

Electrokinetic Remediation of a Nitrate-contaminated Soil

by

Krishnapillai Manokararajah

A Thesis submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfilment of the requirement of the degree
of

Doctor of Philosophy

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ABSTRACT

The potential for groundwater contamination by inorganic forms of nitrogen from intensive livestock operations has become a major concern for surrounding communities that use groundwater as their water supply. The traditional pump-and-treat method is ineffective in medium to fine textured agricultural soils due to their low hydraulic conductivity. Application of an electrical potential gradient results in the movement of charged particles and water in soil. A diffuse double layer formed around hydrated clay particles is the basis for the electrokinetic phenomena. Three sets of laboratory experiments were conducted to assess the effectiveness of electrokinetic methods in remediating a nitrate contaminated soil i.e. the first set of experiments tested denitrification of nitrates, the second looked at retarding nitrate ion movement, and the third evaluated the complete remediation of a nitrate contaminated soil using electrokinetics.

The first set of laboratory experiments showed that the nitrates in soil can be converted to other forms using electrokinetic treatment. The conversion occurred at the cathode (negative electrode) and in the surrounding soil. After nine days of electrokinetic treatment, compared to control, the nitrate concentration at the inflow end and at a relative distance of 0.2 in electrokinetic columns were significantly ($p < 0.05$) lower showing successful reduction of nitrates near the cathode end.

The second set of laboratory experiments showed that nitrate ion movement can be retarded by applying an electrical potential gradient. The retardation occurred at the anode (positive electrode). The application of the electrical potential gradient induced a

nitrate ion barrier around the anode against a hydraulic gradient of 1.25. Nitrate concentration at a relative distance of 0.2 from the anode was significantly lower ($p < 0.05$) than that in the hydraulic column even after thirteen days of treatment.

The third set of experiments showed that by changing the polarity of the electrodes after a period of time, the nitrate levels in a contaminated soil can be brought to below $10 \text{ mg NO}_3\text{-N L}^{-1}$ which is the Maximum Acceptable Concentration (MAC) for nitrate in drinking water in Canada. Six days after switching polarity, the nitrate concentration at a relative distance of 0.2 from the cathode was significantly lower ($p < 0.05$) than that in the hydraulic column. The nitrate concentrations in the entire treatment columns were brought to $< 5 \text{ mg NO}_3\text{-N L}^{-1}$ and significantly lower ($p < 0.05$) than control by the twelfth day. Electrokinetic treatment retarded nitrate movement against a hydraulic gradient of 1.25, and effectively restored a medium textured soil contaminated with $\text{NO}_3\text{-N}$. To achieve optimum results in the field, the electrodes have to be located based on contamination location and the direction of the hydraulic gradient.

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1. INTRODUCTION

1.1 Problem statement

The contamination of groundwater by excess fertilizer and livestock waste application is a problem associated with modern agricultural practices. One specific problem arising from excessive application is the presence of high concentration of nitrates in groundwater. Nitrogen is a valuable part of agriculture and is applied to the soil as fertilizer and livestock waste to increase crop production. The nitrates formed from the fertilizer and decomposition of livestock waste can be transported and reach water sources far away from the contamination location. Nitrates play a vital part in plant growth. But when found in excess, nitrates can easily move within the soil and reach groundwater. The presence of high levels of nitrates in drinking water can be a health hazard. High levels of nitrates in drinking water is related to methaemoglobinaemia in infants. The condition is caused by the bacterial conversion of nitrate into nitrite which combines with haemoglobin in the blood stream. This reduces the oxygen carrying capacity of the blood resulting in "blue baby syndrome". The Canadian Guidelines for Drinking Water limits the Maximum Acceptable Concentration (MAC) of nitrates in drinking water to 10 mg L^{-1} as $\text{NO}_3\text{-N}$ and 1 mg L^{-1} as $\text{NO}_2\text{-N}$ (Health and Welfare Canada 1993). Agriculture accounts for the majority of nitrates that enter the groundwater. When over twenty six percent of the population in Canada depends on the groundwater as their source for drinking water, the problem of groundwater contamination becomes even more important (Hess 1986).

1.2 Treatment technologies

Hunter (2001) described various technologies used to treat nitrate contaminated drinking water. Several treatment processes including ion exchange, biological denitrification, chemical denitrification, reverse osmosis, electrodialysis, and catalytic denitrification can remove nitrates from water with varying degrees of efficiency, cost, and ease of operation (Kapoor and Viraraghavan 1997).

Nitrate-contaminated waters are commonly treated by ion exchange or reverse osmosis. Nitrate ions can be removed from the water on an ion exchange resin. A high excess of regenerant, most notably NaCl, has been required to regenerate the resin periodically. The collected nitrate ends up in the waste solution resulting from the brine regeneration process. Disposal of the waste solution that is high in nitrate concentration may create significant costs and regulatory problems (Van der Hoek *et al.* 1988).

In reverse osmosis, water pressure is used to force water through a thin-film cellulose membrane. Reverse osmosis is capable of reducing nitrate concentration. Resulting brine with high nitrate content, however, cannot be discharged into a river or a deep well.

Ion-exchange and reverse osmosis, however, are not *in-situ* methods. Electrokinetic remediation of a nitrate-contaminated soil essentially would be an *in-situ* method for denitrifying nitrates in the soil.

1.3 Use of electrokinetics in moving contaminants in soil

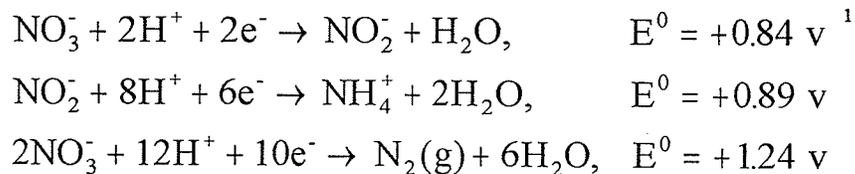
The most common means of reducing soil chemical pollution potential is to remove the chemicals via leachant water using a surface drainage system. Leaching,

however, can be a slow process requiring large volume of water. The traditional pump-and-treat method is ineffective in medium to fine textured agricultural soils due to the low hydraulic conductivity. Electrokinetics is known to be used to enhance or retard flow in such soils.

The electrokinetic technique uses direct current potential difference applied to the soil to transport soil water and dissolved substances. An electrical potential gradient initiates movement by electro-osmosis (movement of fluid), electromigration (charged chemicals movement), electrophoresis (charged particle movement), and electrolysis (chemical reactions due to electric field). Electrokinetic technique has many valuable applications in construction industry and in remediating heavy metal contaminated water.

1.4 Nitrate reactions resulting from electrokinetics

Segall and Bruell (1992) while studying biological treatment of gasoline and other organic contaminants attempted to transport phosphates, nitrates and other nutrients, and bacteria through fine-grained soils. In a series of laboratory experiments, solutions containing phosphates and nitrates were placed in column-influent reservoirs. Clay and soil mixtures were prepared with distilled water. Column effluents were monitored on a daily basis and nutrient distribution in the column was measured by destructive sampling. Nitrates dissolved in column influent water moved through a column and was reduced at the cathode as follows (Segall and Bruell 1992):



These half-reactions provide a basis for converting (denitrifying) nitrates present in the groundwater. Application of a voltage to the soil draws the water toward cathode while nitrate ions move toward anode. The hydrolysis of water changes the pH surrounding the electrodes. Therefore, the aim of this study was to identify conditions favouring these different processes to help in the remediation of a nitrate-contaminated soil.

1.5 Objectives

The objectives of this study were to investigate the use of electrokinetics as a means of restricting the nitrate movement and converting nitrates to other forms to remediate a nitrate-contaminated soil. The specific objectives of this study were:

1. To determine the ability of electrokinetics to remove nitrate from a nitrate-contaminated soil and to retard the flow of contaminated water from contaminated to uncontaminated area.
2. To retard nitrate movement using electrokinetics to establish a nitrate ion barrier to reduce the contaminant spread and concentrate nitrates in a location.
3. To determine the use of electrokinetics to retain, move, accumulate, and convert nitrates to other forms so as to completely remediate a nitrate-contaminated soil.

¹ Standard electrode potentials (E^0) for oxidation-reduction half-reactions are a quantitative indication of the relative tendency for a reaction to occur without application of an external potential.

1.6 Organization

This thesis consists of eight chapters. Chapter 1 briefly describes the problem of nitrate contamination of groundwater and the scope of utilizing electrokinetics in remediation of a nitrate-contaminated soil. Chapter 2 reviews literature on nitrate and health, fate of nitrogen in soil, electrokinetic phenomena, and applications of electrokinetics with special reference to previous studies carried out on electrokinetic remediation of nitrates. Chapter 3 describes the electrokinetic denitrification of nitrates. Chapter 4 describes forming a nitrate ion barrier using electrokinetic retention in soil. Chapter 5 describes electrokinetic remediation of a nitrate-contaminated soil. Conclusions are presented in Chapter 6. Recommendations for future work are given in Chapter 7. Contribution to knowledge is described in Chapter 8.

2. LITERATURE REVIEW

2.1 Introduction

The problems associated with groundwater contamination has gained prominence during the past two decades. In response, new technologies have been developed for restoring contaminated soils and groundwater. As the knowledge and understanding of the principles of electrokinetics advanced during the past decade, its potential use in remediating contaminated soils and groundwater have been explored. Electrokinetic technology has been demonstrated in remediation of metal-contaminated soils.

The principal objective of agricultural-related electrokinetic research has been the removal of salts from saline soils. Early studies showed that the application of an electrical potential gradient resulted in increased salt content in drainage water and salt accumulation near the cathode. It was found that solute flow increased with greater electrical voltage and that lower voltage potential was required with closer electrode spacing. Nitrate-N poses the broadest contamination threat due to the widespread use of fertilizers. Some researchers attempted to concentrate nitrates at a location for further treatment. In other studies, attempts were made to move nutrient and microorganisms to enhance biological remediation. Only a few studies have been carried out in converting nitrates using electrokinetic techniques. Thus far, no studies have been carried out to present a comprehensive protocol to remediate a nitrate-contaminated soil using electrokinetic techniques.

In this chapter, a review of fate of nitrogen in soil with special reference to nitrates is presented. Then a review of electrokinetic phenomena is presented, followed by a

review of different applications of electrokinetics. This is followed by a detailed review of electrokinetic phenomena on nitrates.

2.2 Nitrate and health

Like many substances, nitrate is essential to life, but a nuisance and possibly a hazard in the wrong place at the wrong time. Nitrate readily dissolves in water and is found in most natural waters - in rain, in rivers and lakes, in the sea and importantly in water stored in porous rocks such as chalk and sandstone (Addiscott *et al.* 1992). Our drinking water may come from any of these sources. One reason for the interest in nitrate is that concentrations of nitrate in these natural waters have been increasing steadily over the past 30 years. This increase has coincided with increasing use of nitrogen fertilizers. Nitrate itself is not toxic. Nitrate becomes a problem only when it is converted into nitrite. When that happens we have to consider two problems, the 'blue-baby' syndrome and stomach cancer (Addiscott *et al.* 1992).

The 'blue-baby' syndrome or methaemoglobinaemia, can occur when children less than about one year old consume too much nitrate. Microbes in the stomach convert nitrate to nitrite and when this reaches the bloodstream it reacts with haemoglobin, the agent that transports oxygen around the body. Normal oxyhaemoglobin, which contains iron in the ferrous form, becomes methaemoglobin in which the iron is in the ferric form. As a result, the oxygen-carrying capacity of the blood is decreased. Infants are susceptible because foetal haemoglobin, which has a greater affinity for nitrite than normal haemoglobin, persists for a while in the bloodstream, and because their stomachs are not acid enough to inhibit the microbes that convert nitrate to nitrite.

Stomach cancer has also been associated with the concentration of nitrate in potable water. There are good theoretical reasons for supporting this association. Nitrite produced from nitrate could react in the stomach with an organic compound called a secondary amine coming from the breakdown of meat. This union would result in an N-nitroso compound. Unfortunately, N-nitroso compounds can cause cancer because they are capable of modifying certain components of the DNA (Addiscott *et al.* 1992).

2.3 Importance and fate of nitrogen in soil

Nitrogen is vital to the growth of plants. There are several other nutrients that play vital role in crop growth. All nutrients increase the growth and yield of crops but nitrogen has by far the largest effect. Crops that have insufficient nitrogen are stunted, yellowish, and sickly-looking. Even a small amount of nitrogen given at the right time relieves these symptoms, and larger amounts can increase the yield of grain by a factor of five or six in cereal crops (Addiscott *et al.* 1992). Within the range in which nitrogen increases yield the farmer will get roughly 20 kg of extra grain for each kilogram of nitrogen fertilizer applied. The grain to fertilizer ratio of 20 kg kg⁻¹ does not go on indefinitely. There is a point, described as the 'optimum' at which applying extra nitrogen fertilizer ceases to be worthwhile. The extra nitrogen is largely wasted and it is likely to contribute to nitrate pollution. Manures and slurries are excellent sources of nitrogen. The nutrient analysis of manure nitrogen is in the range of 2 - 8% nitrogen on a dry matter basis and exists in organic N or inorganic N forms (Haynes 1984). Perennial application of manure to agricultural lands leads to excess nitrogen in soil and likely to contribute to nitrate pollution.

It is necessary to understand the fate of nitrogen in the soil and groundwater environment. There are many possible fates of nitrogen including crop uptake, immobilization, mineralization, ammonia volatilization, nitrification, surface runoff, nitrate leaching, and denitrification. After nutrients leave the rooting depth the two main processes by which nitrogen is lost from the system include denitrification and leaching.

2.3.1 Crop uptake

Most of the nitrogen requirements of plants are taken up by roots in the form of mineral nitrogen as ammonium and nitrate. Plant uptake of nitrogen can account for $100 \text{ kg ha}^{-1} \text{ y}^{-1}$ or approximately 5% of the total soil N for high-yield arable crops (Killham 1994). Nutrient uptake values will vary with soil and climatic conditions as well as crop type and stages of growth. Plant nutrients removed by crops (in both seed and straw) can range from values as low as 73 and 75 kg ha^{-1} for flax and wheat to values as high as 319 and 325 kg ha^{-1} for fababeans and forages, respectively (Western Canada Fertilizer Association 1992). When nitrogen is applied in excess, plants can accumulate excessive amounts of NO_3^- , which can be toxic to humans and animals if ingested (Beegle and Lanyon 1994).

