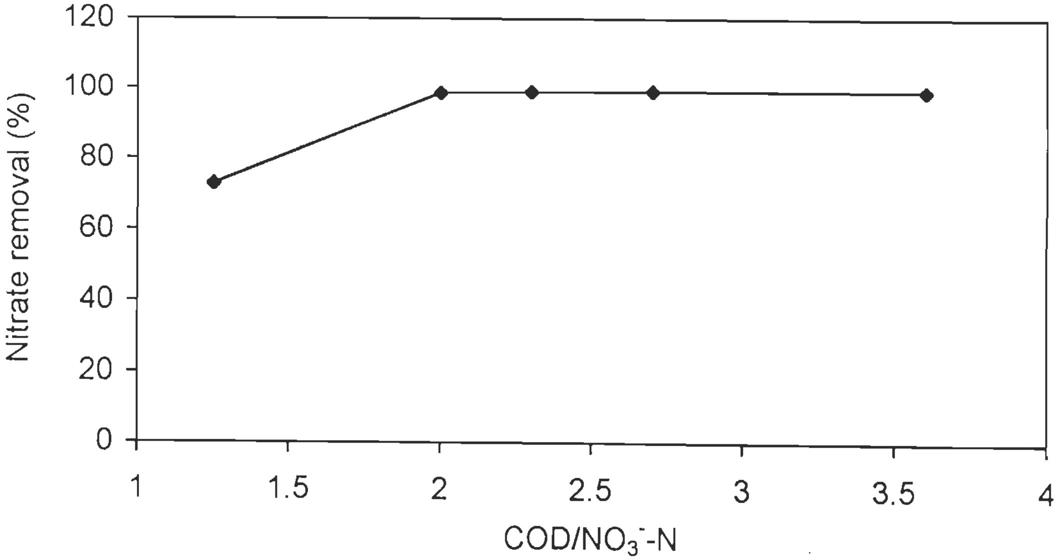


Fig. 4.50 Effect of COD/NO_3^--N Ratio on Nitrate Removal

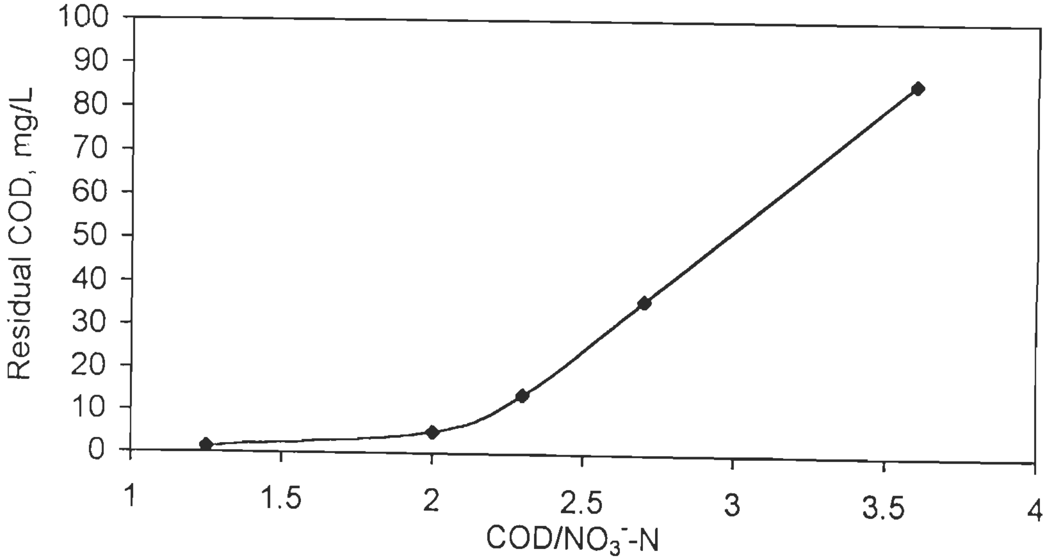


Fig. 4.51 Variation of Residual COD in the Denitrified Water Samples with COD/NO_3^--N Ratio

Accumulation of nitrites was observed within six minutes of reaction at the beginning of the reaction time, in all cases. It increased from 4.2 to 32 mg/L with increase of COD/NO_3^--N ratio [Figs. 4.46(a-e)]. However, after the first hour of the reaction time it significantly reduced and, at the end the reaction time the residual concentrations in the effluent were in the range of 0.01 to 0.45 mg/L, the maximum being at COD/NO_3^--N ratio of 1.25. This observation was also supported by increase of pH and alkalinity (to 8.1 and 505 mg/L respectively) in the effluent, which was measured during routine performance monitoring, indicating occurrence of complete denitrification (Christensen and Harremoës, 1977; Glass and Silverstein, 1998). Intermediate nitrite accumulation followed by subsequent reduction, and good nitrate removal (up to 86% removal in the first hour) were also reported by other investigators (Wilderer et al., 1987; Tam et al., 1992; Lin and Chen, 1995; Glass and Silverstein, 1999) in denitrification of wastewaters. Narkis et al. (1979) and Sauthier et al. (1998) also observed similar effect of C/N ratio on denitrification. Æesøy et al. (1998) reported higher requirement of ethanol equivalent to COD/NO_3^--N ratio of 4.5 in denitrification of wastewater by packed bed biofilm reactor in a temperature range of 9-11°C. Skrinde and Bhagat (1982) found that the optimum COD/NO_3^--N ratio for methanol was 2.5. According to Narkis et al. (1979) when the concentration of the organic matter is expressed as BOD the optimum C/N ratio was 2.3 for methanol and sodium acetate. Accordingly, the optimum COD/NO_3^--N ratio of 2.00 found in this study for ethanol was relatively low. This might be due to: (i) differences in concentration of dissolved oxygen (in this study it was completely purged out), (ii) differences in denitrifier microorganism composition (Lee and Park, 1998), (iii) differences in operating conditions, and (iv) denitrification rate of ethanol is more compared to methanol (Æesøy et al., 1998).

4.3.2 Denitrification Efficiency of Sequencing Batch Reactor (SBR) at Various Initial Nitrate Concentrations

This study was carried out to evaluate the denitrification efficiency of SBR at initial nitrate concentrations varying in the range of 40 to 250 mg/L (as N), and to find out the anoxic reaction times (ARTs) at which both nitrate and nitrite concentrations would be reduced to the acceptable levels at each initial nitrate concentration. Reactors were operated at the optimum COD/NO_3^--N ratio of 2.00 found earlier, ART of 9 hours, and nitrate loading rates of 0.04, 0.08, 0.12, 0.16, 0.20, and 0.25 kg N/m^3.d corresponding to initial nitrate concentrations of 40, 80, 120, 160, 200, and 250 mg/L respectively. After attaining steady state, nitrite, residual nitrate and COD were measured with maximum intervals of 2 hours, in each case. Other details of the experimental procedures are discussed in Sections 3.8.1 and 3.8.2. The results are presented in Tables 4.26A and 4.26 B and plotted in Figs. 4.52 - 4.55. At all values of initial nitrate concentrations (40 to 250 mg/L as N) studied, the general trend of denitrification and COD profiles [Figs. 4.52(a-f) and 4.53] were similar to the observations discussed in Section 4.3.1. In cases of initial nitrate concentrations of 40 and 80 mg/L (as N), nitrate reduction below 10 mg/L was achieved within one hour of reaction time [Figs. 4.52(a-b)]. Within this time, 87.8 % and 90.2 % nitrate removal was observed at initial nitrate concentrations of 40 and 80 mg/L (as N) respectively [Figs. 4.54(a-b)]. Beyond one hour, nitrate reduction continued at extremely slow rate and by the end of the reaction time only 1.0 and 1.2 mg/L nitrate (as N) appeared in the effluent of waters having initial nitrate concentrations of 40 and 80 mg/L (as N) respectively. High nitrite accumulation was observed initially which decreased substantially within 3 hours of reaction time (Fig. 4.55). Sauthier et al. (1998) also

Table 4.26(A) Denitrification and COD Profiles at Various Initial Nitrate Concentrations

COD/NO_3^--N=2.00

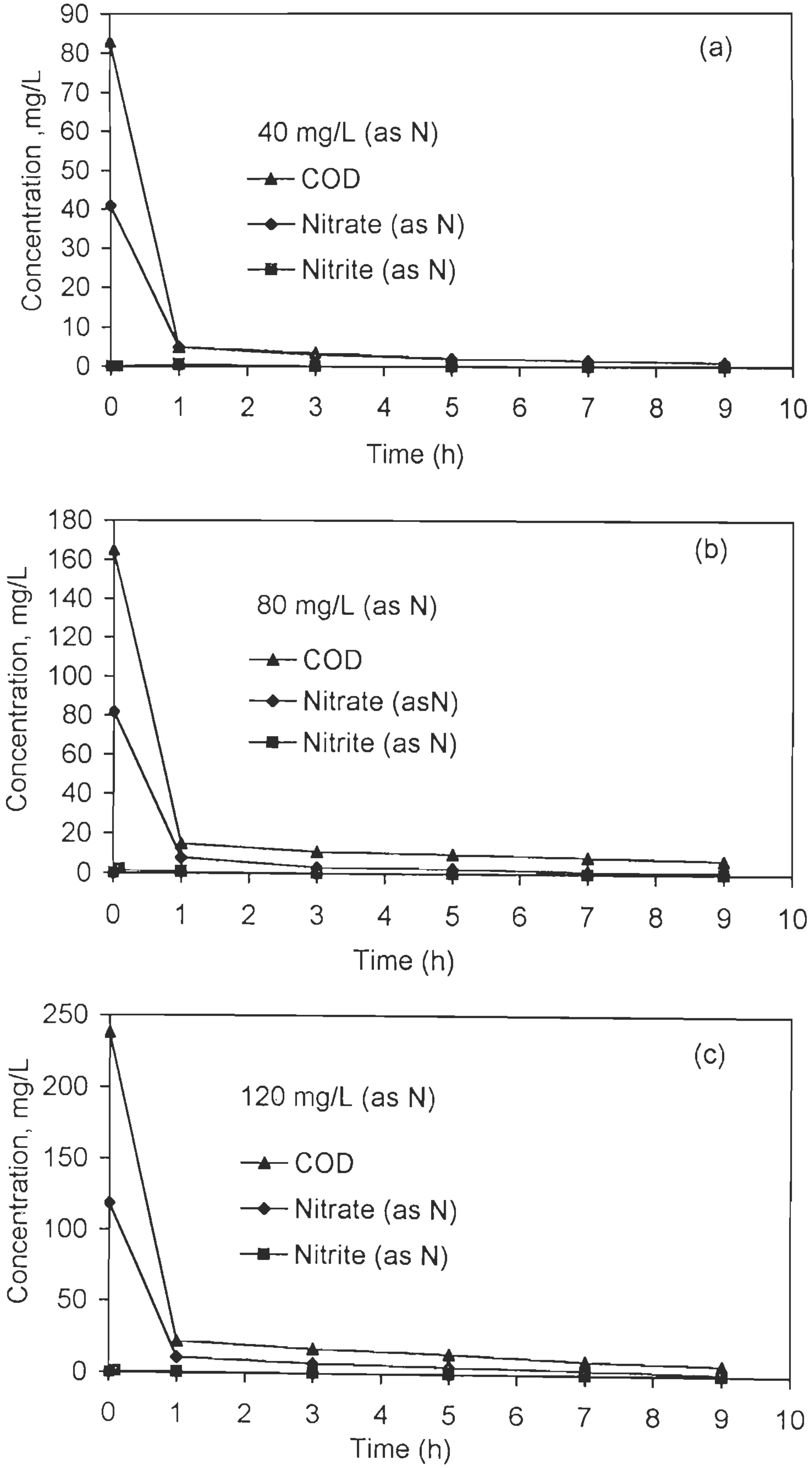
cont-act time (h)	Initial nitrate concentrations, mg/L as NO_3^--N														
	40					80					120				
	Residual concent., mg/L			% removal		Residual concent., mg/L			% removal		Residual concent., mg/L			% removal	
	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD
0	41	0	83	0	0	82	0	165	0	0	119	0	238	0	0
0.1	---	0.03	---	---	---	---	2.1	---	---	---	---	1.85	---	---	---
1	5	0.52	5	87.8	94.0	8	0.85	15	90.2	90.9	11	0.95	22	90.8	90.8
3	3	ND	3.5	92.7	95.8	3	0.01	11	96.3	93.3	7	0.01	17	94.1	92.8
5	2	ND	2	95.1	97.6	2.5	ND	10	97.0	93.9	5	0.01	14	95.8	94.1
7	1.5	ND	1.5	96.3	98.2	1.6	ND	8.5	98.0	94.8	3.5	ND	9.5	97.0	96.0
9	1.0	ND	1.0	97.5	98.6	1.2	ND	7.0	98.5	95.8	1.5	ND	7.5	98.7	96.8

ND – not detected

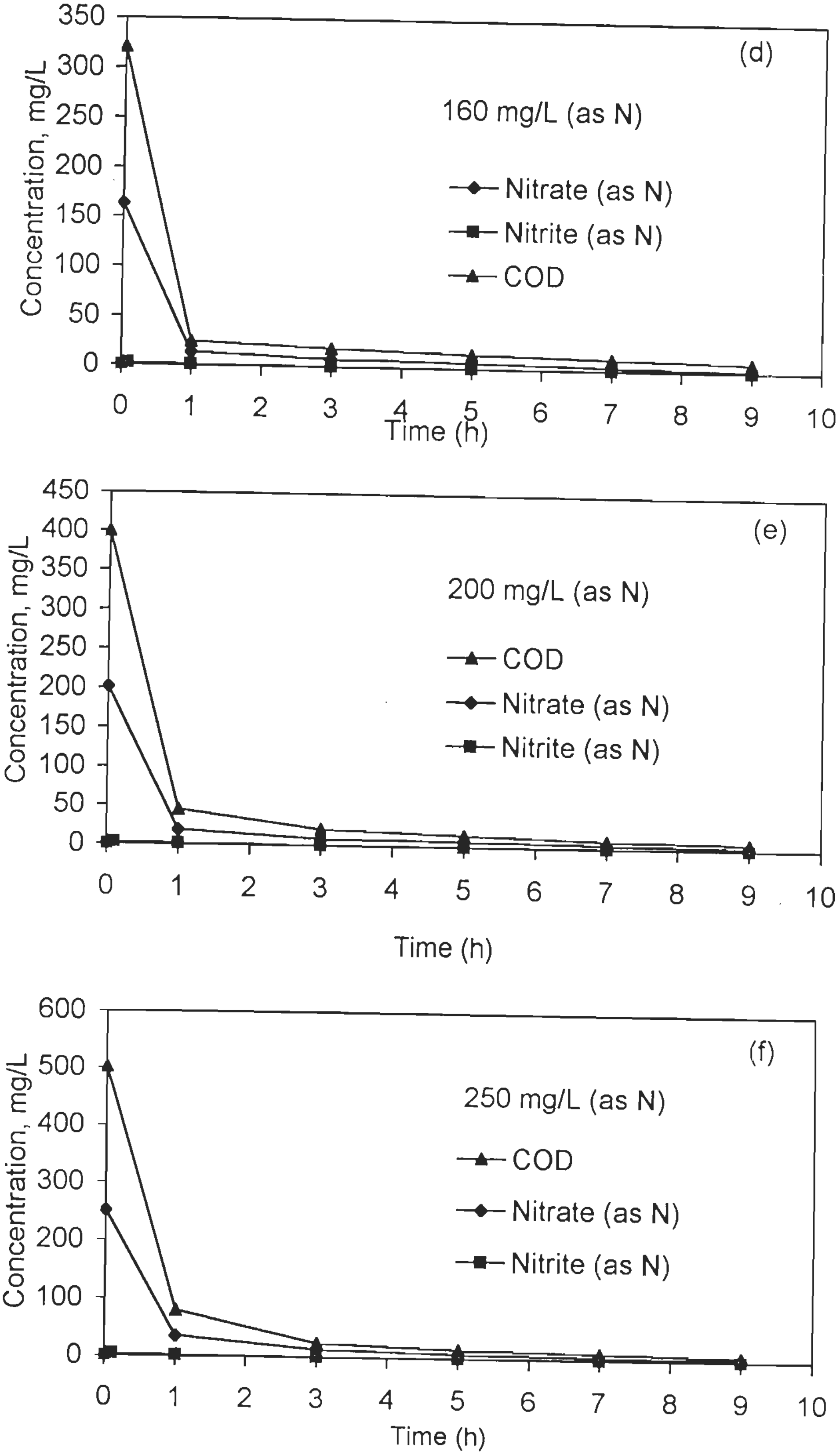
Table 4.26(B) Denitrification and COD Profiles at Various Initial Nitrate Concentrations

COD/NO_3^-- N=2.00

cont-act time (h)	Initial nitrate concentrations, mg/L as NO_3^--N														
	160					200					250				
	Residual concent., mg/L			% removal		Residual concent., mg/L			% removal		Residual concent., mg/L			% removal	
	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD	Nitrate (as N)	Nitrite (as N)	COD	Nitrate	COD
0	164	0	321	0	0	202	0	403	0	0	253	0	502	0	0
0.1	---	2.5	---	---	---	---	3.15	---	---	---	---	3.50	---	---	---
1	14	1.3	25	91.5	92.2	19	1.65	45	90.6	88.8	36	1.85	80	85.7	84.0
3	8.0	0.01	19	95.1	94.1	8.5	0.02	21	95.8	94.8	14	0.25	25	94.4	95.0
5	6.5	0.01	15	96.0	95.3	7.0	0.01	15	96.5	96.2	7.5	0.07	16	97.0	96.8
7	4.0	0.01	12	97.5	96.3	5.0	0.01	10	97.5	97.5	4.5	0.01	12	98.2	97.6
9	2.0	0.01	9	98.7	97.2	3.0	0.01	8	98.5	98.0	4.0	0.01	7.5	98.4	98.5



Figs. 4.52 (a-c) Denitrification and COD Profiles at Various Initial Nitrate Concentrations.