2.3.2 Mineralization and immobilization

An understanding of the mineralization and immobilization processes aids in understanding the fate of manure N in soils. Mineralization refers to the soil processes by which organic nitrogen is converted to mineral nitrogen. Immobilization is the opposite of mineralization, being the conversion of soil mineral nitrogen into organic cellular constituents. The amount of available mineral nitrogen (usually as ammonium and nitrate)

found in soil will largely depend on the difference between rates of immobilization and mineralization (Killham 1994).

2.3.3 Volatilization

Ammonia volatilization from the animal manures is a major mechanism for nitrogen loss from soil-plant-water systems (Sutton 1994). Consequently, losses of ammonia by volatilization may significantly reduce the value of the manure for crop production. Volatilization of ammonia is usually highest under hot, dry, windy conditions in alkaline soils (Killham 1994). In order to maximise the utilization of nitrogen in the manure applied to cropland, management techniques to minimize ammonia volatilization in the field and in storage have been used. Losses of ammonia were greatly reduced if the manure is injected or incorporated into the soil (Smith and Chambers 1993).

2.3.4 Nitrification

Nitrification is the microbial formation of NO_3^- which is the major means whereby plants assimilate nitrogen (Schmidt 1982). If NO_3^- is not used by crops or immobilized by microflora, it is susceptible to loss from the soil by leaching. Nitrification has been defined as a series of reactions resulting in the production of NO_3^- . Nitrification is a necessary prelude to denitrification which leads to nitrogen disappearance from the soil. Biological denitrification cannot occur unless there is an initial oxidation of reduced nitrogen (Killham 1994).

Nitrification is performed by autotrophic and heterotrophic microorganisms. However, it is generally accepted that the dominant form of nitrification in most soils is autotrophic with the two main autotrophic genera including *Nitrosomonas* and

Nitrobacter. *Nitrosomonas* is an ammonium oxidizer whereas *Nitrobacter* is a nitrite oxidizer. Nitrification takes place in virtually all soils where NH_4^+ is present and conditions are favourable with respect to temperature, moisture, pH and aeration. At the field scale, nitrification is strongly controlled by NH_4^+ supply either from fertilizer or from mineralization of organic compounds (Killham 1994).

2.3.5 Nitrate leaching

Although agriculture is not the only source of NO_3^- contamination of groundwater, NO_3^- at levels above 10 mg N L^{-1} have often been associated with agricultural activities (Jones and Schwab 1993; Kimble *et al.* 1972; Knox and Moody 1991; Westerman *et al.* 1987). Nitrate leaching is of great environmental concern as elevated concentrations of NO_3^- in drinking water can have adverse effects on human and animal health. Nitrate-nitrogen concentrations in drinking water that exceeded 10 mg N L^{-1} have been linked to the incidence of methaemoglobinaemia (blue baby syndrome) (Hedlin 1971; Strebel *et al.* 1989) and increased carcinogenic effects from nitrosamine compounds (Selenka 1985). High concentrations of NO_3^- in surface waters, such as estuaries, streams, and lakes, may increase the rate of eutrophication (Sadeghi and Kunishi 1991).

Nitrate leaching tends to increase significantly with increased application rates of available nitrogen, either as manure or commercial fertilizer, to levels exceeding that required by the crop. Hog and poultry manures have a large proportion of nitrogen in readily available forms, increasing the risk of NO_3^- leaching as compared to other manures which have most of the nitrogen tied up in organic forms.

Some studies have shown that manured soils have higher amounts of NO_3^- in their

profiles (Murphey and Smith 1967; Mathers and Stewart 1974; Evans *et al.* 1977), and thus there is a greater risk of NO_3^- leaching on manured soils. Miller and Mackenzie (1978) applied 150 kg N ha^{-1} as ammonium nitrate, hog manure and cattle manure and they found NO_3^- levels were higher on the manured soils the year after application. Other studies found that manured soils result in less NO_3^- leaching to the groundwater than soils fertilized with inorganic fertilizer when applied at recommended rates (Burton 1994; Jokela 1992; Kimble *et al.* 1972; Xie and MacKenzie 1986). Some manured soils had less NO_3^- in their profiles and thus less leaching because of the increased denitrification potential of these soils (Kimble *et al.* 1972; Paul and Beauchamp 1996). Straw and other organic material in manure has the potential to immobilize inorganic nitrogen and enhance denitrification (Burton 1994).

Soils differ in their NO_3^- leaching potentials and soil properties related to water movement play a major role in influencing this (Khakural and Robert 1993). Coarse textured soils experience comparatively more NO_3^- leaching than fine textured soils (Hedlin 1971; Strebel *et al.* 1989; Manitoba Agriculture 1995). Nitrate, an anion, is readily transported through the soil with water and thus, leaching losses occur when there is both a high soil NO_3^- content and water movement. Increased water infiltration through rainfall or precipitation results in a greater potential of groundwater contamination by increased NO_3^- leaching (Chang and Entz 1996). Campbell *et al.* (1983) reported that on the Canadian prairies considerable amounts of NO_3^- leached beyond the rooting zone of cereal crops in years of above average precipitation and also in some relatively dry years with heavy spring rains. Muir *et al.* (1976) also reported that leaching of NO_3^- to the

water table was apparent in most irrigated soils located in low lying areas and in sandy soils.

Soil nitrate data from a study done by King *et al.* (1985) suggested that the application of medium to high rates of swine manure would result in pollution of groundwater with NO_3^- . Evans *et al.* (1977) concluded that applying hog manure for two successive years at a rate of 636 tons ha^{-1} (wet mass) resulted in the rapid movement of NO_3^- below the rooting depth and thus these rates were considered too high for continued annual application. In fact NO_3^- leaching was determined to be high even when recommended manure application rates of 60 Mg ha^{-1} were applied to a clay loam soil in Alberta (Chang and Entz 1996)

2.3.6 Denitrification

Biological denitrification is the dissimilatory reduction of NO_3^- or NO_2^- to gaseous nitrogen either as N_2 or N_2O (SSSA 1997). Denitrification has also been defined as a form of anaerobic bacterial respiration during which nitrogen oxides, principally nitrate and nitrite are reduced sequentially through NO and N_2O to N_2 (Aulakh *et al.* 1992). The bacteria responsible for denitrification are facultative anaerobes and these bacteria have the ability to use both oxygen and oxides of nitrogen as electron acceptors provided sufficient energy sources are available. In the absence of molecular oxygen, nitrogen oxides serve as terminal electron acceptors (Firestone 1982)

Aulakh *et al.* (1992) summarized that denitrification losses were usually in the range of 12 to 20% of the available nitrogen added, however values in excess of 30% had also been reported. Firestone (1982) reported nitrogen losses due to denitrification

ranging from 0 to 70% of the added nitrogen. Annual emissions of 1 to 16 kg N₂O ha⁻¹ in dry regions with low rainfall were reported by McKeeny *et al.* (1980).

2.4 Electrokinetic phenomena

Electrokinetic flow processes in porous media is of great interest to scientists and engineers of different disciplines. The driving force for these processes is an electric field imposed on a porous medium, and the flows may include fluid, electricity, dissolved chemical species, and colloid size solid particles. The basis for these processes is an electrical double layer formed around hydrated clay particles. For a successful application of electrokinetic process in any field, a sound understanding of the basis of electrokinetic process and different electrokinetic processes are important.

A great variety of applications of electrokinetic flow processes can be found in various fields of engineering. Applications range from electrokinetic consolidation in geotechnical engineering to electrokinetic remediation of contaminated sites in environmental engineering. In this study we are looking for an engineering solution to a problem caused by excesses in agriculture sector. That is to use electrokinetic processes as an effective engineering solution to accelerate removal of nitrates from soil

2.4.1 Electrical double layer

Clay minerals are primarily aluminosilicates. In some minerals, some of the silicon positions may be occupied by aluminum ions. The surfaces of clay particles are normally negatively charged because of the isomorphous substitution of silicon with aluminum ions and the presence of broken bonds. Electrical neutrality is maintained by the adsorption of cations to the clay particle surfaces by strong electrostatic forces.

When the clay is placed in water, there is a tendency for the cations to diffuse away to have equal concentration everywhere. This tendency to diffuse is counteracted by the electrical attraction from the negatively charged surfaces of the clay particle. A diffuse layer as shown in Fig. 2.1 is thus formed. Several theories have been proposed on the formation of the diffuse electrostatic double layer. The Stern-Gouy-Chapman theory of diffuse double layer has been widely accepted. Detailed description of this theory of diffuse has been given by Mitchell (1993).

Several electrokinetic phenomena arise in a charged porous medium when there are couplings between hydraulic and electrical driving forces and flows. These phenomena can broadly be classified into two groups by the driving forces causing the relative movement between the liquid and the solid phases. The first group consists of electro-osmosis and electrophoresis, in which the liquid or the solid phase moves relative to the other under the influence of applied electrical potential gradient. The second group consists of streaming potential and migration or sedimentation potential, in which the liquid or the solid phase moves relative to the other under the influence of a hydraulic or gravity force, thus inducing an electrical potential difference across the medium. The four electrokinetic phenomena in clay are shown in Fig. 2.2. Electro-migration is the migration of charged ions towards oppositely charged electrodes under an applied electrical potential gradient. Besides these electrokinetic processes, electrolysis reactions occur at the anode and cathode.

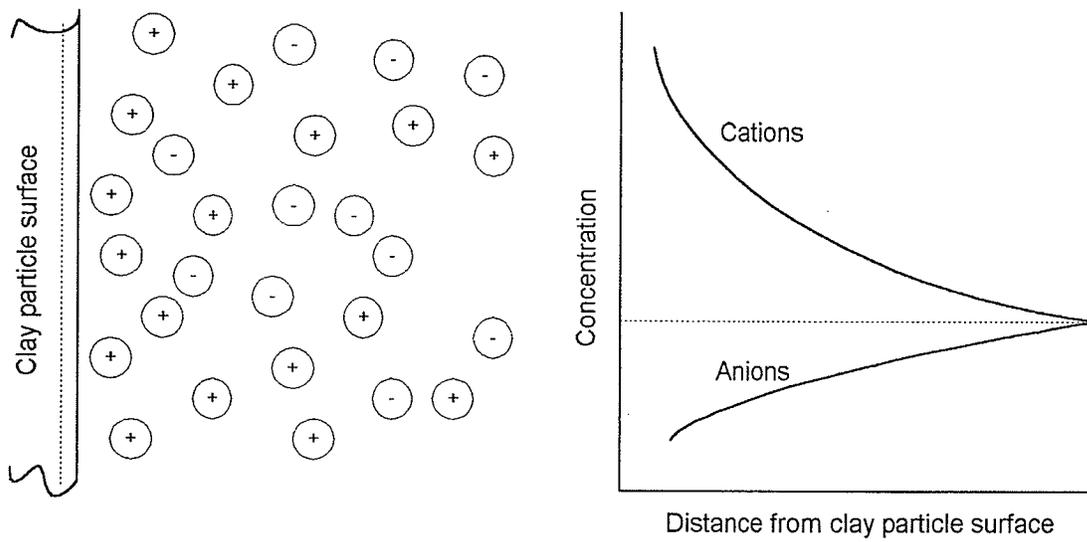


Fig. 2.1 **Distribution of ions adjacent to the surface of clay particles according to the concept of diffuse double layer (adapted from Yeung 1994)**

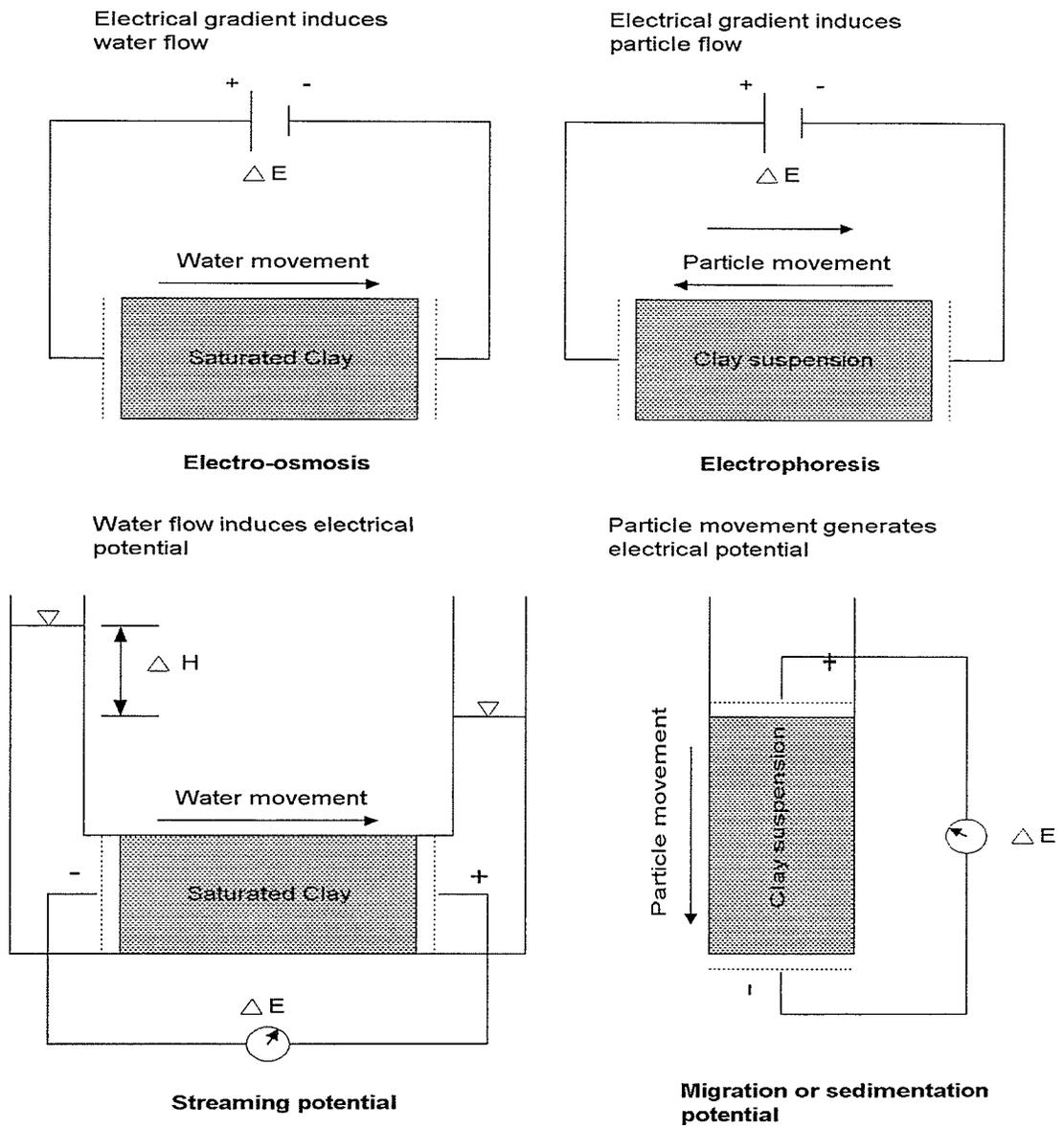


Fig. 2.2 Electrokinetic phenomena in clay (adapted from Yeung and Mitchell 1993)

2.4.2 Electro-osmosis

When an electrical potential gradient is maintained across a sample of wet clay, water is moved from the anode to the cathode as shown in Fig. 2.2. This phenomenon is known as electro-osmosis. The movement of water under the influence of an electrical potential gradient is due to the viscous drag created by the mobile counter ions in the electrical double layer (Yeung 1994). The cations in the pore fluid will drag the water toward the cathode and the anions will drag the water toward the anode. However, due to the presence of a net excess amount of cations in a clay water electrolyte system the net movement of water is more toward the cathode (Mitchell 1991; Yeung 1994). Also, hydrated cations are larger than hydrated anions and hence drag more water molecules with them. Electro-osmotic flow rates can be given by the relation:

$$q_e = K_e \nabla E \quad (2.1)$$

where:

q_e = electro-osmotic flux (m s^{-1})

∇E = electrical potential gradient (V m^{-1})

K_e = electro-osmotic conductivity ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)

The values of hydraulic conductivity can differ by orders of magnitude but the coefficient of electro-osmotic conductivity is generally in the range of 1×10^{-9} to 1×10^{-10} $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ (Mitchell 1993)

Electro-osmotic conductivity depends on several variables. Based on Helmholtz-Smoluchowski model, Casagrande (1949) derived a relationship for electro-osmotic

conductivity in the form of an equation:

$$K_e = \frac{\zeta D \varepsilon n}{\eta \tau} \quad (2.2)$$

where:

- ζ = ²zeta potential (V),
- D = dielectric constant of the fluid (80 for water),
- ε = permittivity of the vacuum (8.854×10^{-12} F m⁻¹),
- n = effective porosity of the medium,
- τ = tortuosity,
- η = viscosity of the fluid (1×10^{-3} N s m⁻²)

The water flow will be towards the cathode if the concentration of cations in the pore fluid exceeds that of the anion (positive zeta potential). According to Yeung (1994) values of ζ will be in the range of +50 to -50 mV. The pH of the soil will determine the zeta potential. For most soils zeta potential will be in the range of 0 to -50 mV (Yeung 1994). A value above 0 mV can occur in highly acidic soils where the electro-osmotic flow will be toward the anode instead of toward the cathode (Eykholt and Daniel 1994). With electro-osmotic flow, there is a pH front that moves along the length of the soil column due to the electrolysis reaction at the electrodes and as a result the zeta potential also changes. Therefore, the electro-osmotic conductivity is not a constant.

² Zeta potential is defined as the potential difference between the shearing surface in the diffuse double layer and the liquid.

Researchers showed that the zeta potential changes linearly with the logarithm of ionic concentration of the pore fluid as described by Kruyt (1952):

$$\zeta = A - B \log_e C \quad (2.3)$$

where:

A & B = constants,

C = the total concentration of the electrolyte.

From Eq. 2.2 it is important to note that unlike the hydraulic conductivity the electro-osmotic conductivity depends mainly on zeta potential and the porosity and not on the pore size or pore size distribution (Probstein and Hicks 1993). Hence, the electro-osmotic flow will be significant in fine-grained soils and the flow distribution will be uniform even in heterogeneous soils (Acar and Alshawabkeh 1993). Electro-osmotic flow occurs both in saturated and unsaturated soils, but increases with increasing water content (Pamucku and Wittle 1992).

2.4.3 Electro-migration

Electro-migration is the migration of charged ions towards oppositely charged electrodes under an applied electrical potential gradient. Positively charged cations move towards the cathode and the negatively charged anions move towards the anode. For instance ammonium ions move towards cathode and nitrate and nitrite ions move towards anode. The rate of migration of ions under an applied electrical potential gradient can be given by:

$$q_{ion} = u_i \nabla E \quad (2.4)$$

where:

q_{ion} = rate of migration of ions (m s^{-1}),

∇E = electrical potential gradient (V m^{-1}),

u_i = ionic mobility in free solution ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)

Ionic mobility can be defined as the velocity of the ion in the soil under the influence of a unit electrical potential gradient. The ionic mobility and the diffusion coefficient of an ion in dilute solution are related by the Nernst-Einstein equation (Koryta 1982):

$$u_i = \frac{D_i z_i F}{RT} \quad (2.5)$$

where:

D_i = diffusion coefficient of species i in dilute solution ($\text{m}^2 \text{s}^{-1}$),

z_i = charge of the chemical species i ,

F = Faraday's constant (96487 C)

R = universal gas constant ($8.314 \text{ kJ kg}^{-1} \text{ K}^{-1}$)

T = absolute temperature (K)

According to Acar and Alshawabkeh (1993), the mass transport rate due to electron-migration will be ten times more than that due to electro-osmosis.

2.4.4 Electrophoresis

When an electrical potential gradient is applied to a suspension of clay particles, the negatively charged clay particles will move toward the anode and positively charged

colloidal particle present in the suspension will move toward the cathode. This phenomena is called electrophoresis (Mitchell 1993).

2.4.5 Streaming potential

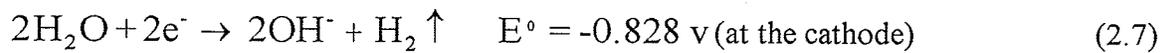
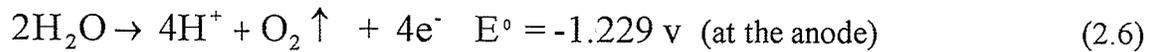
Streaming potential is induced due to the reverse process of the electro-osmosis. When a liquid flows through a column of soil, an electrical potential difference is created between the upstream and downstream ends of the soil column. This potential difference is created due to the transport of mobile ions in the diffuse double layer towards the downstream end of the liquid. This phenomenon is called as streaming potential (Mitchell 1993). The observed electrical potential difference is proportional to the applied hydraulic pressure and is attributed to the separation of oppositely charged ions in the diffuse double layer by the hydraulic pressure (Glasstone 1946).

2.4.6 Migration potential

Migration potential is induced due to the reverse process of electrophoresis. When a charged clay particle or colloidal particle settles down in a soil suspension, an electrical potential difference is created between the top and the bottom of suspension. This electrical potential difference created due to the settlement of charged particles in one end of the suspension is called migration potential (Mitchell 1993).

2.4.7 Electrolysis of water

When an electrical potential gradient is applied across a column of soil, electrolysis reactions take place at the anode and cathode. Electrolysis of water releases H^+ ions at the anode and the OH^- ions at the cathode. The electrolysis of water is given by Eqs. 2.6 and 2.7:



A sharp acid-base front develops due to the electrolysis of water (Acar *et al.* 1993; Eykholt and Daniel 1994; Mise 1961). The acid front will move towards the cathode by advection (due to electro-osmosis), diffusion (due to chemical gradients) and ionic-migration (due to electrical potential gradients). The base front will migrate in the opposite direction towards the anode. Because the ionic mobility of H^+ ions is 1.75 times that of the OH^- ions, the H^+ ions will dominate the system chemistry (Acar and Alshawabkeh 1993). As a result, the migration of the acid front from the anode and the base front significantly impacts the electrochemical properties of the soil and removal of contaminants (Alshawabkeh and Acar 1996; Eykholt and Daniel 1994).

2.5 Applications of electrokinetic phenomena

2.5.1 Electrokinetic remediation

The concept of remediating contaminated soils using electrical fields evolved from several studies conducted during the past decade (Hamed *et al.* 1991; Lageman *et al.* 1989; Probststein and Hicks 1993; Qian 1998; Segall and Bruell 1992; Thomas 1996; Yeung 1990). Electrokinetic remediation involves the application of an electrical potential gradient between electrodes installed in a contaminated zone. Applying an electrical potential gradient causes the movement of water by electro-osmosis and ions by electro-migration. Hydrocarbon contaminants like gasoline can be effectively removed by electro-osmosis. Studies conducted by Bruell *et al.* (1992) showed that the hydrocarbon

contaminants like gasoline and Trichlorethylene (TCE) can be effectively removed from fine-grained soils using electrokinetic remediation. Within three days of treatment 15% of TCE and 15% of benzene were removed. Phenol has a very high retardation coefficient and is less volatile. Hence it is least possible to use remediation techniques like air sparging or vapour extraction to remediate phenol contaminated soil. Studies conducted by Acar *et al.* (1992) showed a removal of 85 - 95% of phenol from contaminated soil using electrokinetic remediation. Electrokinetic remediation can also be combined with remediation techniques like surfactant flushing and bio-remediation for effective removal of hydrocarbon contaminants. Studies conducted by Thomas (1996) and Qian (1998) showed effective removal of hydrocarbon contaminants from fine-grained soils. Acar *et al.* (1996) showed that bio-remediation of hydrocarbon contaminants can be enhanced by injecting microorganisms and nutrients into the soil using electrical fields.

Heavy metal contaminants like lead can also be removed efficiently using this technique. Using electrokinetic remediation Lageman *et al.* (1989) removed more than 80% of lead and copper from an abandoned paint factory site. About 75 - 95% of absorbed lead was removed in a laboratory scale study conducted by Hamed (1991).

2.5.2 Electrokinetic barriers

The movement of water due to an applied electrical potential gradient (electro-osmosis) and the migration of ions toward oppositely charged electrodes (electromigration) can be effectively used to confine or concentrate contaminants for *in situ* remediation. Electrokinetic barriers can be used at refuse sites or abandoned factory sites where the contamination of soil and water has been already detected or in places where

the contamination is likely to occur. Electrical fields have been used to prevent the migration of contaminant like lead, copper, zinc, and cadmium during electrokinetic remediation of an abandoned paint factory site. Studies conducted by Lageman *et al.* (1989) showed that in fine-grained soils like clay, the yearly energy costs of an electrokinetic fence are insignificant.

Yeung (1993) conducted lab scale experiments to study the feasibility of using electrical fields to control the migration of contaminants across a compacted clay liner. Clay liners used in hazardous waste sites may be subject to cracking due to wetting and drying cycles. The cracks developed during this process with time may allow the contaminants present in the clay liner to migrate and cause groundwater contamination. Installing electrodes across this clay liner may prevent the contaminants from spreading. Yeung (1993) found that electrokinetic barriers can effectively prevent the cationic contaminants from migration, but it increased the migration of anions. This is because of the effectiveness of electro-migration in moving the charged ions over electro-osmosis. Proper configuration of electrodes should be used depending on the type of contaminants and the field conditions. It can be inferred from his study that migration of contaminants like gasoline can be effectively controlled by the use of this technique.

Renaud and Probststein (1987) suggested the use of electro-osmosis for diverting the water flowing through hazardous waste facilities. A steady state model developed by them showed, that the groundwater flow due to existing hydraulic gradient can be diverted from flowing through hazardous waste facilities using electro-osmosis. Narasimhan (1999) using laboratory experiment and model studies showed that the electrokinetic

barriers can be used as an effective system for preventing the spread of contaminants.

2.5.3 Electrokinetic consolidation

For many years Civil and Geotechnical engineers used the electrokinetic technique primarily for consolidation of soil and stabilization of the slope. In the field, electrokinetic consolidation is carried out by driving two parallel rows of closely spaced anode and cathode (Esrig 1965). Applying an electrical potential difference between electrodes causes water movement from the anode toward the cathode. The water collected at the cathode compartment is pumped out. As no water is supplied at the anode, the electro-osmotic flow toward the cathode causes consolidation of the soil in between the electrodes.

2.5.4 De-watering and concentration

Wastewater sludges, coal washeries, and mine tailings have high water content. As the suspended particles in these materials are of colloidal size, it might take a longer time for these particles to settle (Yeung 1994). Electrophoresis and electro-osmosis can be effectively used for concentration and de-watering. If an electrical potential gradient is applied on a slurry containing negatively charged colloidal particles, the suspended particles will migrate toward the anode. After sufficient densification has been achieved, further dewatering and consolidation of the sludge can be achieved by electro-osmosis.

2.5.5 Electrokinetic remediation of nitrates

Cairo *et al.* (1995) studied the electromigration of nitrates in soil and observed that the nitrate concentration in saturated soil increased from anode to cathode after the application of a small direct-current electrical field indicating a movement towards the

cathode in saturated soils due to electroosmosis. However, when the soil water content dropped below the saturation level, the nitrates were found to migrate toward the anode due to electro-migration. Budhu *et al.* (1997) tried to transport nitrates through slurried clay in a laboratory experiment to enhance bioremediation. Their experiment showed that the nitrate concentration decreased for the first one-third of the column from the cathode and then increased for the remainder. In laboratory experiment Till *et al.* (1998) showed that Fe(0) can stoichiometrically reduce nitrate to ammonium and that cathodic hydrogen can support autotrophic denitrification. Islam and Suidan (1998) monitored the long-term performance of a biofilm electrode reactor for denitrification. The denitrification efficiency increased with the increase in current and then declined. Chew and Zhang (1998) studied the feasibility of using electrokinetics coupled with a zero valent iron (Fe0) treatment wall to abiotically remediate nitrate-contaminated soil. Under no flow situation, they demonstrated that the electrokinetics/iron wall process can be used to remediate nitrate-contaminated groundwater.

Eid *et al.* (2000) studied the electro-migration of nitrates in a sandy soil under flow against the electrical current, and no flow situations. The system showed that nitrate was concentrated at the anode and the movement was affected by the pH gradient developed. Haugen *et al.* (2002) developed an *in situ* membrane technology to remove nitrate from groundwater. In this technology membrane-fed hydrogen gas was used as an electron donor to stimulate denitrification. Koparal and Ögütveren (2002) investigated electrochemical methods to remove the nitrate from nitrate-contaminated water using electrochemical cells. They reported a process called electrocoagulation to be more cost

efficient than the electroreduction method but the former has a sludge problem associated with it.

2.6 Chapter summary

Nitrogen is an important nutrient that affects crop yield to a great extent. Although application of fertilizer and manure increases the crop yield, excess application can result in presence of excessive nitrogen in the soil system. An understanding of the fate of nitrogen in soil indicates that a considerable proportion of these excess nitrogen can eventually contaminate the soil-water system. Nitrates being highly mobile is an important source of pollution.