Figs. 4.52 (d-f) Denitrification and COD Profiles at Various Initial Nitrate Concentrations.

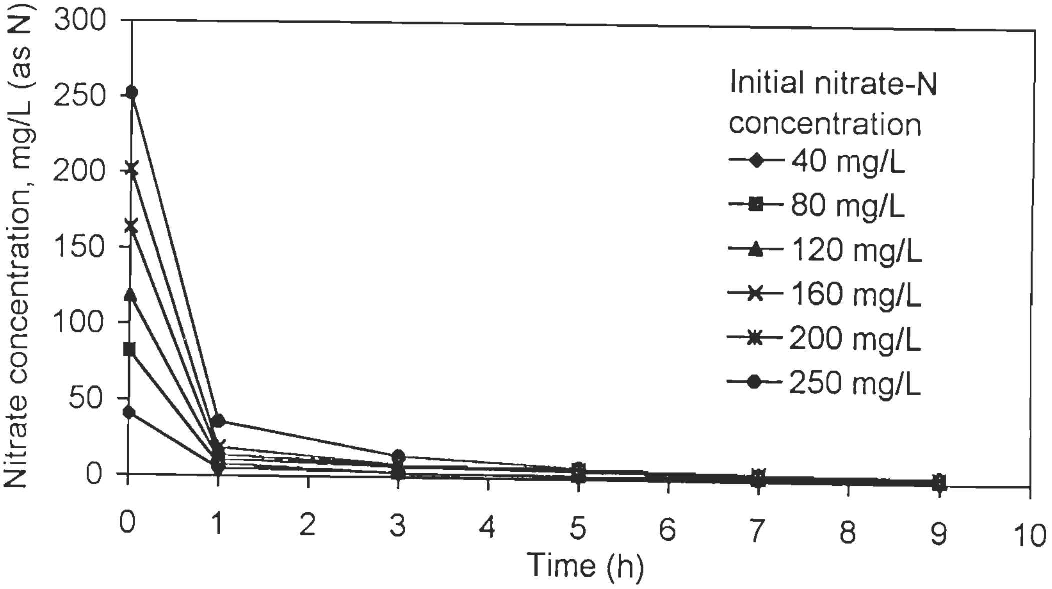
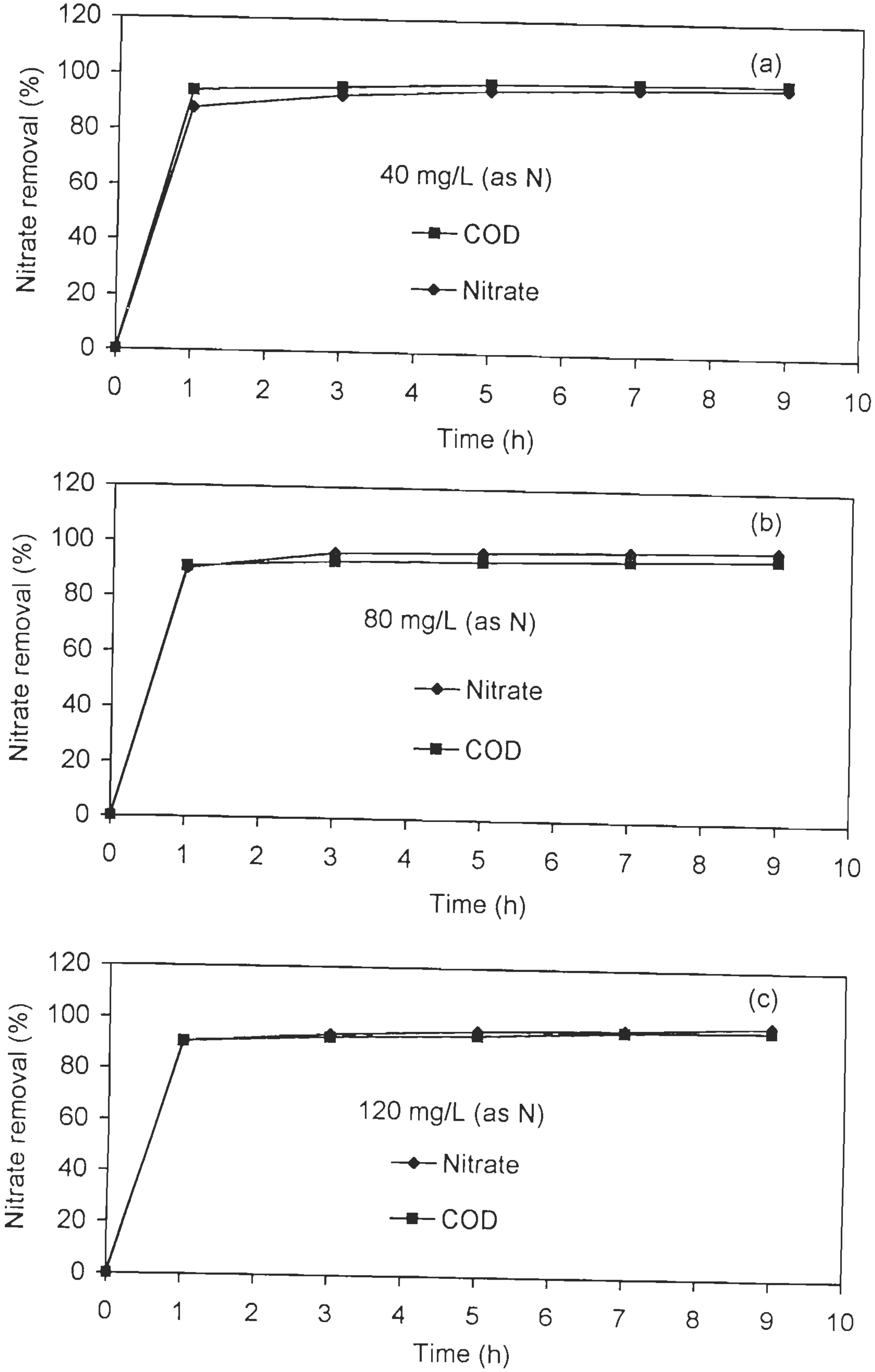
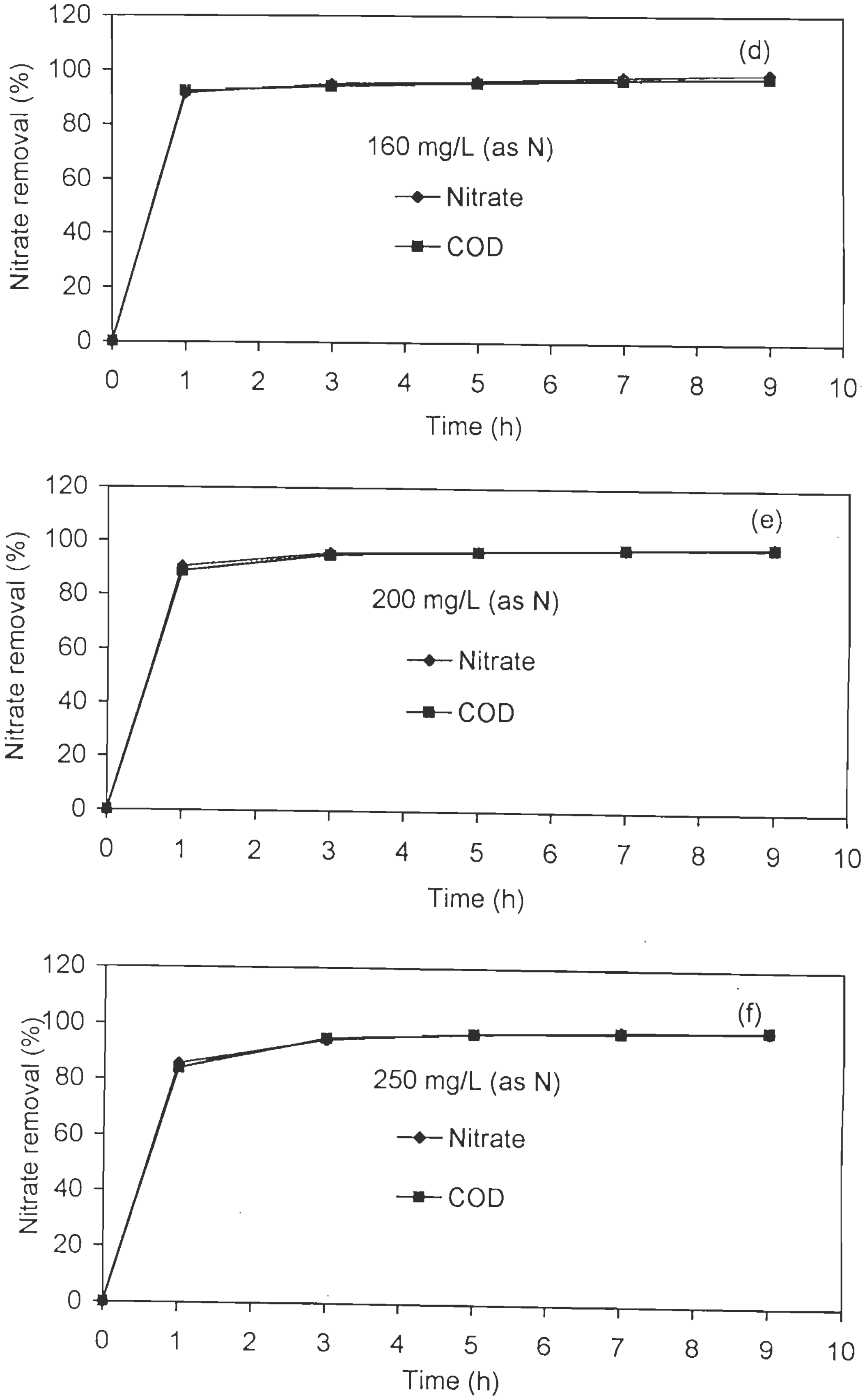


Fig. 4.53 Nitrate Removal Profiles at Various Initial Nitrate Concentrations.



Figs. 4.54(a-c) Percentage Removal of Nitrate and COD at Various Initial Concentrations.



Figs. 4.54 (d-f) Percentage Removal of Nitrate and COD at Various Initial Nitrate Concentrations.

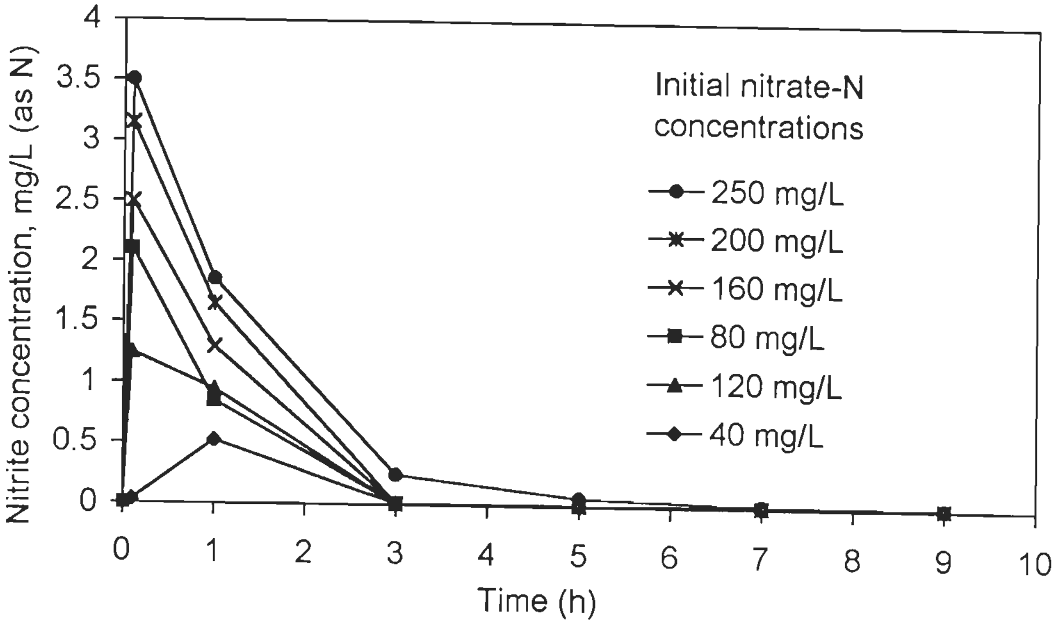


Fig. 4.55 Intermediate Nitrite Accumulation Profiles at Various Initial Nitrate Concentrations.

noted production of nitrite proportional to the nitrate concentration in the reactor. These observations indicate that denitrifcation almost instantly started with initiation of reaction and its path was through a formation of nitrite as a transient intermediate. The same trends of nitrate reduction and nitrite accumulation profiles were also noted for the remaining initial nitrate concentrations (120, 160, 200, and 250 mg/L as N). However, the ARTs required to achieve both the acceptable limits of nitrate and nitrite were 3, 5, and 7 hours for initial nitrate concentrations of 120 to 160, 200, and 250 mg/L (as N) respectively (Tables 4.26A and 4.26B). It could be concluded that to get the water of acceptable quality in terms of nitrate and nitrite ART's of 3, 5, and 7 hours would be required in case of waters having nitrate concentrations of 40 to 160, 200, and 250 mg/L as N respectively. Thus at these ARTs SBR could achieve 92.7 to 98.2% nitrate removal efficiencies (Tables 4.26 A and 4.26 B). At these ARTs, the effluent COD was found in the range of 3.5 to 19 mg/L [Figs. 4.52(a-f)] therefore, possibility of slightly reducing the dose of ethanol could be worked out. This might also eliminate the possibility of sulfide formation in the denitrified water [Fig. 4.62(b)] (Sauthier et al., 1998).

4.3.3 Evaluation of Kinetic Parameters and Sludge Characteristics

Kinetic parameters: Data generated through a series of steady-state experiments at various hydraulic retention times (1.5 to 2.5 days) using test water having an initial nitrate concentration of 120 mg/L (as N) have been used to assess the kinetic parameters. The study was conducted without excess solid recycle (solid concentration in each cycle was maintained constant removing excess solid after settling) for which the cell residence time (CRT) is equal to hydraulic retention time (HRT). Concentration of initial MLVSS was maintained at 200 mg/L at all HRT's. The reactor was operated at COD/NO_3^--N ratio of 2.00. Details of the experimental procedures are given in Sections 3.8.1 and 3.8.2. Since sufficient amount of ethanol was fed to the reactor which resulted in residual COD of ≥ 5 mg/L (Table 4.27) in the effluent, in all cases, it has been assumed that nitrate was the only rate limiting substrate. At each HRT, the concentration of MLVSS was measured at equal interval of time during reaction and averaged. These average concentrations have been used in the analysis of kinetic parameters. Estimation of the Monod kinetic parameters i.e. maximum specific denitrification rate (k_{max}), half saturation coefficient (K_s), yield coefficient (Y), and endogenous decay coefficient (k_d) was attempted by least square regression method using the following equations derived from the Monod kinetic relationships (Metcalf & Eddy, Inc., 1991; Dague et al., 1998).

$$\frac{X.HRT}{S_o - S_e} = \frac{K_s}{k_{\max}} \cdot \frac{1}{S_e} + \frac{1}{k_{\max}} \tag{4.4}$$

where X- biomass concentration, mg VSS/L

HRT- hydraulic retention time, d

S_o- influent nitrate concentration, mg NO_3^--N/L

S_e-effluent nitrate concentration, mg NO_3^--N/L

K_s- half saturation coefficient, mg NO_3^--N/L

k_{max}- maximum specific denitrification rate, mg NO_3^--N/ mg VSS.d, (d^-)

This equation was used to determine the half velocity constant (K_s) and the maximum rate of nitrate utilization (k_{max}) from a linear plot of $\frac{X.HRT}{S_o - S_e}$ versus $\frac{1}{S_e}$. The slope of this plot is equal to $\frac{K_s}{k_{\max}}$ and the y intercept is equal to $\frac{1}{k_{\max}}$.

$$\frac{1}{\theta_c} = Y\frac{S_o - S_e}{X.HRT} - k_d \tag{4.5}$$

where θ_c-cell residence time = HRT (without excess solid recycle), d

Y - Yield coefficient, mg VSS/mg NO_3^--N

k_d-endogenous decay coefficient, d^{-1}

This equation was used to determine the yield (Y) and the endogenous decay (k_d) coefficients from a linear plot of $\frac{1}{\theta_c}$ versus $\frac{S_o - S_e}{X.HRT}$. The slope of this plot is equal to Y and the y intercept is equal to ($-k_d$).

The maximum specific growth rate (μ_m) was calculated as :

$$\mu_m = k_{max}.Y \tag{4.6}$$

The generated laboratory data from denitrifying SBR (without excess solid recycle) and computation conducted to evaluate the kinetic parameters are shown in Table 4.27, while the plot of the regression lines are depicted in Figs 4.56 (a) and (b). The values of kinetic coefficients found from laboratory experimentation (including the results from this study) with various carbon sources are tabulated in Table 4.28.