Application of an electrical potential gradient results in various electrokinetic processes to take place in soil. Diffuse double layer formed around hydrated clay particles is the basis for the electrokinetic phenomena. Electrokinetic technique is being successfully used in many engineering applications. Researchers are investigating the possibility of introducing electrokinetic technology in various other fields.

In the past decade there has been increased attempt to use electrokinetic phenomena to mitigate nitrate contamination. Earlier experiments were designed to move nitrate from one location to another to accumulate nitrates and used non-electrokinetic techniques to eliminate nitrates from a contaminated site. The other researches tried to combine electrokinetic phenomena with another existing nitrate remediating technology to achieve nitrate remediation. Using a zero valent iron wall for nitrate remediation is one such example. Recently electrochemical methods have been developed to remediate drinking water of nitrates. Electrochemical methods can be employed in water purifying

plants.

Few research work has been carried out in converting nitrates in soil to other products or using electrokinetic technology as a comprehensive tool for complete remediation nitrate-contaminated soil. Hence, the objective of this study was to determine the potential of using electrokinetic technique to remediate nitrate-contaminated soils. A series of laboratory experiments were conducted first of all to understand the effect of electrokinetic phenomena on nitrate ion conversion and migration, and then to come up with a set of proposals to use electrokinetic technique as a comprehensive tool for completely remediating nitrate-contaminated soils.

3. ELECTROKINETIC DENITRIFICATION OF NITRATES AND RETARDING CONTAMINATED WATER FLOW IN SOIL

3.1 Chapter summary

Nitrates are the most common nitrogen contaminant in drinking water supplies. In rural areas, agricultural activities that use fertilizers and animal manures are major sources of nitrate contamination. In recent times, electrokinetic techniques have been increasingly used for remediating various contaminated sites. Electrokinetic technique may also provide a safe way of denitrifying nitrates into other products thus remediating nitrate contaminated soils. This chapter describes the use of electrokinetics to remove nitrate from groundwater safely, and to retard the flow of contaminated water in the soil. Therefore, the specific objectives of this study were to conduct a set of laboratory scale experiments to determine the effect of electrokinetics on a nitrate-contaminated soil and to retard the flow of contaminated water. As pH, apparent electrical conductivity, and ammonia content of the soil may change because of the electrokinetic treatment, these components were monitored while applying a voltage potential gradient across the soil sample.

The laboratory experiment conducted showed that the nitrates in soil could be denitrified to other forms using electrokinetic treatment. The denitrification occurred at the cathode (negative electrode) and in the surrounding soil. After nine days, compared to hydraulic columns, the nitrate concentration at the inflow end and at a relative distance of 0.2 were significantly ($p < 0.05$) lower, showing successful reduction of nitrate near the cathode end. In the field situation, the cathode has to be located so as to denitrify as much

nitrate as possible in a nitrate-contaminated soil. The electrokinetic treatment did not affect the natural ammonia-nitrogen present in the soil nor did it convert nitrates into ammonia-nitrogen. The soil pH near the electrodes changed by over 30% because of the invariable hydrolysis taking place at the electrodes. Suitable buffer amendments have to be identified to neutralize these pH changes. The inclusion of Time Domain Reflectometry (TDR) mini-probes in these experiments enabled continuous monitoring of water content and apparent electrical conductivity (EC_a) in a non-destructive way. The movement of nitrate can be tracked from the changes in EC_a data, before doing the expensive and tedious nitrate analysis. The application of an electrical potential gradient caused water to accumulate near the cathode. Thus by appropriately locating the electrodes, an electrokinetic barrier can be formed so as to increase the time taken for the contaminated water to spread to other areas.

Keywords: electrokinetic reduction, nitrates, TDR, apparent electrical conductivity

3.2 Introduction

Nitrates are the most common nitrogen contaminant in drinking water supplies. In rural areas, agricultural activities that involve the use of fertilizers and animal manures are major sources of nitrate contamination. Several *ex situ* processes are currently available that can effectively remove nitrate from contaminated water. Systems that are suitable for small rural communities include reverse osmosis, ion exchange, and electrolysis. However, all of these systems move nitrate from water supply and concentrate it in reject water or brine. Disposal of the reject water can be a major expense as well as an environmental issue.

Segall and Bruell (1992) while attempting to transport phosphates, nitrogen and other nutrients, and bacteria through fine-grained soils for biological treatment of gasoline showed that nitrates were invariably reduced at the cathode. As a result, there has been increased interest in using electrokinetic technology for removal of nitrates in soil. Most of the researchers tried to transport nitrate from a contaminated soil so that the concentrated nitrates may be treated using other non-electrokinetic techniques such as biological treatment (Budhu *et al.* 1997; Cairo *et al.* 1995; Eid *et al.* 2000). Some others combined electrokinetic treatment with another abiotic process such as zero-valent iron wall process (Chew and Zhang 1998).

As a first step in determining the effect of electrokinetics on nitrates, this study used electrokinetics to remove nitrate from ground water safely, and also to retard the flow of contaminated water. Therefore, the objectives of this study were to conduct a set of laboratory scale experiments to determine the ability of electrokinetics to remove nitrate from a nitrate-contaminated soil and to retard the flow of contaminated water from contaminated to uncontaminated area. As pH, apparent electrical conductivity, and ammonia content of the soil may change because of the electrokinetic treatment, it was decided to monitor these components while applying a voltage potential gradient across the soil columns.

Soil columns were used to conduct the laboratory experiment. An equal hydraulic gradient of 1.25 was applied to all soil columns to simulate a natural water movement in the soil columns. The nitrate contaminant was added to the constant head reservoir connected at the upstream inflow end of the columns and the nitrate concentration profile

along the length of the column was monitored. Because the nitrate reduction is known to occur at the cathode, the cathode was placed at the inflow end of the treatment columns. The anode was located at the outflow end. As the cathode is known to pull water towards it, this configuration ensured testing both electrokinetic reduction of nitrates and retardation of contaminated water flow through the soil.

3.3 Materials and methods

A laboratory scale experiment was designed to determine the effect of electrokinetic treatment on the nitrate concentration of the pore water. The laboratory equipment used in the study consisted of:

1. six plexiglass columns outfitted with four pore water extraction ports along the length
2. a constant head flow device
3. a flow rate measuring system at the outflow end
4. a constant voltage source
5. a data acquisition system consisting of a 24-channel multiplexer (fabricated in the Department of Biosystems Engineering) for measuring the voltage distribution along the soil column
6. Time Domain Reflectometry (TDR) mini-probes (fabricated in the Department of Biosystems Engineering) to monitor water content and apparent electrical conductivity (EC_a)

3.3.1 Plexiglass soil columns

Six Plexiglas columns were used in the experiment where three columns were used as a control and referred to as hydraulic columns (H Columns) and the other three columns were subjected to electrokinetic treatment and referred to as electrokinetic columns (EK+H Columns). The columns were 0.30 m long and had 0.03 m long spacers at both inflow and outflow end to provide influent and effluent reservoirs, respectively. The length of the soil column was thus 0.24 m having an internal diameter of 45 mm. Each column had two removable endplates that had one port each for solution inflow to the column and outflow from the column. An O-ring kept the seal between each endplate and the column. In order to take pore fluid samples, each column had four ports spaced 0.060 m apart along the length of the column starting at 0.045 m from the inflow end. Four additional holes of 14 mm internal diameter were located 0.060 m apart, along the length starting at 0.015 m from the inflow end to insert Time Domain Reflectometry (TDR) mini-probes to monitor water content and EC_a . All six columns had ports above spacers at both ends to facilitate the removal of entrapped gases and also to extract fluid samples.

In addition, the electrokinetic columns had four additional ports at the same distances but radially at right angles to the pore fluid collection ports. Platinum electrodes were inserted into these ports to monitor electrical potential along the length. The endplates of the electrokinetic columns contained a port for installing the negative electrode (cathode), for the inflow end plate, and the positive electrode (anode), for the outflow end plate. A schematic diagram of the electrokinetic column is shown in Fig. 3.1.

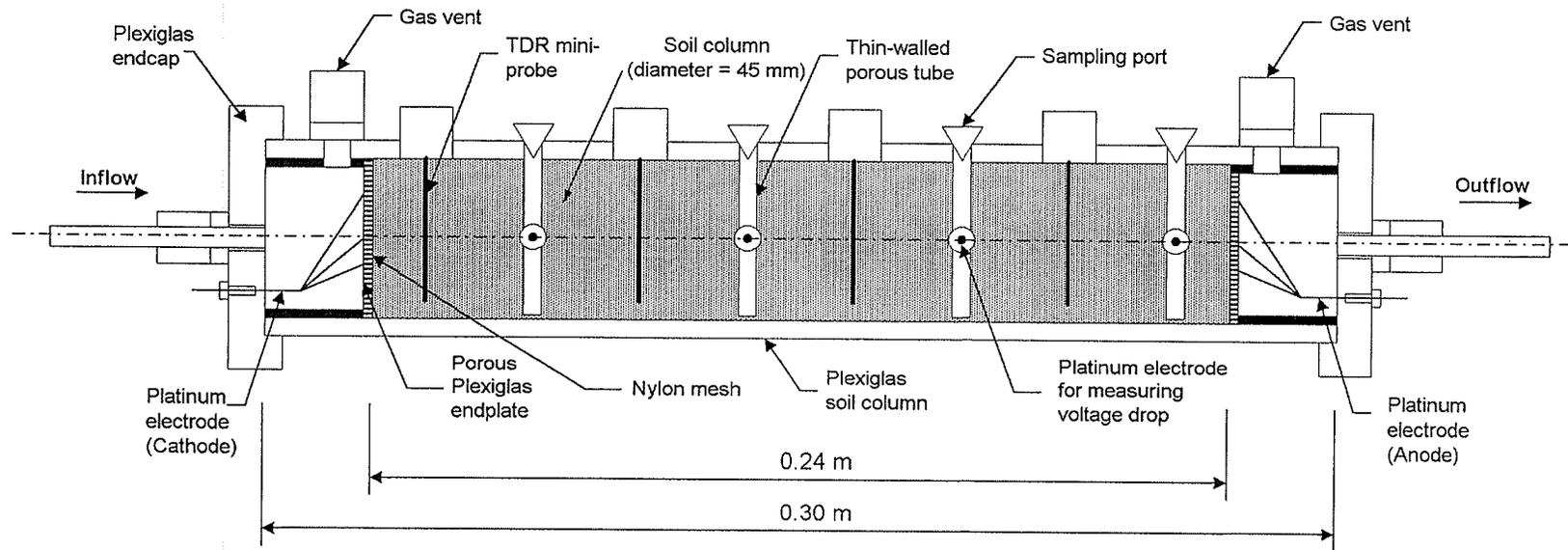


Fig. 3.1 Schematic diagram of the electrokinetic column (EK+H column) used in the electrokinetic experiment.

3.3.2 Hydraulic flow and measurement

The constant head at the upstream end of the sample was provided by an inverted Carboy over a cylindrical reservoir. There were six outlets in the reservoir which were connected to the inlet ends of the six soil columns through chemical resistant nylon pipe fittings. The outflow ports of the end plates were individually connected to thin-walled glass tubes (2.4 mm diameter and 1 m length) that were mounted horizontally on a graduated scale. This arrangement ensured a constant hydraulic gradient for the columns at the downstream end and facilitated the measurement of flow rates through each column by tracking the movement of inserted air bubbles. These flow rates were used to calculate hydraulic conductivity.

3.3.3 Voltage application and data acquisition

The electrokinetic columns were attached to control devices to apply the potential difference to the column and to monitor the drop in electrical potential difference along the length of the column. Platinum electrodes of 0.5 mm diameter were used for this purpose. Platinum electrodes were used to minimize corrosion under varying pH conditions created by the electrolysis.

The constant voltage across the soil sample was supplied and maintained by a BK Precision® DC Power Supply 1610 (BK Precision, Yorba Linda, CA). A specially designed 24-channel multiplexer was coupled with a Hewlett Packard® Multimeter (Model 34401 A, Hewlett Packard, Palo Alto, CA) to measure voltage drops along the columns and the current in the samples. A computer controlled data acquisition/control system was used to continuously monitor the voltage distribution along the length of the soil columns.

The system can apply a DC voltage continuously or in a cycle. The voltage potential gradients along the soil sample were also measured using platinum electrodes. The four voltage drop measurement ports were spaced at 0.060 m apart starting at 0.045 m from the upstream end of the soil column.

3.3.4 Time Domain Reflectometer (TDR) mini-probes

Four holes of 14 mm internal diameter were located 0.060 m apart, along the length starting at 0.015 m from the upstream to insert TDR mini-probes to monitor water content and apparent electrical conductivity of the soil. A TDR mini-probe consists of three 1.5 mm diameter stainless steel of 0.035 m length. A two metre coaxial cable was used to connect the TDR mini-probe to the TDR cable tester. A Tektronix® 1502B metallic TDR cable tester (Tektronix, Beaverton, OR) was used to obtain waveforms from TDR mini-probes for water content and EC_a determination.

3.3.5 Experimental soil

Nitrate levels in groundwater are becoming a major concern in Southern Manitoba. Soil used for the laboratory-scale experiment was obtained from the Manitoba Crop Diversification Centre in Carberry Manitoba. The soil was collected from a depth of 0.40 - 0.60 m. The collected soil was air dried and the clods were broken using a mallet. The dry soil was then sieved through a 2 mm sieve and the soil retained on the 2 mm sieve was discarded. Soil passing through the 2 mm sieve was retained for the electrokinetic experiments.

3.3.6 Properties of the soil

3.3.6.1 Particle size distribution

A wet sieve analysis and a hydrometer analysis was performed on the soil particles passing through 2 mm sieve to determine the particle size distribution. A sample of known dry weight was dispersed using sodium hexametaphosphate and washed through No.200 sieve (Canadian Standard Sieve Series). The particles retained on the No.200 sieve were dried in the oven and shaken through a series of standard sieves. The percentage by weight of soil passing through each sieve was calculated by measuring the weight of the soil retained on each sieve. The particle size distribution of the soil passing through No.200 sieve was determined by the hydrometer method (Klute 1982). The particle size distribution was found to be 20% sand, 54% silt and 26% clay. Based on the textural triangle of the USDA classification scheme, the soil can be classified as a silt loam.

3.3.6.2 Particle density

The particle density (specific gravity) of the soil used in the experiments was found by using a specific gravity bottle (Klute 1982). The specific gravity bottle was filled with distilled water at room temperature. Then the specific gravity bottle was partially emptied and a known weight of oven dried soil sample was transferred to the specific gravity bottle. The specific gravity bottle was slightly agitated to release any entrapped air bubble. After allowing the soil to settle, the specific gravity bottle was again filled with water till the water is near the neck. Then the specific gravity bottle was weighed again. The difference in weight is the volume of the water displaced by the soil. Using this

method, the particle density of the soil was found to be $2.65 \times 10^3 \text{ kg m}^{-3}$.

3.3.6.3 Soil pH

Soil pH is a measure of the activity of hydrogen ions in the soil solution. The pH of the soil is indicative of the chemical properties of the soil. Measurement of soil pH in solution of CaCl_2 is the most satisfactory method. Fifteen grams of soil was measured out into a 50 mL beaker. Thirty millilitres of 0.01M CaCl_2 was added and the suspension was stirred and the sediment was allowed to settle. The soil was stirred at regular intervals of 30 minutes. The pH of the soil was measured by immersing the pH electrode into the partly settled suspension. The pH of the soil suspension was found to be 7.5

3.3.6.4 Soil electrical conductivity

Electrical conductivity of the soil is used for the determination of total soluble salts present in the soil. Two hundred grams of soil was placed into a 400 mL plastic beaker. Distilled water was added to the soil while stirring until it is nearly saturated. The sample was allowed to stand for one hour to permit the soil to imbibe water, and then more water was added to achieve a saturated paste. At saturation the soil paste glistens and reflects light, flows slightly when the container is tipped. The sample was then transferred to a Buchner funnel fitted with a Whatman No.1 filter paper. Vacuum was applied and the filtrate was collected in a test tube. The electrical conductivity of the soil-water was measured using the YSI Model 32 conductance meter (Yellow Springs Instruments Inc., Yellow Springs, Ohio). The electrical conductivity of the soil-water extract was found to be 9.5 dS m^{-1} at 25°C .

3.3.7 Experimental procedure

3.3.7.1 Soil column preparation

In packing the soil columns, care was taken to ensure a uniform bulk density across the columns. The columns were packed, with air-dried soil that had passed through a 2 mm sieve, in 10 mm sections to achieve uniformity. The soil was tamped using a tamping device. After packing each section, the surface was scarified to prevent formation of any distinct and denser layers in between. A thin piece of nylon mesh material was placed between the soil in the column and the perforated spacer to prevent soil being washed out. The amount of soil packed was used to determine the bulk density. The bulk densities of the soil columns were in the range of $1.20 - 1.27 \times 10^3 \text{ kg m}^{-3}$. The bulk densities and the porosity of the hydraulic columns and the electrokinetic columns are given in Table 3.1.

3.3.7.2 Saturation of the soil columns

The soil columns were saturated using de-ionised and de-aired water. The soil columns were mounted on a specially designed column holder vertically. While saturating the column, care was taken not to trap air that may hinder the saturation process. To avoid the formation of air pockets, the columns were flushed with carbon dioxide for two days so as to displace the air from pore spaces. This would prevent the formation of air pockets as carbon dioxide is more soluble in water than air. After two days, the columns were connected to a tank of de-ionized and de-aired water supply with the inflow at the bottom. The movement of the wetting front was maintained at less than 10 mm h^{-1} by controlling the flow into the soil columns.

Table 3.1 Bulk density and porosity of the soil columns for the first set of experiments

Sample No.	Bulk density ($\times 10^3 \text{ kg m}^{-3}$)	Porosity (%)
Hydraulic columns:		
H ₁₁	1.23	53.6
H ₁₂	1.27	52.1
H ₁₃	1.22	54.0
Electrokinetic columns:		
E ₁₁	1.26	52.4
E ₁₂	1.26	52.4
E ₁₃	1.20	54.7

After complete saturation, the orientation of the columns was changed to the horizontal position. Instrumentation was then added to the columns. Platinum electrodes for electrical columns were inserted and connected to the data acquisition system. TDR mini-probes were inserted, sealed in place using silicone and connected to their coaxial cables. Reservoirs were created for pore fluid extraction. Thin walled perforated plastic tubes were inserted into the reservoir to prevent the collapse of soils into these reservoirs. The soil columns continued to receive water for a week to stabilize the system.

3.3.7.3 Hydraulic conductivity measurements

After saturating the sample, the initial hydraulic conductivities of the soil columns were measured. The rate of movement of the water meniscus in the outflow glass tube was measured for a known time period. Then the hydraulic conductivity of the soil columns was found using:

$$K_h = \frac{a\Delta x}{A\left(\frac{dh}{dx}\right)\Delta t} \quad (5.1)$$

where:

- K_h = hydraulic conductivity ($m\ s^{-1}$),
- Δx = distance moved by the water meniscus (m),
- a = cross-sectional area of the glass tube (m^2),
- A = cross-sectional area of the soil column (m^2),

dh/dx = hydraulic gradient,

Δt = time to move the meniscus over a distance of Δx (s).

The hydraulic conductivities of the columns were monitored throughout the duration of the experiment. Measuring the hydraulic conductivity of the electrokinetic columns was a challenging task as the gas liberated from the electrolysis affected the bubble movement.

3.3.7.4 Monitoring water content and apparent electrical conductivity

The changes in the water content and EC_a were monitored daily by connecting the TDR mini-probes individually to a TDR cable tester. The individual waveforms were stored in a computer and a Quick Basic Computer program was used to extract water content and EC_a values from these waveforms. As application of a voltage may affect TDR measurements, the TDR measurements were made only when the voltage was not applied to the electrokinetic columns.

3.3.7.5 Voltage drop measurements

The voltage drop along the length of the soil column and the current flowing through the soil sample were measured by using a computer controlled data acquisition program. The voltage potential drop along the soil sample was measured using the current passing through the sample. A 100Ω resistor connected in series to the electrokinetic columns was used as a reference resistor to measure the current passing through the sample. The current passing through the sample was determined by measuring the voltage drop across the 100Ω resistor by using Ohm's law. With the help of the data acquisition program the electrical potential gradient can be applied

intermittently or continuously based on the experimental needs.

In this study the electrical potential gradient was applied intermittently. The electrical control and data acquisition systems were set up to apply a 24 V DC potential difference on a two-hour ON, two-hour OFF cycle to the electrokinetic columns. When the power supply was switched ON the voltage drop along the length of the columns were monitored at 30-minute intervals.

3.3.7.6 Nitrate contamination and electrokinetic treatment protocol

Once the flushing of the columns with de-ionized water was completed, the experiment was started by introducing a 500-mg $\text{NO}_3\text{-N L}^{-1}$ potassium nitrate solution at the upstream end in place of the de-ionized water. A constant hydraulic gradient of 1.25 was maintained throughout the experiment in all the columns. After introducing the KNO_3 solution at the inflow end, the voltage application and data acquisition system controlled by a computer program was activated. The electrical control and data acquisition systems were set up to apply a 24-V DC potential difference on a two-hour ON, two-hour OFF cycle to the electrokinetic columns and to monitor the voltage drop along the length for every 30 minutes. The intermittent application of electrical potential was continued for a nine-day period.

3.3.7.7 Pore water sampling and soil column sectioning

The distribution profile of nitrate and ammonium ions in the columns, and pH were measured in two ways. To monitor changes during the experiment pore water samples were extracted from the ports that were located 0.060 metres apart along the length of the column starting at 0.045 m from the upstream end. A one-mL syringe was used to extract

the fluid sample. To avoid cross-contamination while sampling, syringes were assigned to each port and were not interchanged. After every sampling each syringe was thoroughly rinsed with de-ionized water. The sampling was done before the start of the experiment (Day 0), one day after the start of the experiment (Day 1) and thereafter every other day until the end of the experiment. A sample of 0.4 mL was extracted and diluted by 15 times using an electronic scale. Samples showed varying degrees of opaqueness because of the fine soil particles present in them. Because nitrate and ammonium chemical analyses were based on colorimetric principles, these particles may interfere with their determination. Therefore, the samples were centrifuged at 10000 rpm for ten minutes to remove these particles. The supernatant was then stored in a refrigerator prior to analysis.

At the end of the experiment a destructive analysis of the columns was done to verify the nitrate and ammonium, and pH profiles of the column. The columns were sectioned at regular intervals to chemically analyse the soil sections to study the contaminant migration under coupled hydraulic, electrical, and chemical gradients. Soil samples were refrigerated to prevent nitrogen losses.

The contaminant was introduced at the cathode end and hence the section starting from the cathode would have higher concentration of contaminants. Hence, the sample was pushed from the cathode end to avoid the contamination of less contaminated soil portion. Care was taken to avoid cross contamination of samples. The soil column was sectioned into approximately six equal sections. Each sample section was again divided into two equal parts. From these portions, small portions were immediately transferred to moisture cans for water content determination. The balance portion was stored in the

refrigerator for pore fluid extraction for further chemical analyses.

The samples were transferred to 250 mL beakers and 15 mL of de-ionised water was added to the samples and mixed to prepare the soil paste. After allowing the samples to stand for four hours, the pore fluid was extracted using the procedure described in Section 3.3.6.4. The addition of water for extracting the ions reduced the actual concentration of the ions present in the soil. Hence, a dilution factor had to be used to calculate the actual concentration of the ions. The dilution factor was found by:

$$DF = \frac{V_w + V_p}{V_p} \quad (5.2)$$

where:

- DF = dilution factor,
V_w = volume of water added (mL),
V_p = volume of pore fluid present in the soil (mL).

The volume of the pore fluid present in the soil section was found from the soil moisture and the soil section used for fluid extraction, using the formula:

$$V_p = \frac{\theta_m}{(100 + \theta_m)} \times \frac{M_s}{\rho_w} \quad (5.3)$$

where:

- θ_m = dry basis water content of the soil (%),
M_s = mass of the wet soil section (kg),
 ρ_w = density of the water (kg m⁻³).

For accurate determination of the nitrate and ammonium concentrations, the extracted pore fluid was duplicated before chemical analysis was done. The measured concentrations were multiplied by the respective dilution factor of the sections to find the actual pore water concentrations.

3.3.7.8 Chemical analysis for nitrate ions

Nitrate content of the diluted samples were analysed using a Technicon® autoanalyzer II Colorimeter (Technicon Instruments Corporation, Tarrytown, NY). The principle used in this method is that the nitrate present in the sample is reduced to nitrite by passing the sample through a column of granular cadmium coated with copper. Nitrite ions form a reddish-purple azo dye at pH 2.0 - 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride. The colour is measured at a wavelength of 520 nm. In this analysis a low calibration range of 2 - 20 mg NO₃/NO₂-N with a detection limit of 0.2 mg N L⁻¹ was used. The procedure adopted is explained below:

1. A nitrate calibration stock solution of 1000 mg KNO₃-N/L was prepared by dissolving 1.8045 g KNO₃, (which was previously dried for 24 hours at 105°C and desiccated), in de-ionized water and the volume was brought to 250 mL.
2. Nitrate standards in the high range were prepared as 2.0, 5.0, 10.0, 15.0, and 20.0 mg KNO₃ L⁻¹ from nitrate stock solution through appropriate dilution. These solutions were prepared ahead of time and stored in the refrigerator.
3. In the autoanalyzer the calibration standards were run first followed by quality control standards. A sample time of 35 s and total time of 80 s were used. Once

the calibration is verified, samples brought to room temperature were placed on the autosampler and run. If the nitrate concentration in the sample was not within the working range of the autoanalyzer then they were further diluted. After every 25 samples blanks and standard 3 solution ($10.0 \text{ mg KNO}_3 \text{ L}^{-1}$) were introduced to do a baseline correction.

4. Measured values were first multiplied by a constant to convert the values to $\text{NO}_3\text{-N}$ mg L^{-1} units. Then they were multiplied by appropriate dilution factor to obtain actual nitrate concentration in the pore water or soil section.

3.3.7.9 Chemical analysis for ammonium ions

Ammonium content of the diluted samples were analysed using the Technicon® autoanalyzer II Colorimeter. Ammonia is measured by means of the Berthelot reaction in which a blue-coloured compound related to indophenol is formed with phenol and sodium hypochlorite. Sodium nitroprusside is added to enhance the intensity of the colour. The colour is measured at a wavelength of 630 nm. In this analysis the calibration range was 0.1 - 1.2 mg $(\text{NH}_4)_2\text{SO}_4\text{-N}$ with a detection limit of 0.01 mg N L^{-1} was used. The procedure adopted is explained below:

1. An ammonia calibration stock solution of $100 \text{ mg } (\text{NH}_4)_2\text{SO}_4\text{-N L}^{-1}$ was prepared by dissolving $0.2358 \text{ g } (\text{NH}_4)_2\text{SO}_4$, (oven dried for 4 hours at 105°C and desiccated), in de-ionized water, and a $2 \text{ mL } 25\% \text{ H}_2\text{SO}_4$ solution was added and the volume was brought to 500 mL .
2. Ammonia standards in the range were prepared as $0.1, 0.2, 0.4, 0.8,$ and $1.2 \text{ mg } (\text{NH}_4)_2\text{SO}_4\text{-N L}^{-1}$ from ammonia stock solution through appropriate dilution.

These solutions were prepared ahead of time and stored in the refrigerator.

3. In the autoanalyzer the calibration standards were run first followed by quality control standards. A sample time of 35 s and total time of 80 s were used. Once the calibration is verified, thawed samples were placed on the autosampler and run. If the ammonia concentration in the sample was not within the working range of the autoanalyzer then they were further diluted. After every 25 samples blanks and standard 3 solution ($0.4 \text{ mg } (\text{NH}_4)_2\text{SO}_4 \text{ L}^{-1}$) were introduced to do a baseline correction.
4. Measured values were first multiplied by a constant to convert the values to $\text{NH}_4\text{-N mg L}^{-1}$ units. Then they were multiplied by appropriate dilution factor to obtain actual ammonia concentration in the porewater or soil section.

3.3.7.10 Other measurements

pH of the solution was measured using a Corning® pH meter 130 (Corning, Corning, NY). Electrical conductivity of the pore fluid was measured with a conductance meter (YSI Model 32).

3.4 Results and discussion

3.4.1 Nitrate-N concentrations

Figure 3.2 shows a series of graphs showing the changes in nitrate concentration that occurred during the experiment, along the lengths of the columns shown here as relative distance from the cathode inflow end. Relative distance of a port from the cathode was the ratio of a port's distance from cathode to the total length of the soil column.