Table 4.27 Data for Analysis of the Biological Kinetic Parameters Initial MLVSS- 200 mg/L, Initial Nitrate-N- 120 mg/L, COD/NO_3^--N=2.00

HRT (d)	Average X mg VSS/L	Residual nitrate-N (S_e), mg/L	Residual COD, (mg/L)	Nitrate removed (S_o-S_e)	X.HRT mg VSS/ d.L	$\frac{X.HRT}{S_o - S_e}$ (d)	$\frac{1}{S_e}$ (mg/L)$^{-1}$	$\frac{1}{HRT}$ (d^{-1})	$\frac{S_o - S_e}{X.HRT}$ (d)
1.50	235	6.0	13.5	114	352	3.10	0.17	0.67	0.33
1.75	268	3.0	8.0	117	469	4.00	0.33	0.57	0.24
2.00	275	1.5	5.5	118.5	550	4.64	0.67	0.50	0.21
2.25	282	1.0	5.0	119	634	5.32	1.00	0.44	0.18
2.50	285	0.6	5.5	119.4	715	5.98	1.67	0.40	0.16

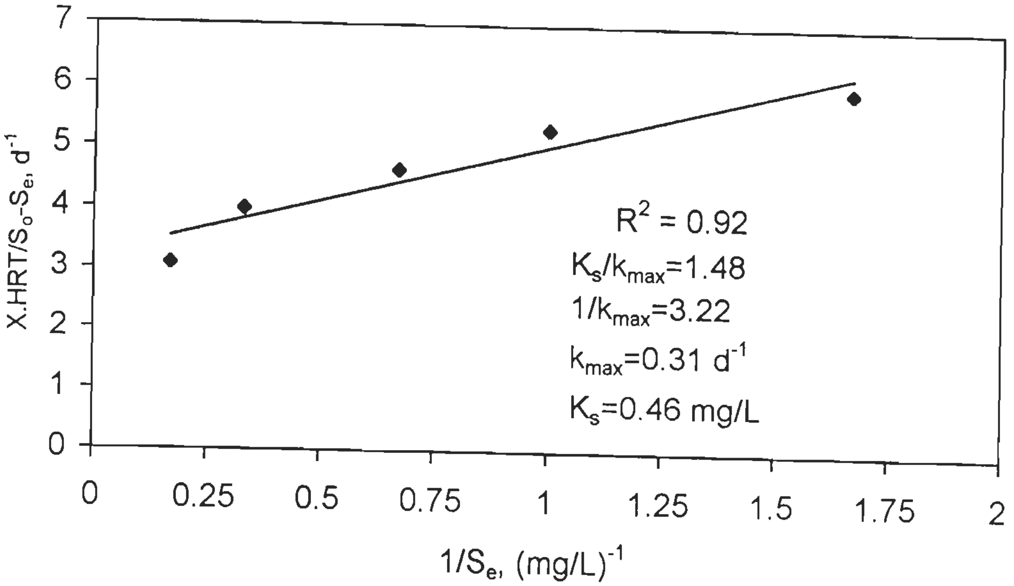


Fig. 4.56 (a) Linear regreasion of X.HRT/S_o-S_e Versus 1/S_e.

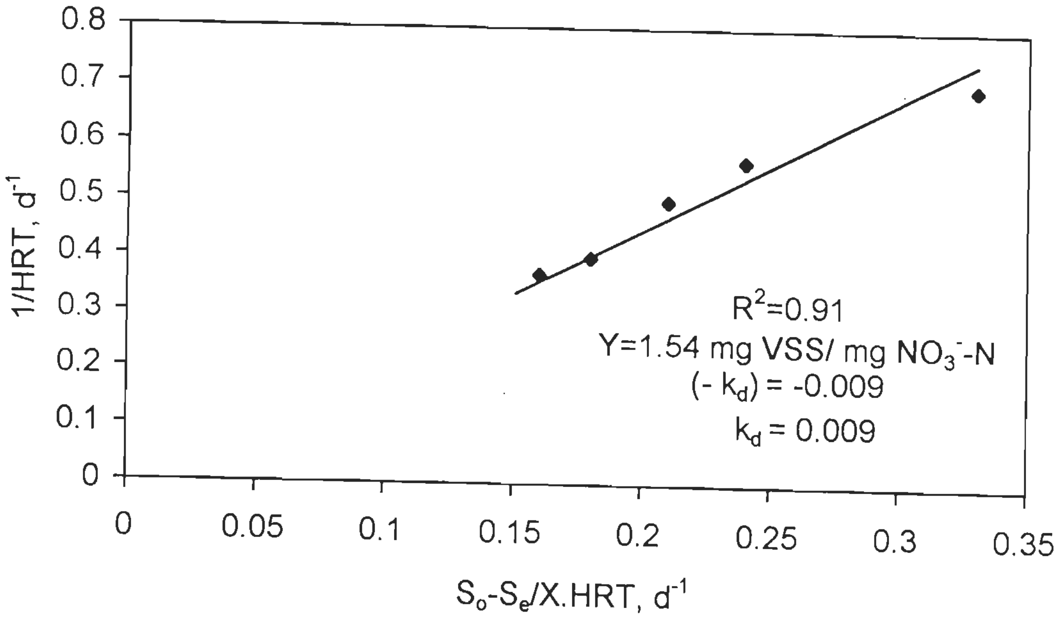


Fig. 4.56 (b) Linear regression of 1/HRT Versus S_o-S_e/ X.HRT.

Table 4.28 Kinetic Coefficients for Denitrification Process

Coefficient	Basis	Values with carbon sources as stated			
		Ethanol*	Methanol** (Beccari et al., 1983)	Glucose** (Beccari et al., 1983)	Wastewater** (With methanol as additional carbon source) (Metcalf & Eddy, Inc., 1991)
k_{max}	d^{-1}	0.31	0.32	0.062 - 0.070	---
K_s	mg NO_3^--N/L	0.46	0.08	0.6	0.06 - 0.20
Y	mgVSS/mgNO_3^--N	1.54	0.55 - 1.40	0.7	0.4 - 0.9
k_d	d^{-1}	0.009	---	---	0.04 - 0.08
μ_m	d^{-1}	0.48	---	5.7 - 6.8	0.3 - 0.9

* Present work

** Referenced

Sludge settling characteristics: Settling characteristic of the sludge was determined by settling a sample for 1 hour in a 1-L graduated cylinder and recording the interfacial height of the settling sludge at various time intervals (Cornwell and Susen, 1987) (Fig. 4.57). The sludge volume index (SVI) was calculated based on the sludge volume after 30 minutes settling. It was observed that the sludge settling was completed within the first 30 minutes showing good settling characteristic with SVI of 74. Christensen and Harremoës (1977) have reported SVI of denitrified sludge in the range of 25-300. The values of turbidity (3.0 to 4.9 NTU) of the denitrified water [Tables 4.30 (A-F)] were also low indicating good settling.

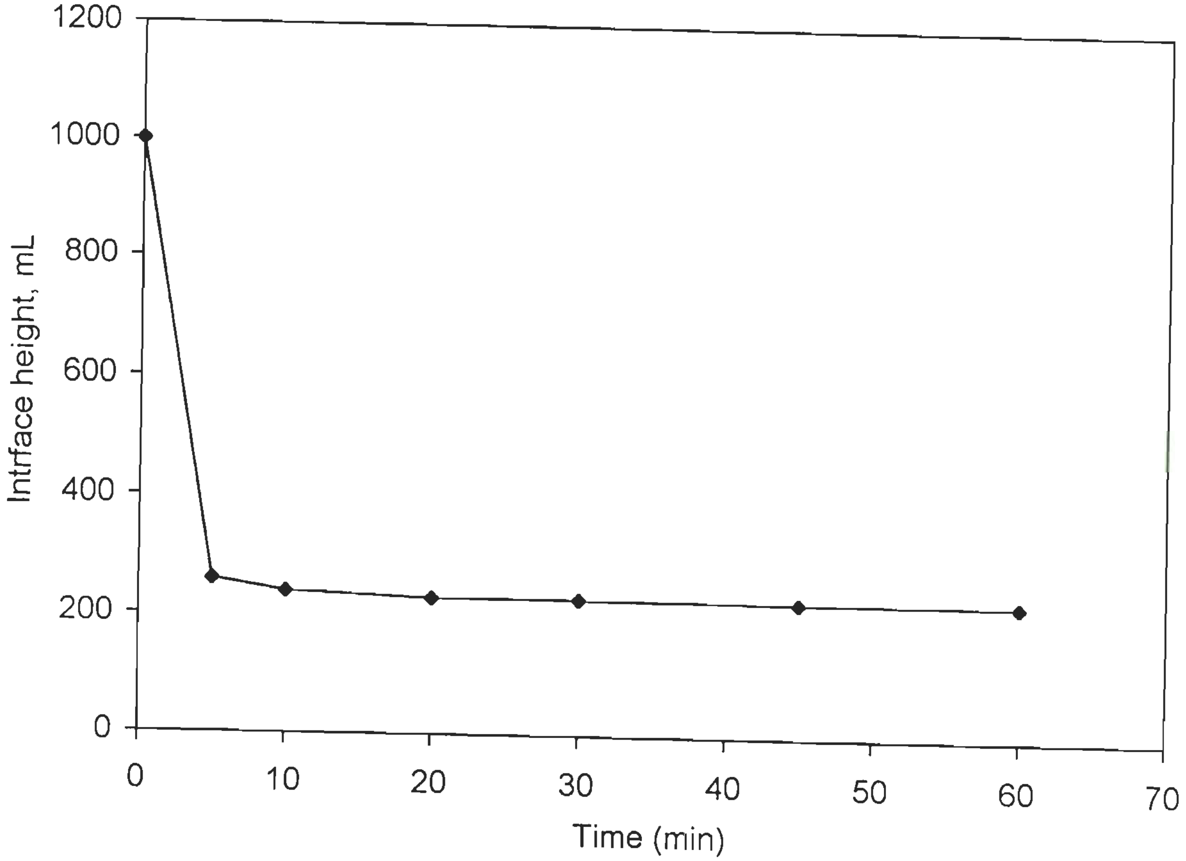


Fig. 4.57 Interfacial Sludge Height Versus Settling Time.

4.3.4 Effect of Length of Idle Time between the Operation Cycles on Denitrfication

As discussed in Section 4.3.2, the denitrifying SBR was found to be efficient in reducing initial nitrate concentration of water in the range of 40 to 250 mg/L (as N) to the allowable limit for drinking water within 3 to 7 hours reaction time depending on the initial nitrate concentrations. Thus, an SBR can be used with number of cycles per day. Accordingly length of idle time between the cycles may vary. Effect of length of idle time on denitrfication has not been studied previously. Therefore, this study was planned to examine the effect of variation in length of idle time on denitrification efficiency. The SBR was fed with water having a nitrate concentration of only 80 mg/L (as N), and COD/NO_3^--N ratio of 2. It was operated at ART of 3 hours and treated water was allowed to settle for 1 hour. Idle time gaps between two cycles studied were 1, 3, 6, and 14 hours. The complete details of the experimental procedures are given in Sections 3.8.1 and 3.8.2. The results are presented in Table 4.29. Significant difference in reduction of nitrate was not observed for length of idle times ranging from 1 to 14 hours. However, accumulation of slightly higher nitrite concentration at the shorter idle hour time gaps (1 and 3 hours) was noted. It can be concluded that duration of idle time has very insignificant effect on denitrfication.

Table 4.29 Effect of Length of Idle Time on Denitrification

Contact time (h)	Idle time (h)											
	1			3			6			14		
	Nitrate (mg/L as N)	Nitrite (mg/L as N)	Nitrate removal (%)	Nitrate (mg/L as N)	Nitrite (mg/L as N)	Nitrate removal (%)	Nitrate (mg/L as N)	Nitrite (mg/L as N)	Nitrate removal (%)	Nitrate (mg/L as N)	Nitrite (mg/L as N)	Nitrate removal (%)
0.0	78.5	0.0	0.0	81.0	0.0	0.0	79.0	0.0	0.0	78.0	0.0	0.0
0.1	---	1.9	---	---	2.4	---	---	3.2	---	---	1.85	---
3.0	8.0	0.08	89.8	7.5	0.05	90.7	6.0	0.01	92.4	5.0	0.01	93.6

4.3.5 Effect of Fluoride on Denitrification

The overall objective of this work was to develop an integrated biological and physicochemical treatment process for fluoride and nitrate removal. However, information regarding the effect of fluoride on the denitrification process is lacking. Hence, this investigation was carried out to examine the effect of different concentrations of fluoride i.e. 0 (control) to 20 mg/L on denitrification. Study was conducted using water sample having an initial nitrate concentration of 160 mg/L (as N) only and different concentrations of fluoride (as sodium fluoride) were added to the influent before it was fed to the denitrifying reactor as per experimental procedures outlined in Sections 3.8.1 and 3.8.2. At each fluoride concentration, the reactor was first acclimatized and then at steady-state nitrate, nitrite, COD, and pH were monitored for 9 hours reaction time with maximum intervals of two hours. The results are presented in Tables 4.30A and 4.30B. Average pH profile is plotted in Fig. 4.58. Results indicated that fluoride in the concentration range studied had no adverse effect

Table 4.30(A) Effect of Fluoride on Denitrification COD/NO_3^--N=2.00, Initial Nitrate ≈160 mg/L (as N)

Contact time (hour)	Fluoride concentration, mg/L																	
	0 (control)						6						10					
	Nitrate mg/L (as N)	Nitrite mg/L (as N)	COD mg/L	pH	Percent nitrate remov.	Percent COD remov.	Nitrate mg/L (as N)	Nitrite mg/L (as N)	COD mg/L	pH	Percent nitrate remov.	Percent COD remov.	Nitrate mg/L (as N)	Nitrite mg/L (as N)	COD mg/L	pH	Percent nitrate remov.	Percent COD remov.
0	164	0.0	321	7.15	0.0	0.0	158	0.0	319	7.10	0.0	0.0	163	0.0	322	7.15	0.0	0.0
0.1	---	2.5	---	8.25	---	-------	-------	2.35	------	8.20	--------	---------	--------	2.40	-------	8.30	--------	--------
1	14	1.3	25	8.85	91.5	92.2	12.5	1.15	22	8.90	92.1	93.1	13.5	1.05	26	9.05	91.7	91.9
3	8	0.01	19	8.60	95.1	94.1	7	0.01	17	8.70	95.6	94.6	7.5	0.01	19	8.85	95.4	93.8
5	6.5	0.01	15	8.50	96.0	95.3	5.5	0.01	15	8.50	96.5	95.3	5.0	0.01	16	8.60	96.9	95.0
7	4	0.01	12	8.40	97.5	96.3	3.5	ND	12	8.45	97.8	96.2	4.0	0.01	14	8.50	97.5	95.6
9	2	0.01	9	8.30	98.7	97.2	1.5	ND	8.5	8.35	99.1	97.3	2.5	ND	11	8.45	98.5	96.5

ND- not detected

Table 4. 30(B) Effect of Fluoride on Denitrification COD/NO_3^--N=2.00

Initial Nitrate ≈160 mg/L

Contact time (hour)	Fluoride concentration, mg/L											
	15						20					
	Nitrate mg/L (as N)	Nitrite mg/L (as N)	COD mg/L	pH	Percent nitrate remov.	Percent COD remov.	Nitrate mg/L (as N)	Nitrite mg/L (as N)	COD mg/L	pH	Percent nitrate remov.	Percent COD remov.
0	162	0.0	325	7.10	0.0	0.0	160	0.0	321	7.18	0.0	0.0
0.1	---	2.60	---	8.25	---	---	---	2.50	---	8.20	---	---
1	11	1.40	24	9.10	93.2	92.6	12	1.10	28	8.95	92.5	89.3
3	6.5	ND	19	8.95	96.0	94.2	9.5	0.01	21	8.75	94.1	93.4
5	5	ND	15	8.80	96.9	95.4	8	0.01	17	8.65	95.0	94.4
7	3	ND	11	8.70	98.1	96.6	6.5	ND	14	8.40	95.9	95.6
9	1	ND	7	8.55	99.4	97.8	5	ND	11	8.30	96.9	96.6

ND- not detected

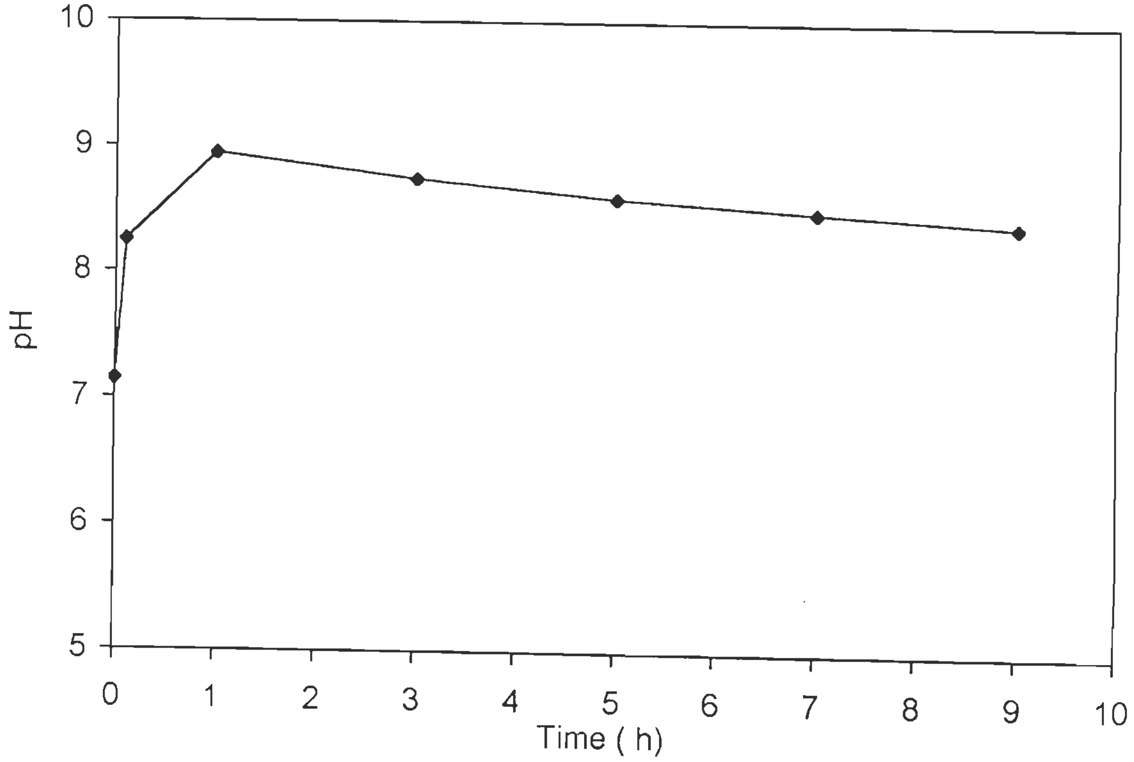


Fig. 4. 58 Average pH Profile of the Denitrification Process.

on denitrification. Traverso and Cecchi (1989) have reported that high concentration of sodium results in accumulation of nitrite concentration while in this study sodium fed along with fluoride did not show adverse effect on the process. This might be due to either the low concentration of sodium or the type of the microorganisms used in the study (Traverso and Cecchi, 1989). The average pH profile of the denitrification process (Fig. 4.58) showed increase of pH until one hour of reaction time, of which almost half of the total increase was within the first six minutes. After one hour, it decreased gradually (by 0.6 to 0.7 pH units) until the end of the reaction. Fang and Zhou (1999) observed that in anaerobic condition and in the presence of nitrate even though denitrification was the predominant process, at low values of nitrate relative to the COD concentration, methanogenesis also occurred. Hendriksen and Ahring (1996) also reported simultaneous occurrence of denitrification and methanogenesis in a UASB reactor in the presence of nitrate. Chen and Lin (1993) and Lin and Chen (1995) studied the possibility of coexistence of methane formation bacterias and denitrifiers in a mixed culture and coimmobilized mixed culture system respectively and concluded that methane formation could occur after completion of dentrification. In this case also with the reduction of nitrate concentration to a certain low value possibly methanogenesis occurred and resulted in reduction of pH.