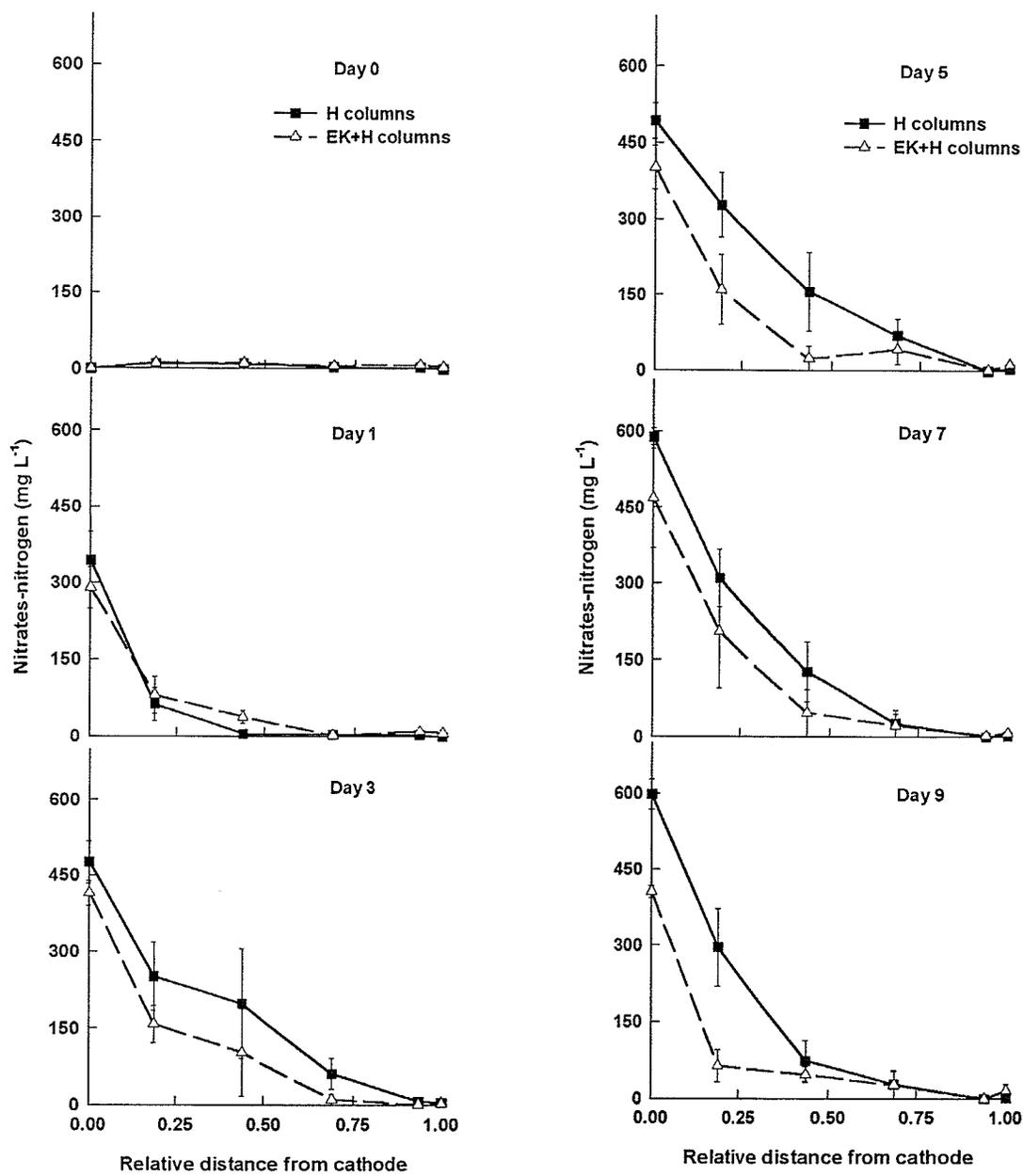


Fig. 3.2 Nitrate concentrations in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error from three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

In Fig. 3.2. graph Day 0 shows the nitrate concentrations before the 500 mg L⁻¹ nitrate nitrogen solution was introduced at the inflow end.

The graph on Day 1 shows nitrate concentrations along the length a day after the nitrate solution was introduced at the inflow end (cathode) and the application of voltage commenced. The concentration at the inflow end was about 290-340 mg L⁻¹ nitrate-nitrogen indicating that all of the de-ionized water from the inflow compartment had not been replaced by the nitrate solution. The nitrate concentrations at the 0.2 and 0.4 relative distance from cathode began to rise in all columns indicating the movement of nitrate through the columns. No apparent difference was visible between the hydraulic and electrokinetic columns. On Day 3, the nitrate concentration at the inflow end rose to about 415-475 mg L⁻¹. Further movement of nitrate through the columns was shown by the increase in concentrations at relative distances of 0.2, 0.4, and 0.7 corresponding to ports 1, 2, and 3, respectively. The electrokinetic columns showed a decline in the nitrate concentration values compared to those of the hydraulic columns showing some of the nitrates being denitrified near the cathode end. In Fig. 3.2 graph Day 5 and graph Day 7 the same pattern followed but the nitrate concentrations at the inflow end and at the relative distance of 0.2 for electrokinetic columns were not significantly ($p < 0.05$) lower than those from hydraulic columns.

After nine days, the nitrate concentration at the inflow end and at the relative distance of 0.2 were significantly ($p < 0.05$) lower than those from hydraulic columns showing a successful reduction near the cathode end (Table 3.2). During the testing period no ammonia smell was detected from the gas produced.

Table 3.2 Nitrate concentrations in soil columns as affected by the electrokinetic treatment (cathode at the inflow end).

Day	Relative distance (from cathode)	Mean nitrate-N (mg L ⁻¹)		CV	R ²
		H Column	EK+H Column		
1	0.0	343.0	290.0	16.0	0.84
	0.2	81.0	63.0	16.0	0.98
	0.4	105.0	5.0	155.0	0.65
	0.7	42.0	4.0	212.0	0.60
	0.9	10.0	3.0	56.0	0.77
	1.0	7.0	0.1	23.3	0.60
3	0.0	476.0	415.0	4.5	0.95
	0.2	252.1	105.8	17.0	0.97
	0.4	198.5	164.0	104.0	0.32
	0.7	61.6	11.0	105.0	0.80
	0.9	58.5	8.0	188.0	0.70
	1.0	93.6	5.0	228.0	0.60
5	0.0	492.9	402.6	2.5	0.99
	0.2	328.0	209.0	53.2	0.90
	0.4	156.0	24.0	98.7	0.76
	0.7	69.0	42.0	40.3	0.92
	0.9	0.9	0.0	244.0	0.60
	1.0	73.0	4.0	197.6	0.60
7	0.0	589.0	339.0	39.2	0.70
	0.2	310.0	206.0	25.6	0.90
	0.4	127.0	47.0	92.3	0.70
	0.7	26.6	22.0	212.0	0.25
	0.9	2.4	0.0	244.0	0.60
	1.0	38.5	2.2	184.0	0.60
9	0.0	598.7	470.8*	8.5	0.93
	0.2	296.0	69.2*	40.1	0.91
	0.4	93.0	17.0	111.9	0.25
	0.7	28.0	27.0	5.1	0.99
	0.9	-	-	-	-
	1.0	17.0	2.2	149.0	0.63

* Mean comparisons are significantly different ($p < 0.05$). All the other mean comparisons are not significantly different (SAS version 8.02). CV = Coefficient of variation. R² = Coefficient of determination. Relative distance of a port from the cathode was the ratio of a port's distance from cathode to the total length of the soil column.

This was further confirmed by doing an ammonia analysis for all the samples along with analysis for nitrate. The test conducted on samples did not show any treatment effect on ammonia production due to electrokinetic process.

3.4.2 Ammonia-N concentrations

Figure 3.3 shows a series of graphs describing the changes in ammonia concentration that occurred during the experiment, along the lengths of the columns shown here as relative distance from the cathode. In Fig. 3.3. graph Day 0 shows the ammonia concentration before the 500 mg L⁻¹ nitrate nitrogen solution was introduced at the inflow end. Graph on Day 1 shows ammonia concentrations along the length a day after the nitrate solution was introduced at the inflow end (cathode) and the application of voltage commenced. Before the start of the experiment, the ammonia concentration in the column varied between 1-9 mg L⁻¹ ammonia-nitrogen. The ammonia-N concentrations between the groups of columns, or along the columns were not significantly different ($p < 0.05$) from the other. The other graphs in Fig 3.3 show that throughout the experiment the ammonia nitrogen concentrations in electrokinetic and control columns were not significantly ($p < 0.05$) different. This suggested that the nitrate nitrogen in the columns were not converted to ammonia nitrogen. The electrokinetic treatment therefore did not have any effect on ammonia nitrogen concentration.

3.4.3 Apparent electrical conductivity (EC_a)

In Fig. 3.4 the changes in apparent electrical conductivity as measured by TDR mini-probes are illustrated. Before the experiment started both types of columns show similar EC_a values. The EC_a values were from 9.6 to 11.4 dS m⁻¹.

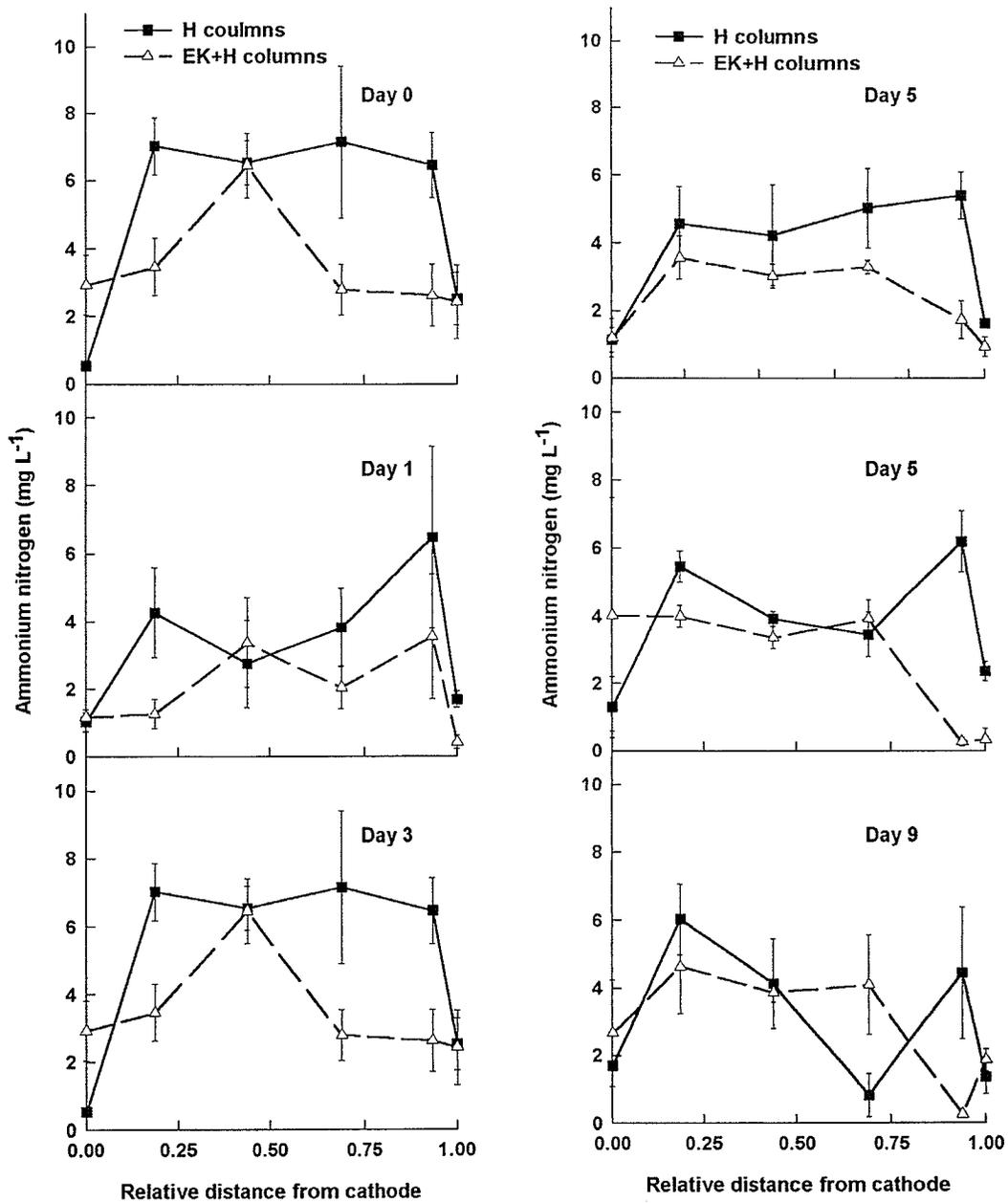


Fig. 3.3 Ammonia concentrations in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error from three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

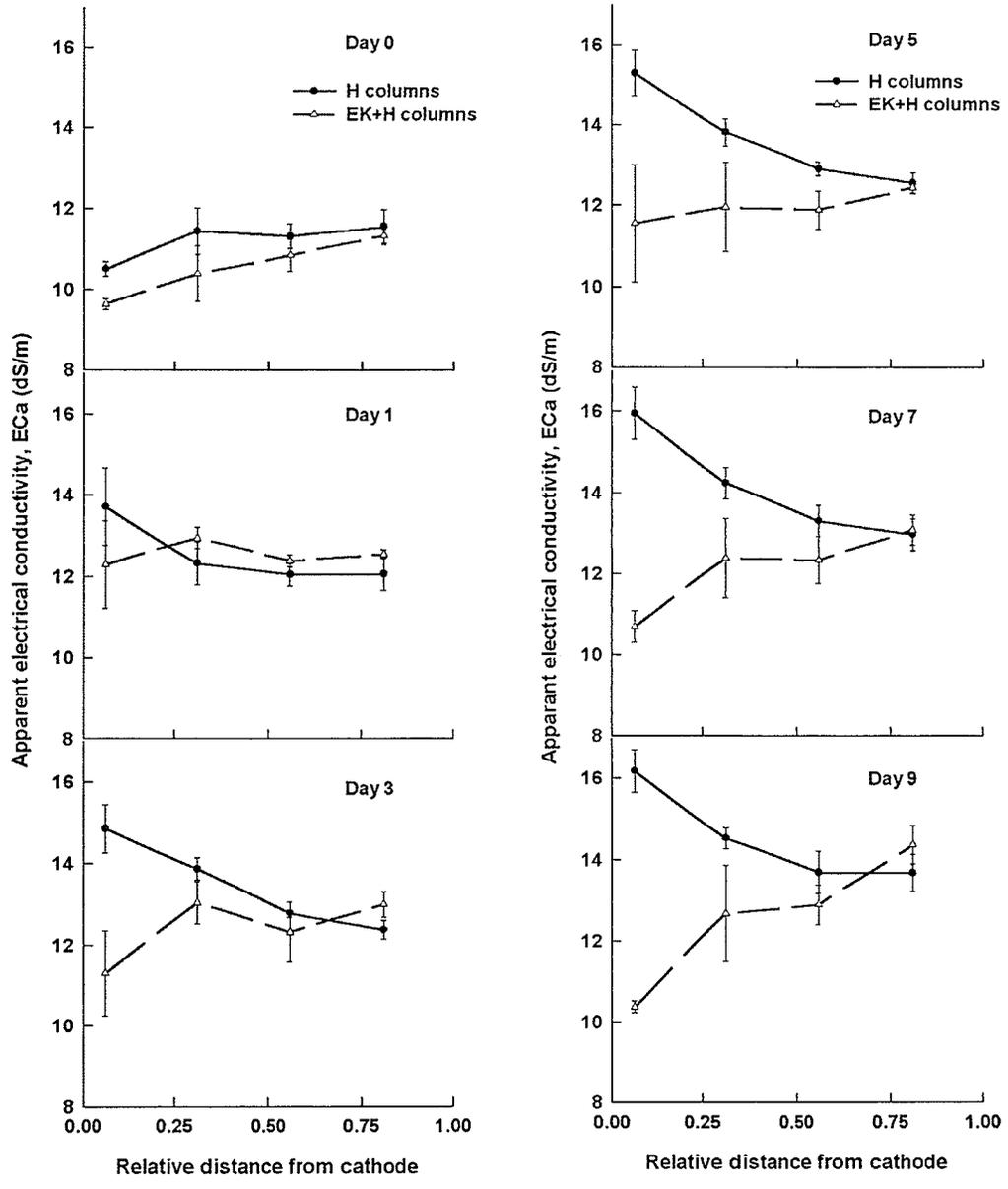


Fig. 3.4 Apparent electrical conductivity (EC_a) in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error from three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