4.4 INTEGRATED NITRATE AND FLUORIDE TREATMENT PROCESS

4.4.1 Evaluation of Sequence of the Treatment Process

There could two possibilities relating to this sequence of treatment: (i) defluoridation followed by denitrification, and (ii) denitrification followed by defluoridation. In wastewater treatment usually physicochemical treatment precedes biological processes. However, in this case, denitrification-defluoridation was thought technically a better choice for the following reasons:

(i) Defluoridation using alum-PAC slurry works best in the pH range of 5.8 to 6.5. Hence, the pH of the defluoridated water after treatment by alum-PAC slurry would be in the range of 5.8 to 6.5 which is relatively low if it is to be fed into a denitrification reactor (for which the optimum pH ranges from 7 to 9) (Christensen and Harremoës, 1977).

(ii) The alkalinity drops when alum-PAC slurry is added for defluoridation. To compensate this, alkalinity is adjusted using lime for effective fluoride removal. On the other hand alkalinity is produced during denitrification. If denitrification precedes defluoridation, addition of lime could either be reduced or completely avoided.

(iii) Since denitrification is a biological process and ethanol and nutrients are added at that stage, the denitrified effluent may contain residual amounts of turbidity, COD, sulfide, nitrogen, and denitrifying microorganisms. Since, during defluoridation, alum-PAC slurry is added, the contents are mixed, and the alum-fluoride flocs are allowed to settle along with coated or uncoated PAC, these residuals from the denitrifying reactor may also be removed along with fluoride. This would eliminate the need of additional treatment.

(iv) The defluoridated effluent contained a high concentration of sulfate (maximum of 400 mg/L) compared to influent (20 mg/L). This was within an acceptable limit (WHO 1984). However, if denitrification were to be followed by defluoridation, this could result in conversion of sulfate to sulfide and build up of excessive concentrations of sulfide in the effluent, as well as leading to deterioration of water quality as it is known to be toxic (Sauthier et al., 1998).

Based on the above, the denitrification-defluoridation sequence was thought be better and this is the sequence that was studied.

4.4.2 Overall Efficiency of the Denitrification-Defluoridation Treatment Process

Experiments were conducted to evaluate the overall efficiency of the integrated treatment process in producing potable water quality. Studies were conducted on bench-scale cylindrical denitrifying-defluoridating SBRs having working volumes of 5-L and 1-L respectively (Fig. 3.4). The reactors were operated at optimum conditions (operation procedures, COD/NO_3^--N ratio, ARTs, alum and PAC doses, and pH) studied previously. Details of the experimental setup and test procedures are given in Sections 3.8 and 3.9. Twenty four water samples with nitrate concentrations of 40, 80, 120, 160, 200, and 250 mg/L (as N) and fluoride concentrations of 6, 10, 15, and 20 mg/L in various combinations were investigated. For all the twenty four water samples, the optimum alum doses studied previously (Section 4.2.3) i.e. 500, 600, 800, and 900 mg/L along with 100 mg/L of PAC were initially tried for fluoride concentrations of 6, 10, 15, and 20 mg/L respectively. Thereafter, the alum dose was increased to 600, 800, and 850 mg/L for the three water samples having 80 mg/L of nitrate and initial fluoride concentrations of 6, 10, and 15 mg/L respectively, to reduce initial fluoride concentrations to 1.5 mg/L. It was also increased to 700 and 900 mg/L for the two water samples having 120 mg/L of nitrate and initial fluoride concentrations of 6 and 10 mg/L respectively, to reduce initial fluoride concentrations below 2 mg/L. Along with fluoride and nitrate, nine other related water quality parameters i.e. nitrite, COD, sulfate, sulfide, aluminum, alkalinity, pH, turbidity, and MPN were analyzed in the influent, and the effluents from denitrification and defluoridation stages. The results are presented in Tables 4.31(A-F) and 4.32, plotted in Figs. 4.59 through 4.67 and discussed below.

Fluoride and nitrate concentrations in treated water samples are shown by Fig. 4.59 (a) and (b) respectively. Fluoride concentrations varied from 1.35 to 7.05 mg/L whereas nitrate concentrations varied from 2.5 to 8.5 mg/L (as N). While nitrate concentration was reduced to a value below the acceptable level for all the 24 water samples, fluoride concentration was observed to be less than 1.5 mg/L only in case of 3 water samples. Fluoride in water samples having initial fluoride concentrations of 6, 10, and 15 mg/L along with 40 mg/L of nitrate-N was reduced below 1.5 mg/L [Fig. 4.59(a)]. However, in the case of water samples having an initial fluoride concentration of 20 mg/L, it was reduced only to 3.05 mg/L. Fluoride in water samples with concentrations of 6, 10, and 15 mg/L along with 80 mg/L of nitrate-N was reduced to the level of below 2 mg/L [Fig. 4.59(a)]. However, because of excessive alkalinity of the denitrified effluent (545 to 560 mg/L as $CaCO_3$) [Fig. 4.60(a)], fluoride could not be reduced to the level of 1.5 mg/L by alum-PAC slurry using the optimum alum doses i.e. 500, 600, and 800 mg/L of alum along with 100 mg/L of PAC for initial fluoride concentrations of 6, 10, and 15 mg/L respectively. Fluoride concentration of 20 mg/L was reduced only to 3.25 mg/L. When the alum doses were increased to 600, 800, and 850 mg/L (from originally tried values of 500, 600, and 800 mg/L) for initial fluoride concentrations of 6, 10, and 15 mg/L respectively along with 100 mg/L of PAC, it resulted in reduction of fluoride concentrations ≤ 1.5 mg/L (Table 4.32). Thus, the use of alum-PAC slurry for defluoridation resulted in reduction of alum dose by 40 and 43% (at 40 mg/L nitrate-N) and 20 and 39% (at 80 mg/L nitrate-N) for initial fluoride concentrations of 10 and 15 mg/L respectively compared to defluoridation by alum and lime alone (Fig. 4.61). In cases involving all of the water samples having an initial concentration of nitrate ≥ 120 mg/L, high alkalinity of the denitrified effluent (715 to

1175 mg/L as $CaCO_3$) [Fig. 4.60(a)] inhibited fluoride reduction to 1.5 mg/L by alum-PAC slurry using doses referred to above. In case of an initial nitrate concentration of 120 mg/L, increase of alum doses to 700 and 900 mg/L (from originally tried values of 500 and 600 mg/L) reduced initial fluoride concentrations of 6 and 10 mg/L respectively to the level in the range of 1.5 to 2 mg/L (Table 4.32). For the remaining initial nitrate concentrations (> 120 mg/L), higher doses of alum i.e. 600, 800, 850, and 900 mg/L were not tried as it was found that even with this increase in doses reduction of fluoride to the level of 1.5 mg/L was not possible. Alum doses of > 900 mg/L were not used, as it would have resulted in unacceptable concentrations of both aluminum and sulfate in treated water. In all cases (40 – 250 mg/L as N), initial nitrate concentrations were reduced to a value below the acceptable level (< 10 mg/L as N) [Fig. 4.59(b)]. Thus, the integrated treatment process appeared to be promising for nitrate and fluoride concentrations as high as 80 mg/L (as N) and 15 mg/L respectively. In cases of initial nitrate concentrations of > 80 mg/L (as N), to achieve the acceptable fluoride value of 1.5 mg/L, defluoridation by alum-PAC slurry along with adjustment of optimal alkalinity using acid could be tried.

In most cases, nitrite concentrations were not detected [Fig. 4.62a)] and, in few cases (at nitrate concentrations of ≥ 120 mg/L (as N)), sulfide was found in the denitrified effluent in the concentration range of 0.2 to 0.4 mg/L [Fig. 4.62(b)]. This could be because of reduction of sulfate available in the water (20 mg/L as SO_4^{2-}) to sulfide in the presence of excess COD in the denitrified water [Fig. 4.63(a)]. Sauthier et al. (1998) in their study on denitrification by immobilized culture also observed the reduction of sulfate to sulfide in the presence of excess organic matter. However, it was not found to be present in detectable range in water samples after defluoridation indicating its removal at this stage. In the denitrified-defluoridated effluent, residual COD did not appear in detectable concentrations in the case of initial nitrate concentrations of 40 to 120 mg/L suggesting its removal at the defluoridation stage. Whereas at nitrate concentrations greater than 120 mg/L, residual COD was observed in the range of 1 to 4 mg/L [Fig. 4.63(b)]. This could be attributed to the high pH (> 7) of the denitrified-defluoridated effluent [Fig. 4.64(b)] as the optimum pH for organic removal by alum is less than 7 (Semmen and Field, 1980 ; Randtke, 1988).

Average pH and alkalinity for each nitrate concentration of the denitrified effluent were in the ranges of 8 to 9 [Fig. 4.64(a)] and 445 to 1156 mg/L as $CaCO_3$ [Fig. 4.60(a)] respectively, increasing with increase of initial nitrate concentrations. Thus the pH was in the optimum range (7 to 9) for denitrification reported in literature (Christensen and Harremoës 1977). The average alkalinity production rate of the denitrification process was calculated to be 3.53 mg as $CaCO_3$ per mg of nitrate reduced to nitrogen gas, which nearly approached to the stoichiometric value of 3.57 (Miyaji et al., 1980; Gayle et al., 1989). At an initial nitrate concentration of 40 mg/L (for all the four fluoride concentrations) and 80 mg/L (for fluoride concentration of 20 mg/L), the pH of denitrified-defluoridated effluent was found in the optimum range (5.8 to 6.5). However, at all other initial nitrate concentrations, the pH was above the maximal optimum (6.5), being in the range of 6.6 to 8.2 [Fig. 4.64(b)]. Therefore, the optimum alum doses for initial fluoride concentrations of 10 and 15 mg/L (600 and 800 mg/L) found earlier, during the jar tests, in this case have been increased to 800 and 850 mg/L respectively, to reduce the pH to its optimal value at initial nitrate concentration of 80 mg/L (Table 4.32). The residual alkalinity of the denitrified-defluoridated effluent varied in the ranges of 210 to 935, 185 to 910, 90 to 750, and 45 to 730 mg/L as $CaCO_3$ for initial fluoride concentrations of 6, 10, 15, and 20 mg/L respectively. Alkalinity and pH in the denitrified-defluoridated water samples [Fig. 4.60(b) and 4.64(b)] were found to be increasing and decreasing respectively with increase of initial nitrate and fluoride concentrations. Alkalinity produced at the denitrifcation stage avoided the use of lime at the defluoridation stage, in cases of nitrate values up to 80 mg/L (as N). While it inhibited reduction of fluoride to the desired level of 1.5 mg/L using the doses of alum-PAC slurry referred to above at relatively high nitrate concentrations (≥ 120 mg/L), increasing the pH in the range of 8.45-9.00.

In the denitrified-defluoridated effluent, at initial nitrate concentrations up to 120 mg/L (as N), residual aluminum was in the range of 0.12 to 0.20 mg/L for initial fluoride concentrations of 6, 10, and 15 mg/L respectively. With an initial fluoride concentration of 20 mg/L, higher values in the range of 0.26 to 0.80 mg/L were observed, which increased with decrease of initial nitrate concentration (Fig. 4 65). The pH of the water samples with initial fluoride concentrations of 6, 10, and 15 mg/L varied in the range of 6.05 to 7.25. The pH of the water samples having 20 mg/L of fluoride varied in the range from 5.90 to 6.70, increasing with increase of initial nitrate concentrations in both cases [Fig. 4.64(b)]. At an initial nitrate concentrations ≥ 160 mg/L, an residual aluminum concentration was observed in the range of 0.05 to 2.79 mg/L which increased with increase of initial nitrate concentration for all fluoride concentrations (Fig. 4.65). At these initial nitrate concentrations residual aluminum also increased with decrease of initial fluoride concentrations. The pH of these treated water samples varied in the ranges of 7.85 to 8.20, 7.70 to 8.10, 7.35 to 7.75, and 7.15 to 7.55 for initial fluoride concentrations of 6, 10, 15, and 20 mg/L increasing with increase of initial nitrate concentrations. It also varied in the ranges of 7.15 to 7.85, 7.40 to 7.90, and 7.55 to 8.2 for 160, 200, and 250 mg/L initial nitrate concentrations respectively increasing with decrease of initial fluoride concentrations [Fig. 4.64(b)]. Comparison of Figs. 4.64(b) and 4.65 and perusal of the data of pH and residual aluminum in Tables 4.31 (A-F), in most cases, show very low values of residual aluminum at a pH range of 6.05 to 7.35. A minimum residual aluminum concentration of 0.05 mg/L was observed at pH of 7.15. With increase of pH (> 7.15) of denitrified-defluoridated water samples, residual aluminum concentration also increased to a maximum of 2.79 mg/L at pH of 8.20. On the other hand, for water samples of pH < 7.15, the aluminum concentration increased with decrease in pH to a maximum of 0.8 mg/L at the lowest observed pH of treated water of 5.90. Culp and Stoltenberg (1958) have observed minimum residual aluminum in the pH range of 6.5 to 7.5.

In the denitrified-defluoridated effluent, increase of sulfate concentration almost proportional to the increase in initial fluoride concentrations (and with that the alum dose) was also observed (Fig 4.66). However, it was within the maximum allowable limit of 400 mg/L as SO_4^{2-} (WHO 1984) in all cases. The turbidity of the denitrified effluent varied in the range of 3 to 5 NTU [Fig. 4.67(a)] showing a maximum increase of the water turbidity by 3.7 NTU. However, after defluoridation, this was reduced to the level of the influent turbidity (average 1.3 NTU) or even below it [Fig. 4.67 (b)]. In the denitrified and denitrified-defluoridated water samples, the MPN index/100 mL was found to be less than 1.1 indicating the absence of coliform bacteria in the biocommunity of denitrifiers.