The low EC_a values at a relative distance of 0.06 from the inflow end in all columns may be because of the leaching of solutes from the inflow end resulting from the constant water flow. A day after the nitrate solution was introduced, the EC_a values in the hydraulic columns began to rise corresponding to the movement of KNO_3 solution into the column. The EC_a values in the electrokinetic columns, however, did not rise as much as those in the hydraulic columns. This may be attributed to the production OH^- ions at the cathode and being moved along with hydraulic and electrokinetic gradients. The H^+ production at the anode end did not show much of an increase in the EC_a value as the H^+ ions were moving against the hydraulic gradient. On Day 3, in addition to the above pattern, the EC_a at a relative distance of 0.2 from the anode began to rise as H^+ ions moved against the flow. The same pattern continued for the rest of the experiment. The rise of EC_a values in hydraulic columns corresponded with the KNO_3 solution movement into the column ($R^2 = 0.60$).

The decline of EC_a values in electrokinetic columns from the cathode end was further enhanced by the reduction of nitrate at this end. The high EC_a towards anode may be due to the increase of H^+ ions. These H^+ ions moves against the hydraulic gradient towards the cathode seems to have reached a relative distance of 0.2 from anode. The TDR probes were useful in locating nitrate solution movement approximately, before analysing pore water extracts for nitrate.

3.4.4 Water content

The TDR mini-probes also monitored the changes in the water content in all columns. In Fig. 3.5 the changes in water content as measured by TDR mini-probes are illustrated. Before the experiment started both types of columns showed similar water content values. The volumetric water content values during the experiment period varied between 0.44 - 0.49 $\text{m}^3 \text{m}^{-3}$. The water contents between the groups of columns, or along the columns were not significantly different from the other. The other graphs in Fig. 3.5 showed that throughout the experiment the water contents in two groups of columns were not significantly different.

The application of voltage, however, caused water to accumulate near the cathode in the electrokinetic columns. This was reflected in less time required for pore water extraction near the cathode and more time required for pore water extraction near the anode. This was not the case before starting the application of a voltage gradient. Because TDR probes are less sensitive to changes in water contents near saturation water contents, the changes in water content in the electrokinetic columns were not reflected on the TDR measured water content values.

3.4.5 Hydraulic conductivity

The average hydraulic conductivity of all the soil columns was $0.41\text{E-}6 \text{ m s}^{-1}$ with a range from $0.12\text{E-}6$ to $1.33\text{E-}6 \text{ m s}^{-1}$. With the application of voltage the hydraulic conductivities of the electrokinetic columns decreased compared to those from hydraulic columns.

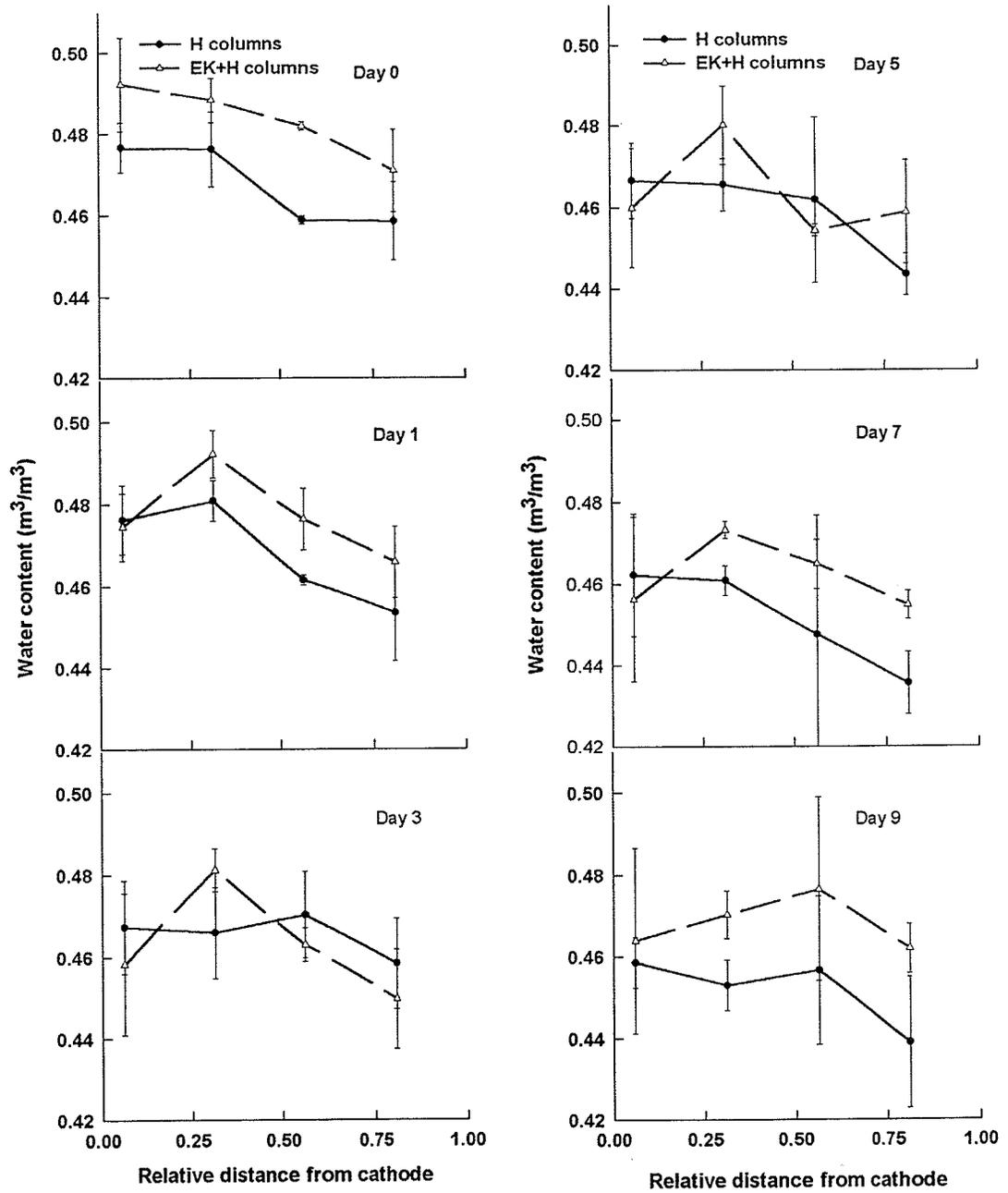


Fig. 3.5 Water content in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error from three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

The hydraulic conductivity values calculated for electrokinetic columns were not considered reliable as the gas pressure in the outflow compartment frequently affected flow determination.

3.4.6 pH

Figure 3.6 shows the changes occurred in pH in the soil columns. The pH in the hydraulic column was about 6.5 and did not change during the experiment. Application of a voltage also causes hydrolysis and OH^- and H^+ ions are produced in the cathode and anode, respectively. On Day 3, the pH near the cathode began to rise and the pH near the anode began to decrease. On Day 5 the pH near the electrodes were significantly different from those of the hydraulic columns.

This graph also showed that the acid front from the anode was fast moving against the hydraulic gradient towards the cathode compared to the base front movement towards anode because of the high mobility of H^+ ions. By Day 9 the pH in the electrokinetic columns increased to about 8.5 near the cathode, and decreased to about 4.0 near the anode. A drastic change in pH may bring undesirable changes in the existing chemical equilibrium of a soil. Besides it may create sites with high electrical resistivity that may render the electrokinetic process less effective. These situations may be “neutralized” by adding appropriate nonpolluting, naturally occurring buffer solutions to stabilize the soil.

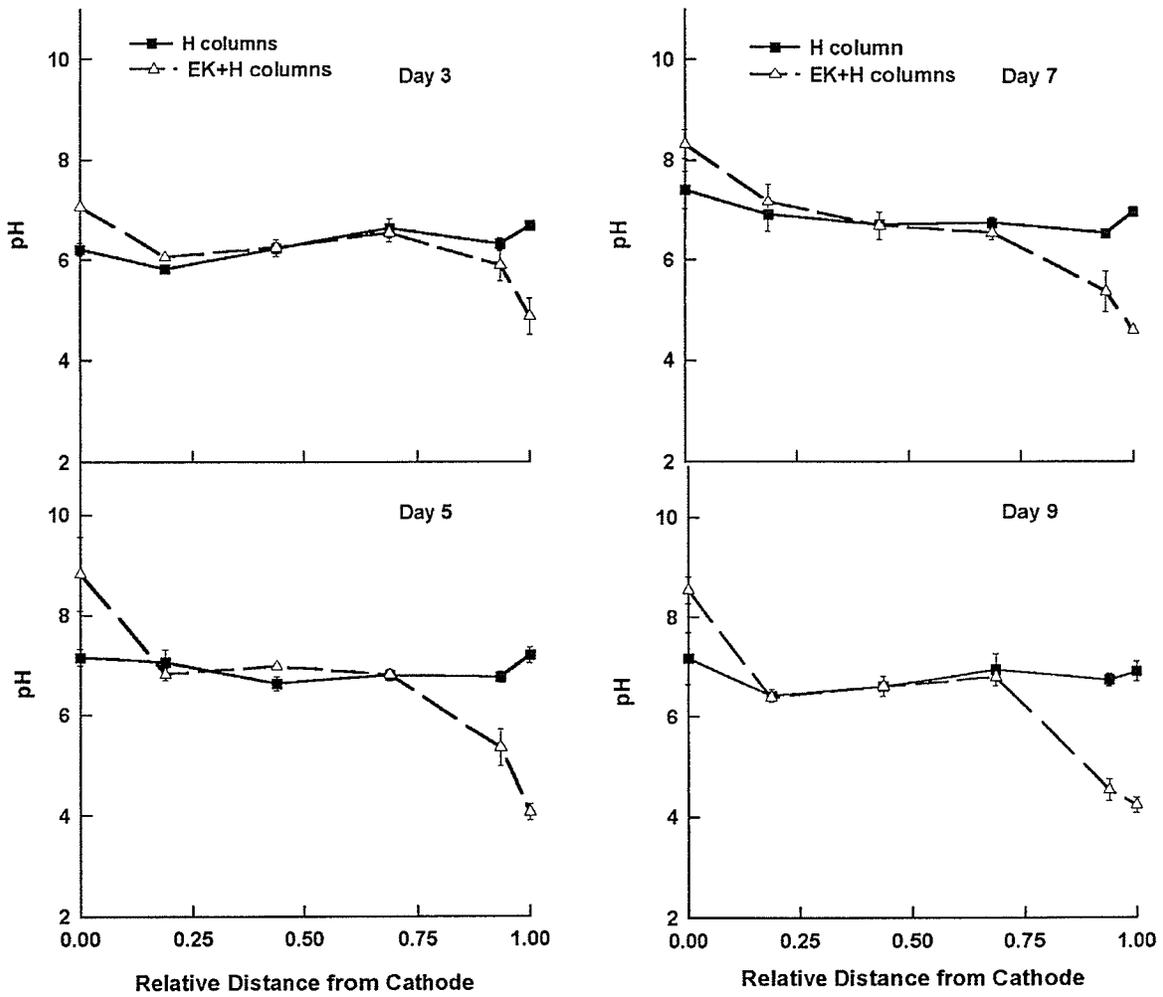


Fig. 3.6 pH in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error from three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

4. FORMING A NITRATE ION BARRIER USING ELECTROKINETIC RETENTION IN SOIL

4.1 Chapter summary

Movement of chemicals through soils to groundwater has become a serious problem in many agricultural and livestock producing areas. One of the major concerns with this chemical movement is the movement of nitrates in soil. Nitrates being anions are free to move in a soil system as they are not adsorbed to the clay particles which are negatively charged. In recent times electrokinetic technique has been used for transporting metal contaminants and other colloids in the soil. By utilizing such a transport process in reverse, application of an electrokinetic potential may retard the spread of nitrate contaminant in a soil.

This study was aimed at using electrokinetics to retard the movement of nitrate ions against flow due to a hydraulic gradient and concentrate nitrates at a desired location so that the water containing concentrated nitrate can be pumped out for further treatment. By restricting the movement of nitrates at certain locations, the spread of nitrate contamination would be limited to a smaller volume of soil. Therefore, the objectives of this study were to conduct a set of laboratory experiments to determine the use of electrokinetics to retard nitrates movement and to establish an electrokinetic barrier to nitrate ion migration to reduce the spread of contaminant.

The results showed that applying electrical potential gradient to soil caused the anode (positive electrode) to attract and accumulate nitrates rapidly at the anode end. In a field situation by having a timed-pumping operation, the pore water containing

concentrated nitrate can be evacuated to a confined, safe location for further treatment. Treatments like biological denitrification systems and catalytic systems can be used for such purpose. These systems convert nitrate to nitrogen gas (Chew and Zhang 1999; Haugen *et al.* 2002; Till *et al.* 1998).