Table 4.31(A) Overall Efficiency of the Denitrification-Defluoridation Treatment Process

Initial Nitrate Concentration- 40 mg/L (as N),   ART for Denitrification -3 h

Alum Doses-500, 600, 800, and 900 mg/L for 6, 10, 15, and 20 mg/L Initial Fluoride Concent. Respectively,   PAC Dose-100 mg/L

Water quality parameters	Unit	Fluoride concentration, mg/L											
		6			10			15			20		
		Influent	Effluent		influent	Effluent		influent	Effluent		influent	Effluent	
			denitrification	defluoridation		denitrification	defluoridation		denitrification	defluridation		denitrification	defluoridation
Fluoride	mg/L	6.00	5.90	1.45	10.00	10.00	1.35	15.00	15.15	1.40	20.00	19.90	3.05
Nitrate (as N)	mg/L	40.00	5.50	5.50	40.00	4.50	4.50	40.00	5.00	5.00	40.00	3.00	2.5
Nitrite (as N)	mg/L	ND	0.01	ND	ND	0.015	ND	ND	0.02	ND	ND	ND	ND
COD	mg/L	81.00	6.00	0.00	80.00	6.50	0.00	82.00	4.00	0.00	79.00	4.00	0.00
Sulfate	mg/L	20.00	20.00	241.00	20.00	20.00	285.50	20.00	20.00	365.00	20.00	20.00	396.80
Sulfide	mg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aluminum *	mg/L	ND	ND	ND	ND	ND	0.15	ND	ND	0.20	ND	ND	0.80
Alkalinity **	mg/L	310.00	430.00	210.00	310.00	440.00	185.00	310.00	450.00	90.00	310.00	455.00	45.00
pH	unit	7.35	8.05	6.55	7.30	8.10	6.35	7.30	8.10	6.05	7.40	8.00	5.90
Turbidity	NTU	1.30	3.50	1.20	1.35	3.00	1.10	1.25	3.20	0.90	1.40	4.20	1.20
MPN	Index	---	---	< 1.1	---	---	< 1.1	---	---	< 1.1	< 1.1	< 1.1	<1.1

* as Al (III)   ** total alkalinity (as $CaCO_3$)   The unit for MPN is index/100 mL   ND- not detected   --- not measured

Table 4.31(B) Overall Efficiency of the Denitrification-Defluoridation Treatment Process
Initial Nitrate Concentration-80 mg/L (as N), ART for Denitrification-3 h
Alum Doses- 500, 600, 800, and 900 mg/L for 6, 10, 15, and 20 mg/L Initial Fluoride Concent. Respectively, PAC Dose-100 mg/L

Water quality parameters	Unit	Fluoride concentration, mg/L											
		6			10			15			20		
		Influent	Effluent		Influent	Effluent		Influent	Effluent		Influent	Effluent	
			denit-rification	defluor-idation		denit-rification	defluor-idation		denit-rification	defluor-idation		denit-rification	defluor-idation
Fluoride	mg/L	6.00	6.00	1.85	10.00	10.10	1.75	15.00	15.00	1.65	19.90	20.00	3.25
Nitrate (as N)	mg/L	80.00	6.50	6.50	80.00	4.50	4.00	80.00	5.50	5.50	80.00	7.00	6.50
Nitrite (as N)	mg/L	ND	0.01	ND	ND	0.015	ND	ND	0.01	ND	ND	0.02	0.01
COD	mg/L	163.00	13.00	ND	161.00	7.00	ND	158.00	8.00	ND	156.00	9.50	ND
Sulfate	mg/L	20.00	18.50	235.00	20.00	20.00	283.00	20.00	20.00	370.00	20.00	19.50	398.00
Sulfide	mg/L	ND	0.25	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aluminum *	mg/L	ND	ND	0.12	ND	ND	0.14	ND	ND	0.14	ND	ND	0.46
Alkalinity **	mg/L	305.00	560.00	345.00	315.00	545.00	265.00	310.00	550.00	185.00	310.00	555.00	155.00
pH	unit	7.35	8.25	6.90	7.30	8.30	6.80	7.35	8.20	6.60	7.30	8.25	6.35
Turbidity	NTU	1.15	3.50	1.20	1.25	3.75	1.15	1.30	4.50	1.20	1.30	4.25	1.25
MPN	Index	----	----	< 1.1	----	----	< 1.1	< 1.1	< 1.1	< 1.1	----	---	< 1.1

* as Al (III), ** total alkalinity (as $CaCO_3$)

Table 4.31(C) Overall Efficiency of the Denitrification-Defluoridation Treatment Process

Initial Nitrate Concentration-120 mg/L (as N), ART for Denitrification-3 h

Alum Doses-500, 600, 800, and 900 mg/L for 6, 10, 15, and 20 mg/L Initial Fluoride Concent. Respectively, PAC Dose- 100 mg/L

Water quality parameters	Unit	Fluoride concentration, mg/L											
		6			10			15			20		
		Influent	Effluent		Influent	Effluent		Influent	Effluent		Influent	Effluent	
			denit-rification	defluor-idation		denit-rification	defluor-idation		denit-rification	defluor-idation		denit-rification	defluor-idation
Fluoride	mg/L	6.00	6.10	2.35	10.00	10.00	3.05	15.00	14.90	2.55	20.00	20.10	4.10
Nitrate (as N)	mg/L	120.00	7.00	7.00	120.00	8.50	8.00	120.00	6.50	6.50	120.00	7.50	7.50
Nitrite (as N)	mg/L	ND	0.01	ND	ND	ND	ND	ND	0.015	0.01	ND	0.01	ND
COD	mg/L	242.00	15.00	ND	236.00	13.00	ND	238.00	15.00	ND	244.00	18.00	ND
Sulfate (SO_4)	mg/L	20.00	18.50	243.00	20.00	19.50	280.00	20.00	18.00	368.00	20.00	19.00	395.00
Sulfide	mg/L	ND	0.35	ND	ND	0.20	ND	ND	0.40	ND	ND	0.25	ND
Aluminum *	mg/L	ND	ND	0.20	ND	ND	0.18	ND	ND	0.17	ND	ND	0.23
Alkalinity **	mg/L	310.00	715.00	480.00	310.00	718.00	450.00	305.00	725.00	380.00	310.00	735.00	345.00
pH	unit	7.40	8.45	7.25	7.40	8.55	7.15	7.35	8.50	6.85	7.35	8.45	6.70
Turbidity	NTU	1.25	4.00	1.20	1.20	4.20	1.30	1.25	3.90	1.30	1.20	3.70	1.40
MPN	Index	----	----	< 1.1	< 1.1	<1.1	< 1.1	----	----	< 1.1	----	----	< 1.1

* as Al (III) ** total alkalinity (as $CaCO_3$)

Table 4.31(D) Overall Efficiency of the Denitrfication-Defluoridation Treatment Process

Initial Nitrate Concentration-160 mg/L (as N), ART for Denitrification-3 h

Alum Doses- 500, 600, 800, and 900 mg/L for 6, 10, 15, and 20 mg/L Initial Fluoride Concent. Respectively, PAC Dose- 100 mg/L

Water quality parameters	Unit	Fluoride concentration, mg/L											
		6			10			15			20		
		Influent	Effluent		Influent	Effluent		Influent	Effluent		Influent	Effluent	
			denitrification	defluoridation		denitrification	defluoridation		denitrification	defluoridation		denitrification	Defluoridation
Fluoride	mg/L	6.00	6.00	2.85	10.00	10.00	4.05	15.00	15.00	4.25	20.00	20.00	5.50
Nitrate (as N)	mg/L	160.00	5.50	5.50	160.00	6.50	6.50	158.00	6.00	6.00	163.00	3.50	3.00
Nitrite (as N)	mg/L	ND	0.02	ND	ND	0.01	ND	ND	ND	ND	ND	ND	ND
COD	mg/L	318.00	16.00	3.50	322.00	14.00	2.50	320.00	12.00	ND	316.00	9.00	ND
Sulfate	mg/L	20.00	18.00	238.00	20.00	19.50	275.00	20.00	20.00	360.00	20.00	18.50	405.00
Sulfide	mg/L	ND	0.30	ND	ND	ND	ND	ND	ND	ND	ND	0.30	ND
Aluminum *	mg/L	ND	ND	0.84	ND	ND	0.71	ND	ND	0.26	ND	ND	0.05
Alkalinity **	mg/L	310.00	850.00	635.00	315.00	855.00	595.00	310.00	860.00	470.00	315.00	875.00	485.00
pH	unit	7.35	8.75	7.85	7.35	8.80	7.70	7.40	8.90	7.35	7.30	8.80	7.15
Turbidity	NTU	1.30	4.50	1.25	1.20	3.90	1.30	1.35	4.20	1.20	1.40	4.10	1.30
MPN	Index	< 1.1	< 1.1	< 1.1	----	----	< 1.1	----	----	< 1.1	----	---	<1.1

* as Al (III) ** total alkalinity (as $CaCO_3$)

Table 4.31(E) Overall Efficiency of the Denitrification-Defluoridation Treatment Process

Initial Nitrate Concentration- 200 mg/L (as N), ART for Denitrification- 5 h

Alum Doses- 500, 600, 800, and 900 mg/L for 6, 10, 15, and 20 mg/L Initial Fluoride Concent. Respectively, PAC Dose- 100 mg/L

Water quality parameters	Unit	Fluoride concentration, mg/L											
		6			10			15			20		
		Influent	Effluent		Influent	Effluent		Influent	Effluent		Influent	Effluent	
			denitrification	defluoridation		denitrification	defluoridation		denitrification	defluoridation		denitrification	defluoridation
Fluoride	mg/L	6.00	6.00	3.45	10.00	10.10	4.55	15.00	15.00	4.95	20.00	19.90	6.10
Nitrate (as N)	mg/L	200.00	6.50	6.50	200.00	5.00	5.00	200.00	8.50	8.50	200.00	4.00	4.00
Nitrite (as N)	mg/L	ND	ND	ND	ND	0.01	ND	ND	0.02	0.01	ND	ND	ND
COD	mg/L	402.00	13.50	3.00	405.00	12.00	1.50	400.00	10.50	1.00	395.00	8.50	ND
Sulfate (SO_4)	mg/L	20.00	20.00	241.00	20.00	19.50	285.00	20.00	20.00	358.00	20.00	19.00	394.00
Sulfide	mg/L	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.25	ND
Aluminum *	mg/L	ND	ND	1.27	ND	ND	1.59	ND	ND	1.19	ND	ND	1.18
Alkalinity **	mg/L	310.00	980.00	765.00	310.00	1005.00	730.00	310.00	995.00	645.00	310.00	990.00	625.00
pH	unit	7.35	8.95	7.90	7.35	8.90	7.80	7.40	8.95	7.55	7.35	8.90	7.40
Turbidity	NTU	1.20	3.80	1.25	1.35	4.10	1.20	1.30	4.10	1.30	1.30	4.00	1.15
MPN	Index	---	---	< 1.1	----	----	< 1.1	< 1.1	< 1.1	< 1.1	----	----	< 1.1

* as Al (III) ** total alkalinity (as $CaCO_3$)

Table 4.31(F) Overall Efficiency of the Denitrification-Defluoridation Treatment Process
Initial Nitrate Concentration-250 mg/L (as N), ART for Denitrification-7 h
Alum Doses- 500, 600, 800, and 900 mg/L for 6, 10, 15, and 20 mg/L Initial Fluoride Concent. Respectively, PAC Dose-100 mg/L

Water quality parameters	Unit	Fluoride concentration, mg/L											
		6			10			15			20		
		Influent	Effluent		Influent	Effluent		Influent	Effluent		Influent	Effluent	
			denit-rification	defluor-idation		denit-rification	defluor-idation		denit-rification	defluor-idation		denit-rification	defluor-idation
Fluoride	mg/L	6.00	5.90	3.70	10.00	10.00	4.85	15.00	15.00	6.10	20.00	20.00	7.05
Nitrate (as N)	mg/L	250.00	4.50	4.50	250.00	2.00	2.00	250.00	3.50	3.50	250.00	5.0	5.00
Nitrite (as N)	mg/L	ND	0.01	0.01	ND	ND	ND	ND	0.01	ND	ND	ND	ND
COD	mg/L	505.00	9.50	4.00	495.00	8.00	3.50	502.00	10.50	2.50	506.00	12.5	3.00
Sulfate (SO_4)	mg/L	20.00	19.50	237.00	20.00	19.00	278.00	20.00	18.50	365.00	20.00	18.5	401.00
Sulfide	mg/L	ND	ND	ND	ND	0.35	ND	ND	ND	0.40	ND	0.35	ND
Aluminum *	mg/L	ND	ND	2.79	ND	ND	2.31	ND	ND	1.69	0.00	0.00	1.63
Alkalinity **	mg/L	310.00	1160.00	935.00	310.00	1175.00	910.00	310.00	1135.00	750.00	310.00	1155.00	730.00
pH	unit	7.40	9.00	8.20	7.40	9.05	8.10	7.35	9.00	7.75	7.35	8.95	7.55
Turbidity	NTU	1.30	4.25	1.35	1.30	4.50	1.40	1.35	4.85	1.40	1.25	4.90	1.35
MPN	Index	---	---	< 1.1	---	---	< 1.1	< 1.1	< 1.1	< 1.1	---	---	< 1.1

* as Al (III) ** total alkalinity (as $CaCO_3$)

Table 4.32 Alum Dose Requirement (Incorporated with 100 mg/L of PAC) to Reduce Initial Fluoride below 2 mg/L at Various Nitrate Concentrations

Initial nitrate-N, mg/L	Initial fluoride, mg/L	Alum dose, mg/L					
		500	600	700	800	850	900
		Residual fluoride concentration, mg/L					
40	6	1.45	---	---	---	---	---
	10	---	1.35	---	---	---	---
	15	---	---	---	1.40	---	---
80	6	---	1.45	---	---	---	---
	10	---	---	---	1.40	---	---
	15	---	---	---	---	1.50	---
120	6	---	---	1.80	---	---	---
	10	---	---	---	---	---	1.70

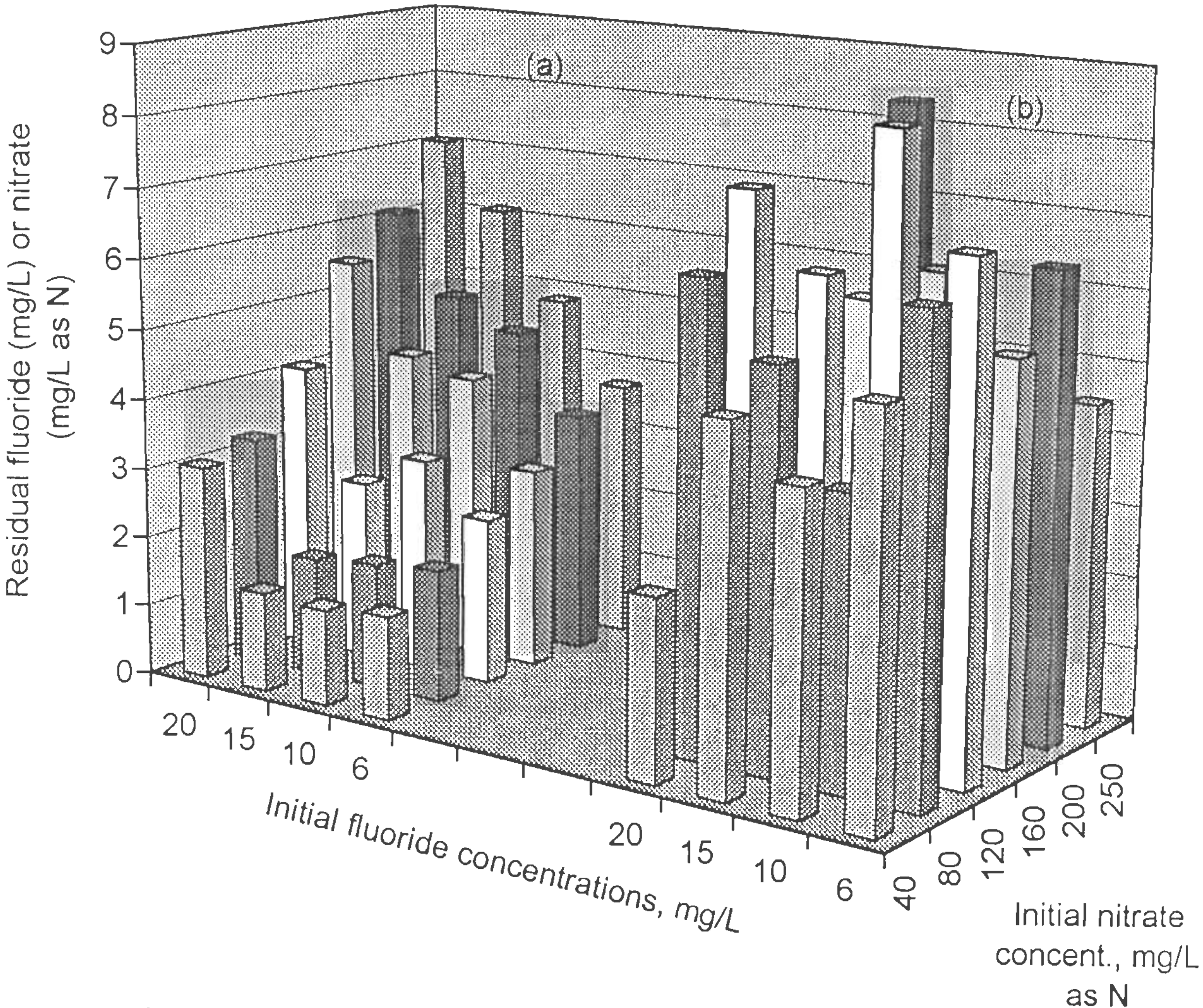


Fig. 4.59 (a-b) Residual Fluoride (a) and Nitrate (b) at Various Initial Fluoride and Nitrate Concentrations in the Denitrified-Defluoridated Water Samples.

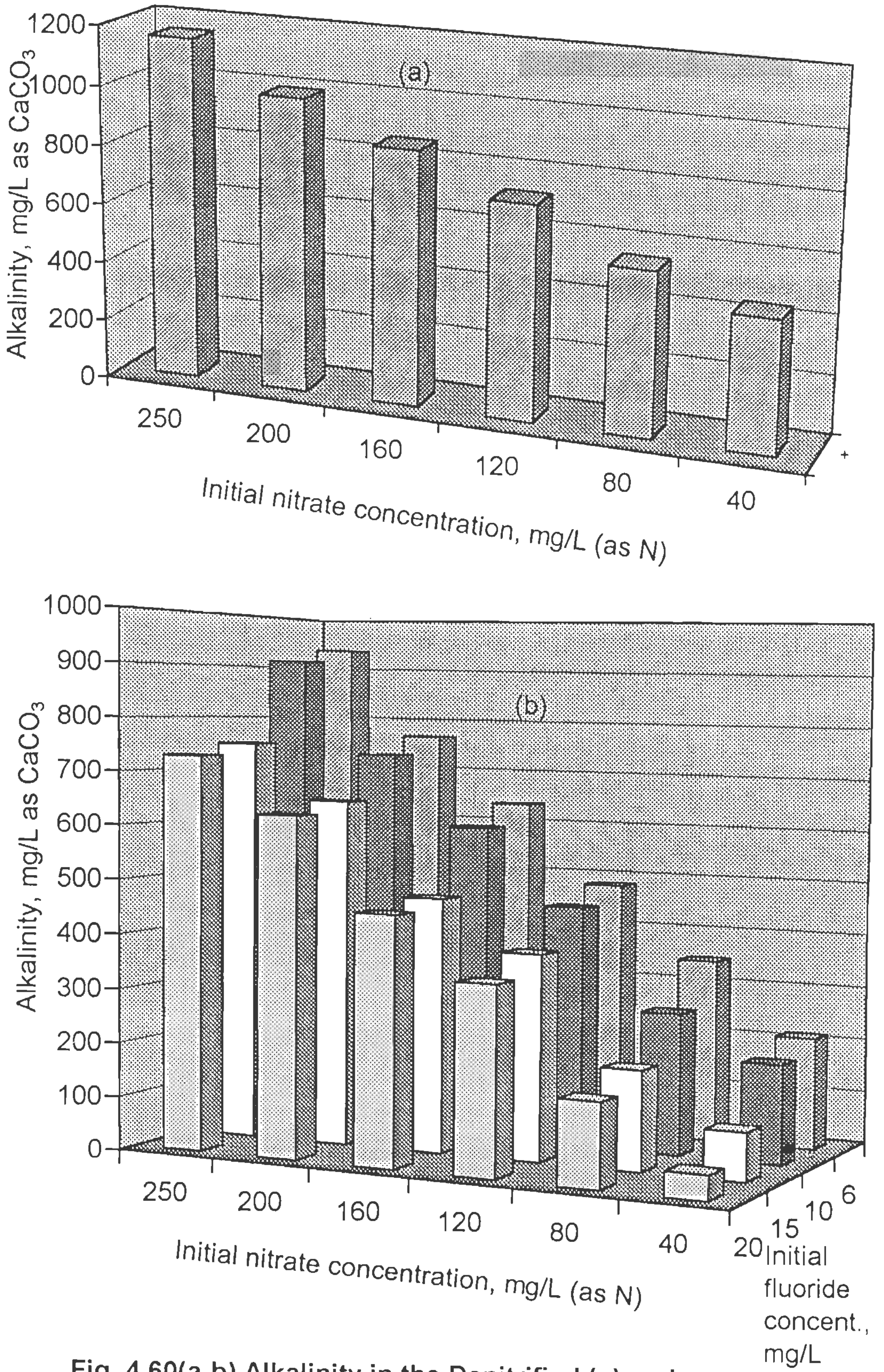


Fig. 4.60(a-b) Alkalinity in the Denitrified (a) and Denitrified-Defluoridated (b) Water Samples.

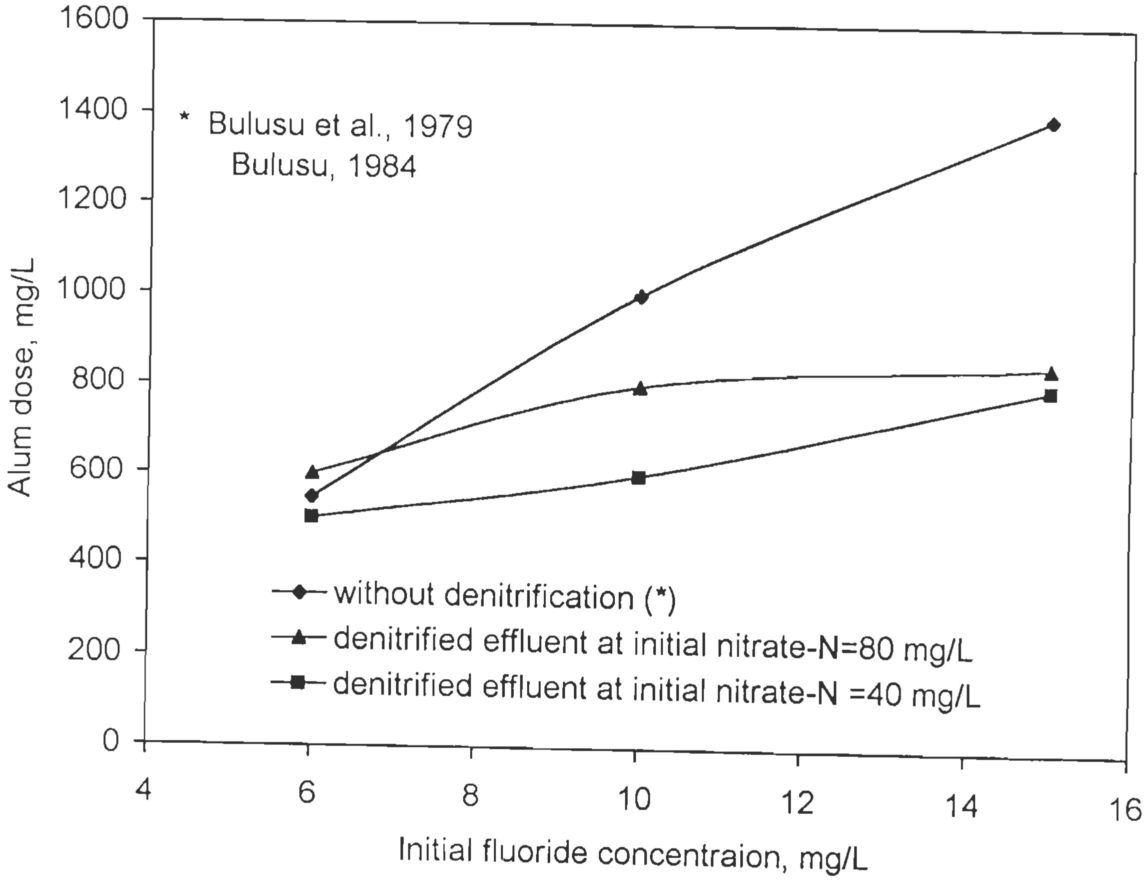


Fig.4.61 Alum Dose Requirement to Reduce Initial Fluoride Concentrations to 1.5 mg/L by Alum-PAC Slurry in the Integrated Nitrate and Fluoride Treatment Process.

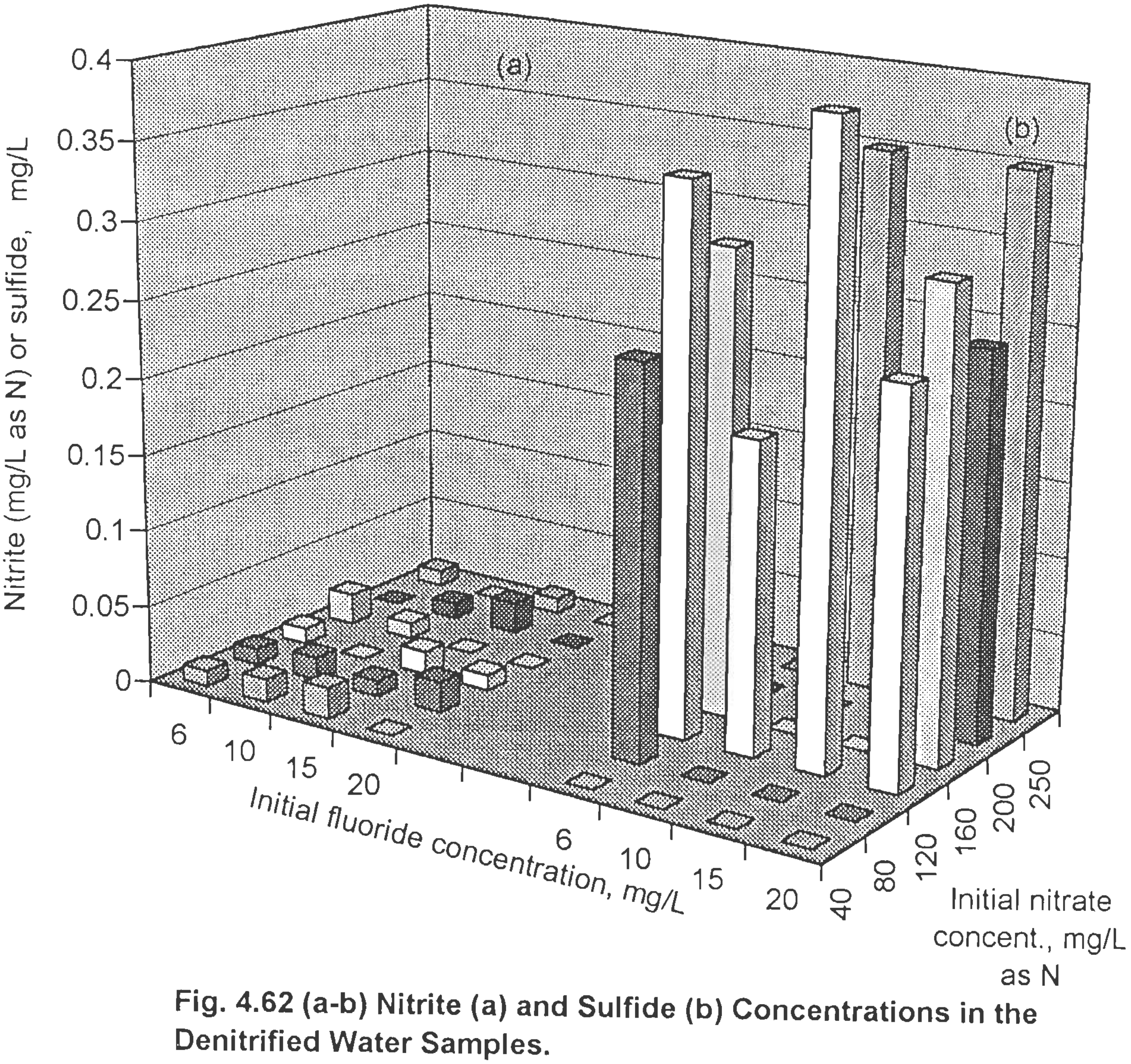


Fig. 4.62 (a-b) Nitrite (a) and Sulfide (b) Concentrations in the Denitrified Water Samples.

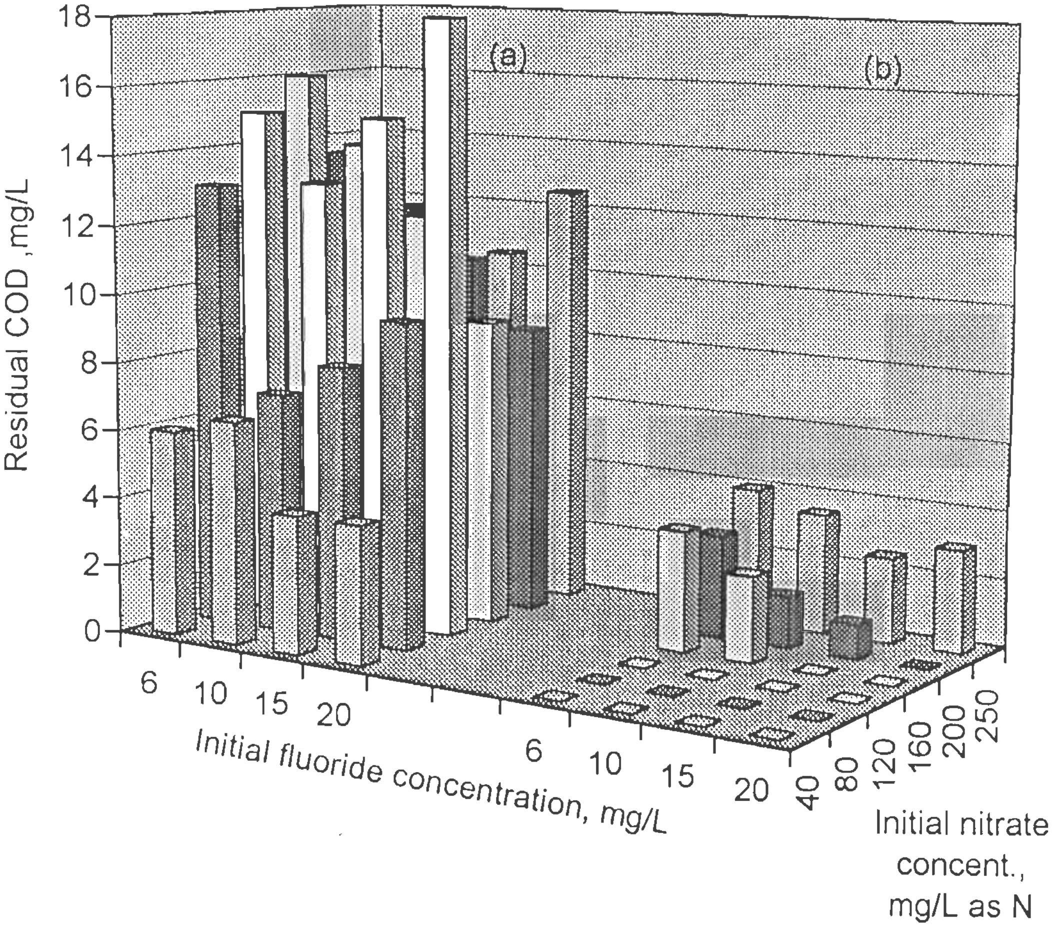
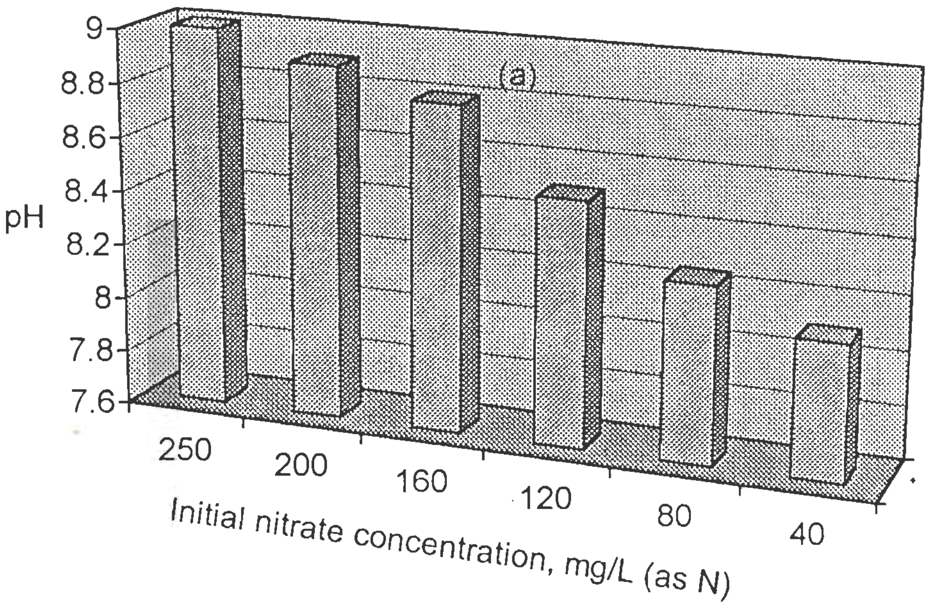


Fig. 4.63(a-b) Residual COD Concentrations in the Denitrified (a) and Denitrified-Defluoridated (b) Water Samples.



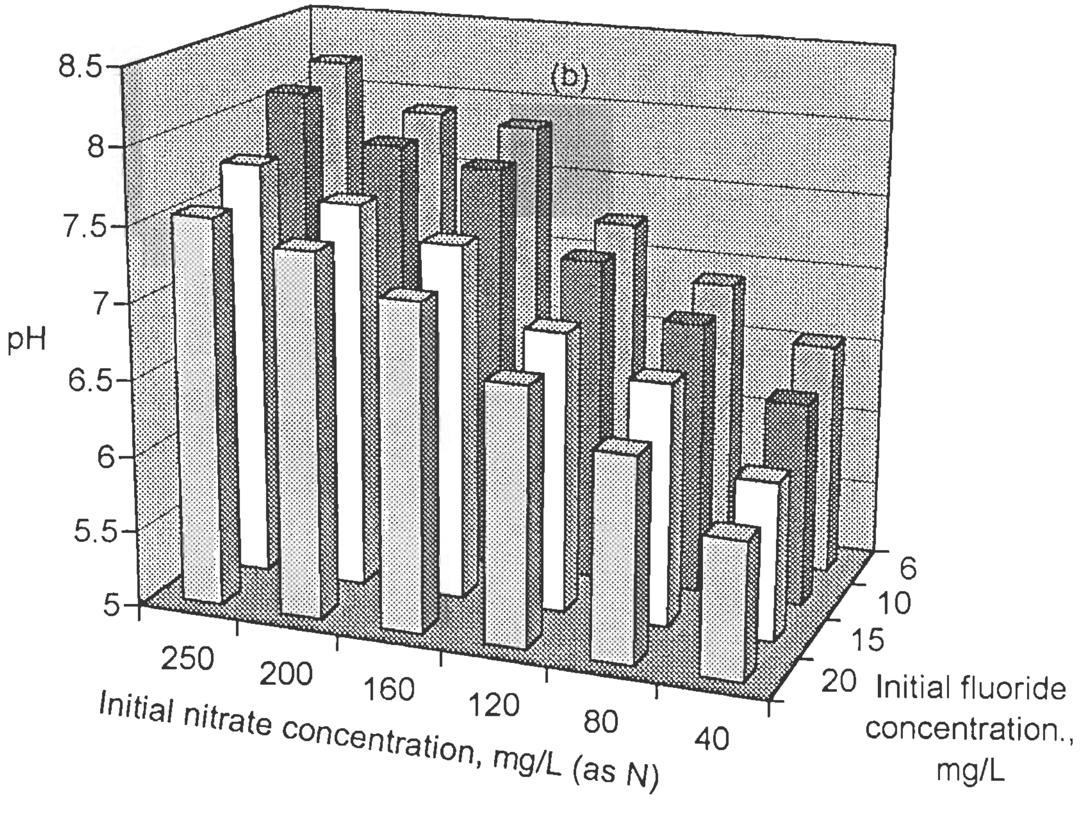


Fig. 4.64 (a-b) pH of the Denitrified (a) and Denitrified-Defluoridated (b) Water Samples.

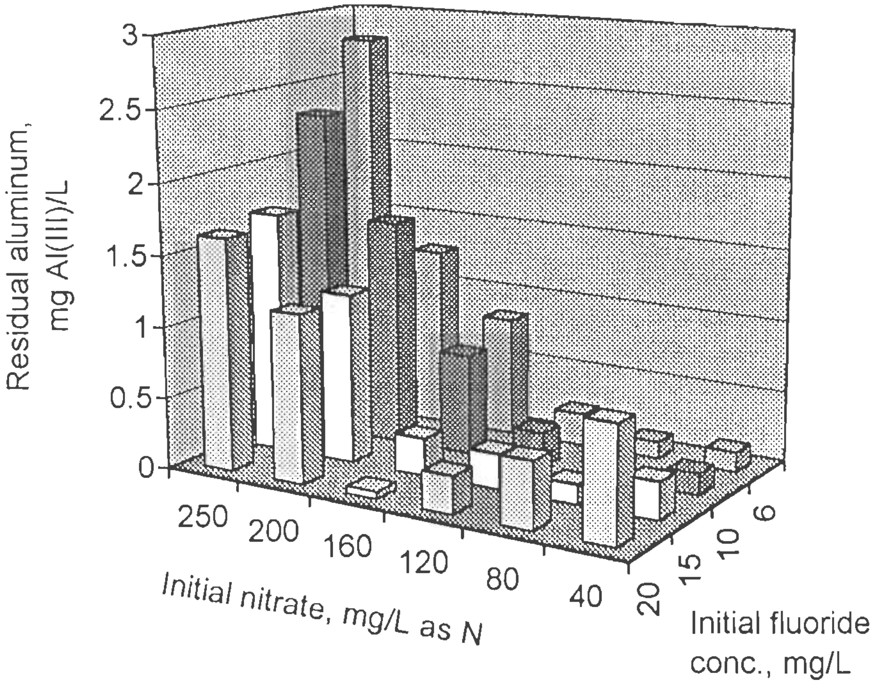


Fig. 4.65 Residual Aluminum Concentration in the Denitrified-Defluoridated Water Samples.

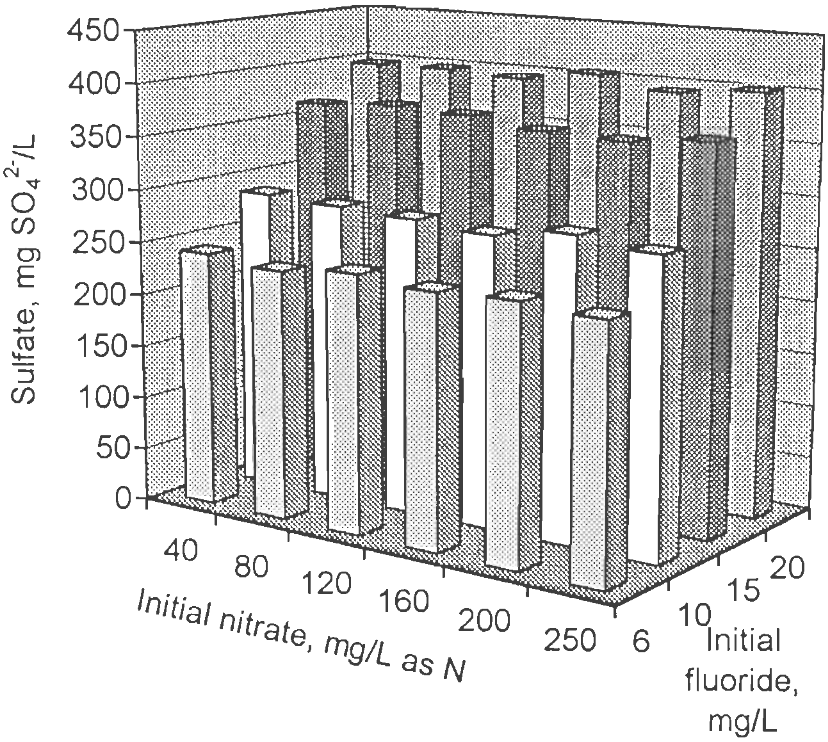


Fig. 4.66 Sulfate Concentration in the Denitrified-Defluoridated Water Samples.

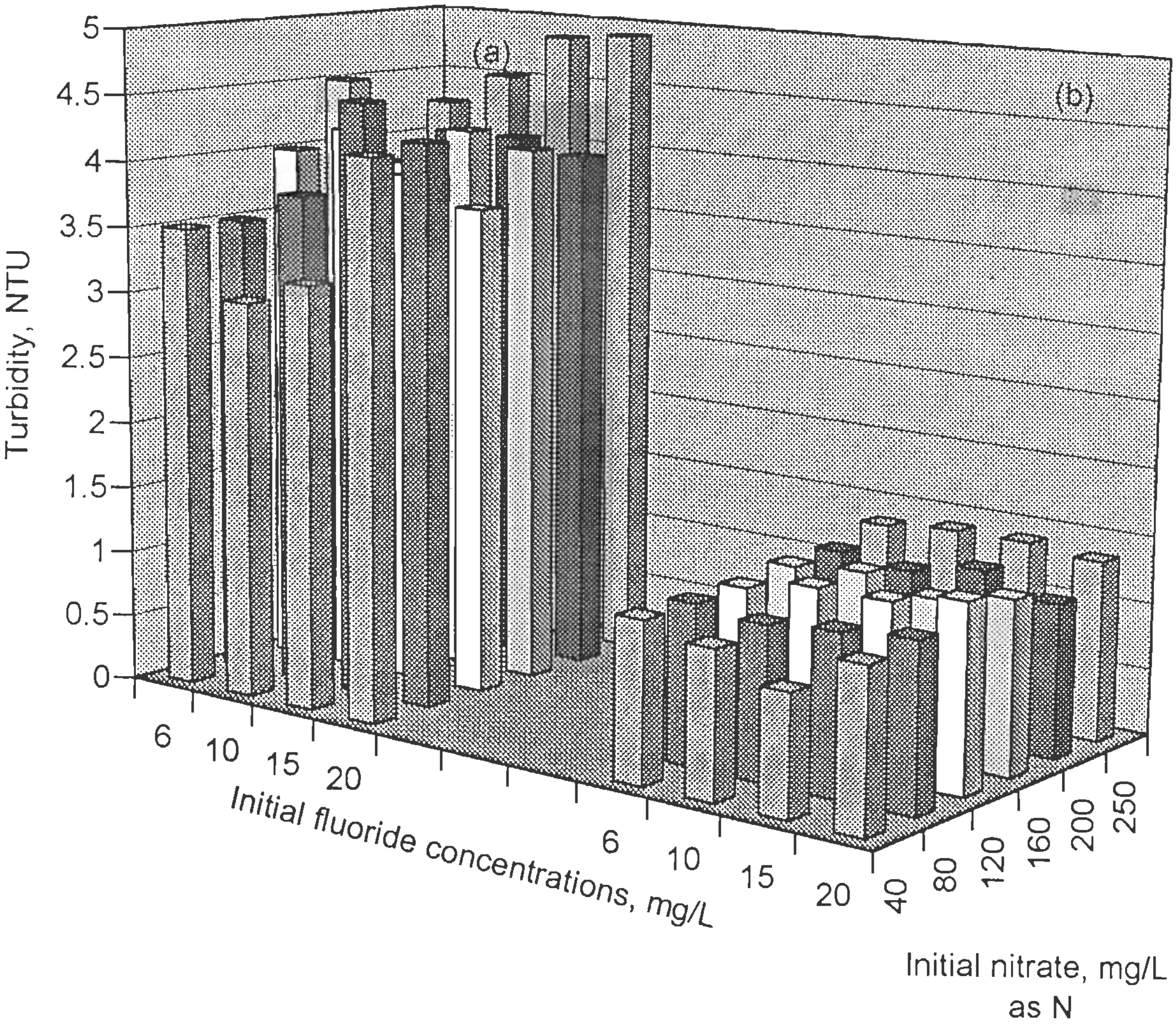


Fig. 4.67(a-b) Turbidity of Denitrified (a) and Denitrified-Defluoridated (b) Water Samples.

In summary, an integrated biological and physicochemical treatment process appeared to be promising for waters having fluorides along with nitrates as high as 15 and 80 mg/L (as N) respectively. At initial nitrate concentrations of 40 and 80 mg/L (as N), alkalinity produced at the denitrification stage was consumed during defluoridation in raising the pH, avoiding the need for lime addition. Even though the quality of the treated water at these concentrations was within the acceptable limit, slight pH adjustment, filtration, and disinfection will also be required before it could be used for potable purposes. However, at initial nitrate concentrations of ≥ 120 mg/L (as N), the production of excessive alkalinity during denitrification inhibited the reduction of fluorides to 1.5 mg/L with reasonable doses of alum and PAC i.e. up to 900 and 100 mg/L respectively. At these nitrate concentrations, in order to achieve the acceptable fluoride value, the feasibility of defluoridation by alum-PAC slurry along with acid neutralization requires further investigation. Sulfide, residual COD, and turbidity, which appeared in the denitrified water, were removed at the defluoridation stage (along with fluoride) avoiding the need of additional special treatment facilities.

4.4.3 Operating Strategy for Typical Integrated Denitrification-Defluoridation SBR Plant

Operating strategy for the proposed integrated denitrification-defluoridation SBR system has been drawn up for a community with population of 2000 assuming water consumption rate of 40 lpcd as per Indian rural community requirement (CPHEEO, 1976). The total daily demand is 80 m^3. The reactors would be equipped with inlet, decanting, nitrogen gas vent (in case of denitrifying reactors), sludge draw off port, and mixing mechanisms. They could be constructed of steel or concrete with circular or rectangular shape. The plant would consist 3 treatment train working in parallel with a total number of six SBRs. Each treatment train should be designed to produce 27 m^3/d. The schematic flow diagram of the plant is shown in Fig.4.68.

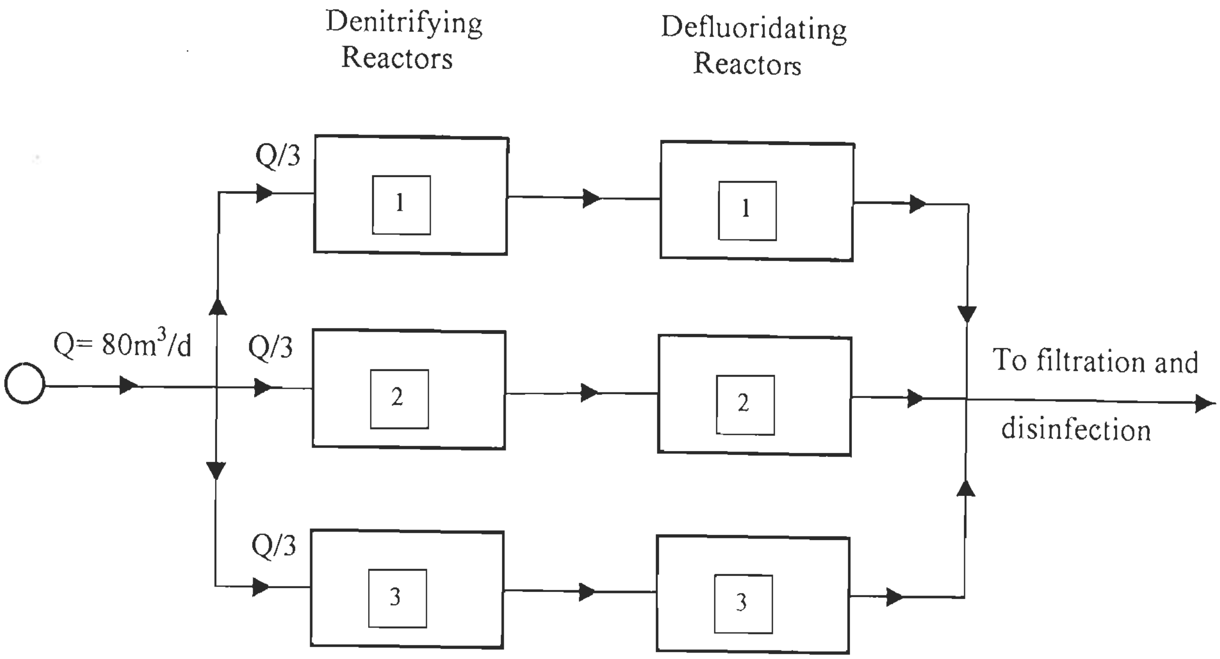
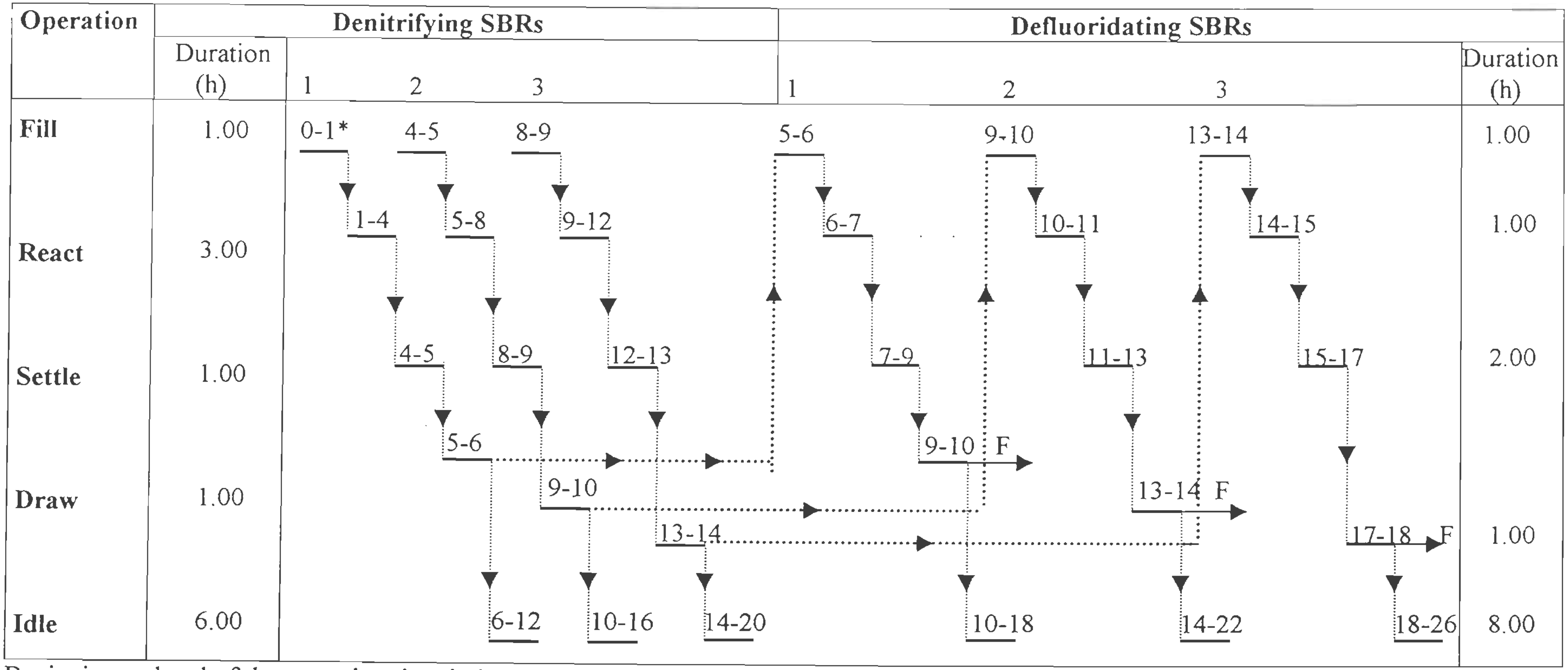


Fig. 4.68 Schematical Flow Diagram of an Integrated Denitrification-Defluoridation SBR System

The SBR process has five basic operating periods i.e. Fill, React, Settle, Decant, and Idle in a time sequence. The operating strategy of the plant is to be planned based on the optimum duration of reaction and settling found for denitrification and defluoridation in this study and assuming one hour of fill and draw. Since the integrated treatment scheme has been found to be suitable only for nitrate (as N) and fluoride concentrations as high as 80 and 15 mg/L respectively, these values have been considered in planning the operating strategy. In addition, it is assumed that each stage of treatment has its own operators working in shifts with minimum staffs. The suggested operating strategies are schematically shown in Fig. 4.69.



* Beginning and end of the operation time in h

F – To filtration and disinfection

Sludge is removed during idle time

Fig. 4.69 Operating Strategy for an Integrated Denitrification-Defluoridation SBR System

Each denitrifying reactor is planned to be filled cyclically after the other reactor completed reaction in order to avoid overlapping of the reaction period which requires closer monitoring by the operator i.e. the operator has to monitor reaction of one reactor at a time. After completion of 80 % of filling, simultaneously the reactor is fed with the required nutrients (Tables 3.5 and 3.7). On completion of filling, the mixers are switched on and the biomass is agitated i.e. the reaction phase starts. The duration of reaction is maintained for 3 hours. During this time the operator has to monitor closely the work of the reactor to ensure prevalence of the optimum operating conditions i.e. pH, mixing, anoxic condition, MLVSS concentration, etc. At the end of reaction it is allowed to settle in quiescent for one hour while simultaneously starting filling of the other reactor. After completion of settling the supernatant (80 % of the content) is decanted to the defluoridating SBR (filling phase for defluoridating SBR). As discussed above, to avoid overlapping of the reaction phase, 6 hours of idle time would be maintained before starting the next cycle for the same reactor. Excess sludge removal is planned during the idle phase. Thus, duration of one cycle for each denitrifying reactor would be 12 hours and all reactors would complete their cycle within 20 hours.

The operation of defluoridating reactor is started by filling denitrified supernatant from the preceding stage i.e. decanting of denitrifying reactor. After completion of filling, the required optimum doses of alum and PAC (Section 4.2.3 & 4.4.2) are added in two stages. First, at rapid mixing (with G value of 260 s^{-1}), alum-PAC slurry (400 mg/L alum + 100 mg/L PAC) is added and mixing continued for 40 minutes. Second, the remaining alum dose (total optimum alum dose - 400 mg/L) is added to the reactor and mixing is continued at G value of 45 s^{-1} (flocculation) for 20 minutes. The operator has to monitor closely the work of the reactor to ensure prevalence of optimum operating conditions at this time (pH, mixing rate, chemical doses, etc.). After completion of reaction it is allowed to settle in quiescent for 2 hours. Finally, the supernatant (90 % of the content) is decanted to the next stages of treatment (filtration and disinfection). In order to avoid overlapping of the reaction phase, 8 hours of idle time would be maintained before starting the next cycle. Sludge would be removed during the idle phase. The duration of one complete cycle (including the idle phase) for the integrated denitrification-defluoridation treatment is 26 hours while within 18 hours, treatment of the daily flow is completed. Since the decant percentages were assumed to be 80 % and 90 % at denitrifying and defluoridating stages respectively, volume of the reactors has to be increased accordingly.

Chapter 5

CONCLUSION

CHAPTER-5

CONCLUSIONS

Conclusions drawn from the present research are summarised below:

5.1 GENERAL

Fluoride and nitrate concentrations in groundwaters exceed the desirable levels of 1.5 mg/L and 10 mg/L (as N) respectively, at various places throughout the world. Barring very few cases, in all the six continents, in majority of the cases, fluoride occurs up to 20 mg/L and nitrate up to 250 mg/L (as N) concentrations. Excessive intakes of these contaminants can cause methomoglobinemia and fluorosis respectively. Simultaneous occurrence of both fluoride and nitrate in high concentrations in groundwaters has been noticed at several places in Asia, Africa, and other continents. Although several treatment methods are known for separate fluoride and nitrate removal, there is a need to explore the possibility of a joint treatment option for water containing both fluorides and nitrates occurring simultaneously. The objective of this work was to study the feasibility of an integrated fluoride and nitrate removal scheme for water having fluoride and nitrate values up to 20 mg/L and 250 mg/L (as N) respectively. Therefore, studies were conducted in phases to develop appropriate options for defluoridation and denitrification when they occur separately, and to utilize the synthesized design values for an integrated denitrification-defluoridation system of treatment to tackle their simultaneous occurrence. Various conclusions drawn for each phase are as follows:

5.2 PHASE-1 STUDY: DEFLUORIDATION

Methods for fluoride removal include chemical precipitation, ion exchange, adsorption, electrodialysis, and reverse osmosis. Alum and lime are used to precipitate fluoride in a defluoridation technique developed in India popularly known as "Nalgonda" technique. The amount of alum required increases with the amount of raw water fluoride value. Alkalinity must be adjusted with lime to ensure that the alum is precipitated. It is simple in operation and can be applied for any size of treatment plants. Large number of such plants are already in operation in India. Technoeconomically, this technique has been found to be suitable for fluoride concentrations up to 5 mg/L but can be utilized up to 10 mg/L.

Waters containing high fluoride concentrations (≥ 10 mg/L) require a high dose of alum, which results in an increase of sulfate and aluminum concentrations in the treated water to unacceptable levels. Although activated alumina can reportedly be used for fluoride concentrations as high as 20 mg/L, the Nalgonda technique has been preferred because of operational problems (particularly at community level) such as chemical (acids and alkalis) handling encountered by activated alumina method. In search for quantifying potential improvements in the Nalgonda technique, this study investigated the feasibility of incorporation of coagulation and adsorption processes using alum and PAC as alum-PAC slurry for defluoridation of water having wide range of fluoride concentrations viz. 6, 10, 15, and 20 mg/L. Specific conclusions drawn on exclusive defluoridation study are:

(i) On the relationship of pH with defluoridation efficiency of alum, PAC, and mixed slurry the optimum pH values were found to be 6.5 - 7.5, 3.00, and 5.8 - 6.5 respectively.

(ii) Design conditions for generating optimal coagulation, flocculation, and adsorption for defluoridation by alum-PAC slurry were synthesized. A total of one hour contact time with 40 minutes of rapid and 20 minutes of slow mixing at G values of 260 s^{-1} (100 rpm) and 45 s^{-1} (30 rpm) respectively along with split alum feeding were found to provide optimal efficiency.

(iii) Studies on requirements of alum and PAC doses at initial fluoride concentrations of 6, 10, 15, and 20 mg/L revealed that:

* At initial fluoride concentrations of 6, 10, and 15 mg/L, an acceptable fluoride value of ≤ 1.5 mg/L was achieved using alum-PAC slurries having 100 mg/L of PAC along with 500, 600, and 800 mg/L of alum with removal efficiencies of 75, 85, and 90 % respectively. Also, alum dose could be reduced by 40 and 43 % at initial fluoride values of 10 and 15 mg/L respectively, compared to defluoridation by alum and lime alone. Increase in PAC dose > 100 mg/L did not improve fluoride removal efficiency.

* Fluoride values beyond 15 mg/L i.e. 16 and 20 mg/L were reduced only to 1.7 and 3.15 mg/L respectively, with reasonable doses of alum (≤ 900 mg/L) and PAC (100 mg/L).

* At relatively lower fluoride concentrations (≤ 6 mg/L), alum-PAC slurry has no significant advantage compared to defluoridation by alum and lime alone.

(iv) On the role of lime in fluoride removal, it was found that lime is to be added during slow mixing only to increase alkalinity and pH, which are reduced during rapid mixing (due to alum addition). The optimal alkalinity required in the treatment process is calculated to be in the range of 0.5 – 0.63 mg/L as $CaCO_3$ for each mg/L of alum added.

(v) Studies on the kinetics of fluoride removal by alum-PAC slurry indicated:

- Alum directly involves in fluoride removal throughout the contact time whereas PAC is directly participating only during rapid mixing.
- At the transition from rapid to slow mixing, small amount of fluoride appeared to desorb from the PAC surface.
- Removal of fluoride by PAC in the presence of alum was relatively less compared to the removal when used alone, suggesting some reduction of fluoride removal efficiency of PAC in combination with alum possibly due to coating of PAC by aluminum hydroxide precipitate.
- Fluoride removal was significant (53 to 65 %) during the first 10 minutes of contact time. Contact periods of 40 minutes and 20 minutes are generally recommended for rapid and slow mixing respectively, to achieve optimal fluoride removal efficiency.
- The data on the contribution of alum and PAC in fluoride removal by alum-PAC slurry does not follow conventional isotherms. Therefore, exact mechanism of removal could not be worked out as it appears to be due to more than one mechanism participating simultaneously.

(vi) Assessment on effects of some water quality parameters on defluoridation by alum-PAC slurry revealed that:

- Sulfate, nitrate, chloride, and organic matter (ethanol) do not have adverse effect within the concentration range studied whereas phosphate and silica do.
- Depending on the initial concentrations, 29.5 to 100 % of ethanol (as COD) was removed along with fluoride without adverse effect to the removal of the latter.

Summary: The existing view on defluoridation of water is that Nalgonda technique is technoeconomically more suitable for fluoride concentrations up to 5 mg/L, but it could be utilized up to 10 mg/L. This research has revealed that for fluoride concentrations in the range of 6 to 15 mg/L, alum-PAC combination, which could be taken as "Modified Nalgonda" technique could treat fluoride values to permissible limit of 1.5 mg/L. In case of fluoride concentrations of more than 15 mg/L, alum-PAC slurry was unable to achieve the permissible value of $\leq$ 1.5 mg/L, and requires further investigations.

5.3 PAHASE- 2 STUDY: DENITRIFICATION

Nitrate is highly soluble in water. It is not treated easily by conventional water treatment processes. Methods for its removal include chemical reduction, electrodialysis, reverse osmosis, ion exchange, and biological denitrification. Of these, ion exchange and biological denitrification are already in use in drinking water treatment, the latter being more preferable due to its relatively lower treatment cost. Biological denitrification brings about microbial reduction of nitrate to nitrogen gas. Due to absence of organics in water, external carbon source (as ethanol) has been used. In the process, pH and alkalinity are increased.

For drinking water denitrification fluidized bed, fixed bed, and upflow sludge blanket reactors have been suggested. Sequencing batch reactor (SBR) system in biological wastewater treatment particularly for small communities is preferred against conventional system lately. Merits of SBR include: (i) simplicity in operation i.e. effluent water quality is easily controlled by manipulating the reaction and settling time and quantity of sludge solids, (ii) cheaper i.e. additional clarifier and sludge return system are not required, and (iii) matching of operation with fill-and-draw type reactor for defluoridation eliminating the need for equalization/storage tank. The SBR system has not so far been tried in water treatment practice. The present research has taken up this proposal. This study was thus undertaken to evaluate the efficiency of SBR in denitrification of drinking water with wide range of nitrate concentrations viz. 40, 80, 120, 160, 200, and 250 mg/L (as N). Conclusions drawn from this study are:

(i) The effort to optimize the requirement of ethanol revealed that ethanol at COD/NO_3^-- N ratio of 2.00 is sufficient to reduce nitrate concentrations to the acceptable values while at the same time minimizing residual COD values.

(ii) Treatability studies through kinetics and sludge settling characteristics have been carried out. The Monod's kinetic coefficients evaluated were: $k_{max} = 0.31\ d^{-1}$, $K_s = 0.46$ mg NO_3^--N /L, Y=1.54 mg VSS/ mg NO_3^--N, $k_d = 0.009\ d^{-1}$, and $\mu_m = 0.48 d^{-1}$. It produced sludge with good settling having SVI value of 74.

(iii) Investigation on denitrification efficiency of SBR at various initial nitrate concentrations (40 to 250 mg/L as N) demonstrated 92.7 to 98.2 % removal reducing nitrate and nitrite values to the acceptable levels or less at anoxic reaction times (ARTs) of 3, 5, and 7 hours for initial nitrate concentrations of 40 to 160, 200, and 250 mg/L (as N) respectively. Depending on initial nitrate concentrations alkalinity and pH were increased in the ranges of 445 – 1156 mg/L as $CaCO_3$ and 8 – 9 respectively.

(iv) On the effect of length of idle time on denitrification, idle hours within the range studied (1 to 14 hours) do not have any significant effect on denitrification.

(v) On the effect of fluoride on denitrification, no noteworthy conclusion has been drawn.

Summary: This study showed SBR could be used for denitrifcation of drinking water having nitrate concentrations in the range of 40 to 250 mg/L (as N) with operational ease.

5.4 PHASE-3 STUDY : DEVELOPMENT OF DENITRIFCATION - DEFLUORIDATION SBR SYSTEM

Feasibility of an integrated nitrate and fluoride removal treatment process using biological and physicochemical methods respectively, through SBR design was investigated in this research by integrating the above separate studies for water containing fluorides along with nitrates. The denitrification process produces excess alkalinity, biomass, turbidity, and residual COD. On the other hand, defluoridation process requires additional alkalinity. Further, the alum-PAC slurry is capable of removing the residual biomass, turbidity, and COD discharged from denitrification. Therefore, denitrification followed by defluoridation was adjusted as the most prudent sequence for an integrated treatment of nitrate and fluoride containing raw waters. The experimental work on an integrated SBR system was limited to nitrate and fluoride concentrations in the ranges 40 to 250 mg/L (as N) and 6 to 20 mg/L respectively. Studies on an integrated SBR system revealed the following:

- Nitrate and fluoride concentrations up to 80 mg/L (as N) and 15 mg/L respectively, can be treated to the acceptable respective residual values.
- At initial nitrate concentrations of 40 and 80 mg/L (as N), alkalinity produced at the denitrification stage along with the natural alkalinity is used up during defluoridation avoiding the need of lime for this purpose.
- Even though the quality of the treated water at these concentrations (40 and 80 mg/L as N) was within the acceptable limit, slight pH adjustment, filtration, and disinfection will be required before it could be used for potable purposes.

- Compared to defluoridation by alum and lime alone, defluoridation by alum-PAC slurry reduces alum dose requirement by 40 and 43 % (at 40 mg/L nitrate-N) and 20 and 39 % (at 80 mg/L nitrate-N) for fluoride concentrations of 10 and 15 mg/L respectively.
- At nitrate concentrations > 80 mg/L (i.e. 120, 160, 200, and 250 mg/L) as N, production of excessive alkalinity at the denitrification stage along with natural alkalinity in the range of 715 – 1175 mg/L as $CaCO_3$ inhibited reduction of fluoride to 1.5 mg/L with reasonable doses of alum (≤ 900 mg/L) and PAC (100 mg/L). This resulted in increase of pH to high values in the range of 8.45 – 9.00 which could not be reduced to the optimal pH values (5.8 to 6.5) of defluoridation by alum-PAC slurry using alum dose as high as 900 mg/L. The average alkalinity production rate is calculated to be 3.53 mg as $CaCO_3$ per mg of nitrate reduced to nitrogen gas.
- Sulfide, residual COD, and turbidity which have appeared in the denitrified water was removed at the defluoridation stage (along with fluoride) avoiding the need of additional special treatment facilities.
- Operating strategy for the proposed integrated denitrification-defluoridation SBR system serving a community of 2000 people has been suggested. Based on this, it was found that treatment (nitrate and fluoride removal) of the daily demand is completed within 18 hours using 3 parallel working treatment trains having a minimum operating staff.

Summary: This study has revealed that an integrated biological and physicochemical process using SBR system could be used for treatment of water having fluorides along with nitrates up to 15 mg/L and 80 mg/L respectively. The treatment process itself produces alkalinity required for defluoridation and sulfide, turbidity, and organics from the denitrification process are removed at the defluoridation stage along with fluoride. However, at initial nitrate concentrations of > 80 mg/L (i.e. 120, 160, 200, and 250 mg/L) excessive alkalinity produced at the denitrification stage along with the natural alkalinity in the range of 715 – 1175 mg/L as $CaCO_3$ inhibited reduction of fluoride to 1.5 mg/L.

5.5 PRACTICAL IMPLICATION OF THE RESEARCH

The findings of this study have the following practical implications:

(i) The broadening of application of the Nalgonda technique in respect of initial fluoride concentration to 15 mg/L (at one-stage treatment) is technically feasible. Thus, this enables the technique to be more comprehensive in respect of initial fluoride concentration even at existing treatment plants without major modification, only facilitating the mixing and other auxiliary devices to work for relatively longer detention times.

(ii) Reduction of alum dose requirement at 10 and 15 mg/L fluoride decreases the risk of contamination of treated water with excess concentration of aluminum and sulfate ions.

(iii) The findings about the efficiency of SBR in nitrate removal from water could lead to its practical application in the field to solve nitrate problem at community level.

(iv) The findings about the feasibility of an integrated denitrification-defluoridation treatment process also could lead to its practical application in the field for treatment of water having fluorides along with nitrates. Moreover, the possibility of incorporation of nitrate removal treatment process with the Nalgonda defluoridation technique could broaden the use of this technique in solving drinking water problems at community level.

5.6 SUGGESTIONS FOR FUTURE RESEARCH WORK

(i) The optimum pH of defluoridation by alum and lime is 6.5 to 7.5. Even though lower pH is favorable for fluoride removal by activated carbon, good fluoride removal at pH of 6.2, and 7 to 8 was also reported by activated carbons prepared from lignite and fish bone respectively. When incorporated, these materials will work efficiently at higher pH. Hence, further study on fluoride removal by alum-PAC slurry could be carried out using PAC having optimum pH of fluoride removal closer to 6.5 to 7.5. This might increase fluoride removal efficiency of alum-PAC slurry, extending its applicability to initial fluoride concentrations of > 15 mg/L. Attention should also be given to relatively cheaper carbons prepared from indigenous carbon sources.

(ii) The effect of alkalinity on fluoride removal by alum-PAC slurry has been studied and it was thought that doses of alum and PAC are specific for each water and thus should be evaluated experimentally. Further study on water samples of different initial fluoride concentrations and alkalinity values would be useful.

(iii) Defluoridation by alum-PAC slurry having PAC doses in the range of 20 to 220 mg/L has been studied. Alum-PAC slurries having doses of PAC above 100 mg/L has shown decrease in fluoride removal efficiency. Further investigations to understand role of PAC are required. Furthermore, the mechanisms of fluoride removal by alum-PAC slurry require to be identified in more detail.

(iv) An integrated denitrification-defluoridation treatment process at the denitrification stage produces alkalinity while at the defluoridation stage it is consumed. This avoided the need for lime addition in defluoridation of water having nitrate concentration up to 80 mg/L (as N). However, at nitrate concentrations > 80 mg/L, the production of excessive alkalinity inhibited the reduction of fluoride to the permissible limit by alum-PAC slurry having doses of alum and PAC up to 900 and 100 mg/L respectively. For these cases, at the defluoridation stage, possibility of using acid-neutralization could be assessed.

(vi) This study has only established the technical feasibility of an integrated denitrification-defluoridation treatment process using physicochemical (alum-PAC slurry) and biological methods for water having initial nitrate and fluoride concentrations up to 80 mg/L (as N) and 15 mg/L respectively. Therefore the work needs to be evaluated on pilot scale and economical feasibility of the scheme may be further assessed.

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