The application of the electrical potential gradient also retarded the nitrate ion movement. The anode retarded the movement of nitrates further into the column despite having a steep nitrate concentration gradient at the inflow end. Nitrate concentrations at a relative distance of 0.2 from the anode in electrical column was significantly lower than the control ($p < 0.05$) showing that anode can effectively retard nitrate movement against a hydraulic gradient of 1.25. As demonstrated, such retardation effectively controls the movement of nitrates against an applied hydraulic gradient and forms an electrokinetic barrier to nitrate around the anode. The anode can act like a trap holding nitrate ions against a relatively high hydraulic gradient. By appropriately locating the electrodes in the field, an electrokinetic nitrate ion barrier can be created against existing local hydraulic gradients.

The inclusion of TDR mini-probes in these experiments enabled continuous monitoring of changes in water content and apparent electrical conductivity (EC_a) in a non-destructive way.

Keywords: electrokinetic retention, electrokinetic accumulation, nitrates, TDR, apparent electrical conductivity.

4.2 Introduction

Movement of chemicals through soils to groundwater has become a serious problem in many agricultural and livestock areas. Over application of fertilizer and livestock waste in agricultural fields contributes to this problem. One of the major concerns in this chemical movement is the movement of nitrates in soil. Nitrates being anions, are not held by the cation exchange systems in the soil. Therefore, when found in excess nitrates can easily move within the soil and reach groundwater.

Electrokinetic technique has been used to transport and retain metal contaminants for removal and further processing. Some of these metal ions are present in complex form in the soil and the soil need to be pre-treated to release the metal ions before moving them. Nitrates are free to move in a soil system.

Electrokinetic technique may provide means of transporting nitrates in the soil. (Budhu *et al.* 1997; Cairo *et al.* 1995; Eid *et al.* 2000). If we can restrict the nitrate movement against a hydraulic gradient, then it may help retard the spreading of nitrate contaminant. Therefore, as a second step in finding the effect of electrokinetics on nitrates, this study was aimed at using electrokinetics to retard the movement of nitrate ions against a hydraulic gradient flow and concentrate nitrates at a desired location so that the pore water containing concentrated nitrate can be pumped out for further treatment. By restricting the movement of nitrates to certain locations, the spread of nitrate contamination would be minimized. Therefore, the objectives of this study were to conduct a set of laboratory experiments to determine the use of electrokinetics as a means of retarding nitrate movement to establish a nitrate ion barrier and to reduce the

contaminant spread and concentrate nitrates to a location.

4.3 Materials and methods

A laboratory scale experiment was designed to determine the effect of electrokinetic treatment on the nitrate movement in a soil system. The aim was to retard nitrate movement against a hydraulic gradient and concentrate them for further treatment. The apparatus that was described in Section 3.3 was used with necessary modification. A detailed description of the materials and methods was given in Chapter 3. Any changes in the procedures or analyses are described below.

Soil columns were used to conduct the laboratory experiment. An equal hydraulic gradient of 1.25 was applied to all soil columns to simulate a natural water movement in the soil columns. The nitrate contaminant was added at the upstream inflow end of the columns and the profile of nitrate concentration was monitored as a function of time and distance. Because the nitrate is known to move towards anode, anode was placed at the inflow end to retard the movement of nitrate ions with hydraulic flow and at the same time to determine the effectiveness of electrokinetics in accumulating nitrates at one location. The cathode was located at the outflow end.

The soil columns were filled with the same experimental soil as described in Section 3.3.5. The bulk densities of the soil columns were in the range of $1.40-1.47 \times 10^3$ kg m^{-3} . The bulk densities and the porosity of the hydraulic columns and the electrokinetic columns are given in Table 4.1.

Ammonia analysis of pore water and soil extract was abandoned for two reasons.

Table 4.1 Bulk density and porosity of the soil columns for the second set of experiments

Sample No.	Bulk density ($\times 10^3 \text{ kg m}^{-3}$)	Porosity (%)
Hydraulic columns:		
H ₂₁	1.42	46.4
H ₂₂	1.42	46.4
H ₂₃	1.40	47.2
Electrokinetic columns:		
E ₂₁	1.46	44.9
E ₂₂	1.40	47.1
E ₂₃	1.47	44.5

Firstly, no nitrate reduction is known to take place at the anode and secondly, the previous experiment did not show any electrokinetic treatment effect on ammonia concentration.

The pH of the solution was measured using a Accumet® Model 15 pH meter (Fisher Scientific Inc., Pittsburgh, PA).

4.4 Results and discussion

4.4.1 Nitrates-N concentrations

Figure 4.1 illustrates the changes in nitrate-nitrogen concentration along the length of the columns during the experiment. The first graph (Day 0) represents the situation before the 500 mg L⁻¹ KNO₃ solution was added at the anode end. A day after the KNO₃ solution was added and the electrical potential applied, the nitrate concentrations in both hydraulic and electrokinetic columns rose to about 400-500 mg L⁻¹. The nitrate concentrations in electrokinetic columns rose slightly more than those in the hydraulic columns (Day 1) and significantly higher ($p < 0.05$) (Table 4.2). In five days, the nitrate concentrations at the anode end of the electrokinetic columns doubled but apparently did not reach the first port located 0.2 relative distance away from anode. Relative distance of a port from the anode was the ratio of a port's distance from anode to the total length of the soil column. The reason for this quick rise in concentration at the inflow ends of electrokinetic columns were due to the accumulation of nitrate from the KNO₃ contaminant source at the anode. In hydraulic columns, the nitrate concentrations at the first ports began to increase and varied between 10-70 mg L⁻¹. On Day 7, the nitrate concentrations at the anode ends in the electrokinetic columns were about two and one-half times those in the hydraulic columns.

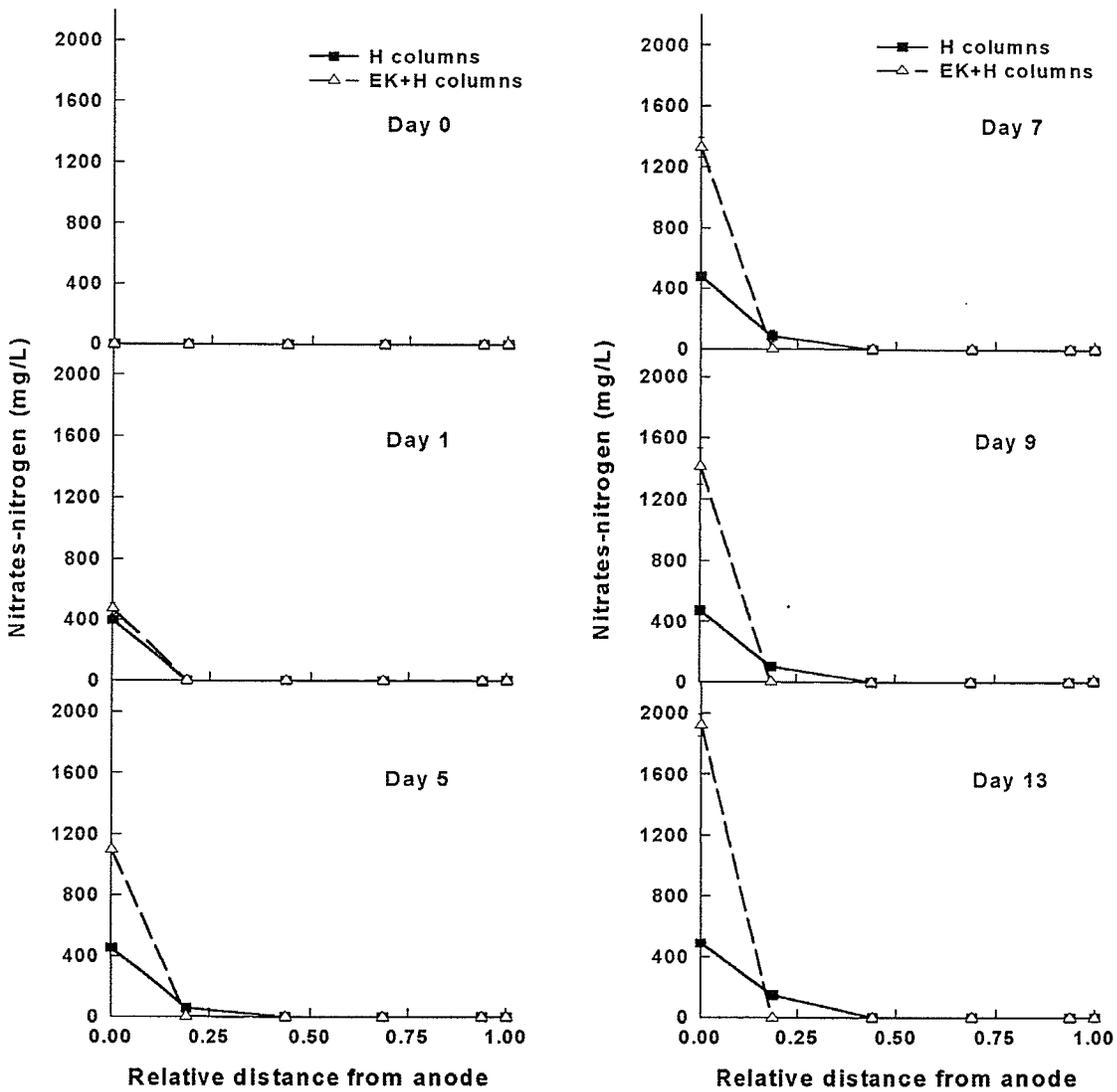


Fig. 4.1 Nitrate-nitrogen concentrations in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error among three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

Table 4.2 Nitrate-nitrogen concentrations in soil columns as affected by the electrokinetic treatment (anode at the inflow end).

Day	Relative distance (from anode)	Mean nitrate-N (mg L ⁻¹)		CV	R ²
		H Column	EK+H Column		
1	0.0	399.0	473.8*	2.3	0.99
	0.2	0.2	0.0	245.0	0.60
3	0.0	452.0	854.0**	5.6	0.94
	0.2	41.7	0.3	97.0	0.80
5	0.0	455.0	1100.0***	3.2	0.99
	0.2	59.1	3.4	95.0	0.75
7	0.0	481.5	1331.5*	6.3	0.99
	0.2	87.8	0.0	108.0	0.78
9	0.0	474.9	1416.0*	15.5	0.97
	0.2	105.0	0.7*	42.7	0.95
11	0.0	478.2	1548.0**	8.0	0.99
	0.2	127.7	0.3*	42.5	0.95
13	0.0	490.2	1922.0**	7.5	0.99
	0.2	148.4	0.2*	38.0	0.95

Mean comparison * significantly different (p<0.05), **significantly different (p<0.01), ***significantly different (p<0.001). All the other mean comparisons are not significantly different (SAS version 8.02). H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns. CV = Coefficient of variation. R² = Coefficient of determination.

The nitrate concentrations at a relative distance of 0.2 in the hydraulic columns continued to rise but not in the electrokinetic columns. Nitrate concentrations at the anode in the electrokinetic columns tripled by the ninth day. Nitrate concentrations at a relative distance of 0.2 from anode in electrical column was significantly lower than control ($p < 0.05$) showing that anode can effectively hold nitrate movement against a hydraulic gradient of 1.25 (Table 4.2). On Day 13, the nitrate concentrations at the anode end of the electrokinetic columns were close to four times to those in the hydraulic columns. The nitrate concentrations at the first ports (0.2 relative distance from anode) in hydraulic columns varied between 95-180 mg L⁻¹, whereas in the electrokinetic column the nitrate did not reach the first ports and was significantly lower ($p < 0.05$). This showed that an anode can act like a electromagnetic barrier holding nitrate ions against a relatively high hydraulic gradient.

Figure 4.2 shows the changes in nitrate-nitrogen at the inflow end during the experiment. The nitrate concentrations in the hydraulic (control) columns were about 500 mg L⁻¹ and did not show any appreciable changes. This shows that in the absence of electrokinetic potential the nitrate-N was uniformly and homogeneously transported along the hydraulic gradient, as would have been expected. The concentrations at the inflow end of the electrokinetic columns rose several folds to about 2000 mg L⁻¹ nitrate nitrogen in thirteen days. As the Figure 4.3 shows, the nitrate in hydraulic columns moved up to the first port (0.2 relative distance from the anode) and the concentration at this point steadily increased. In the electrokinetic columns, however, the nitrate did not reach the first port.

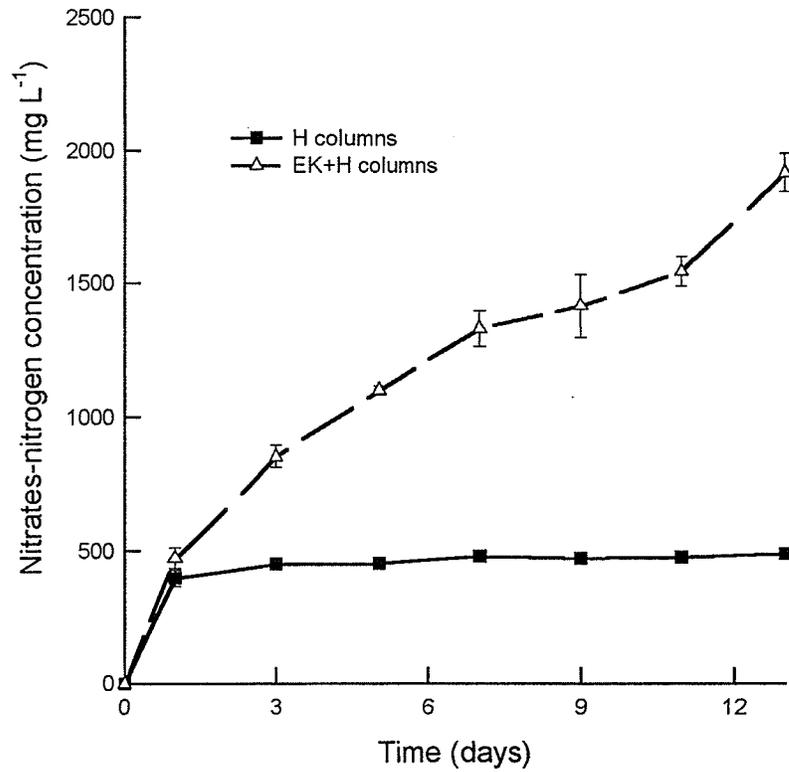


Fig. 4.2 Nitrate-nitrogen concentration at anode as influenced by the electrokinetic treatment. The error bars represent the standard error among three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

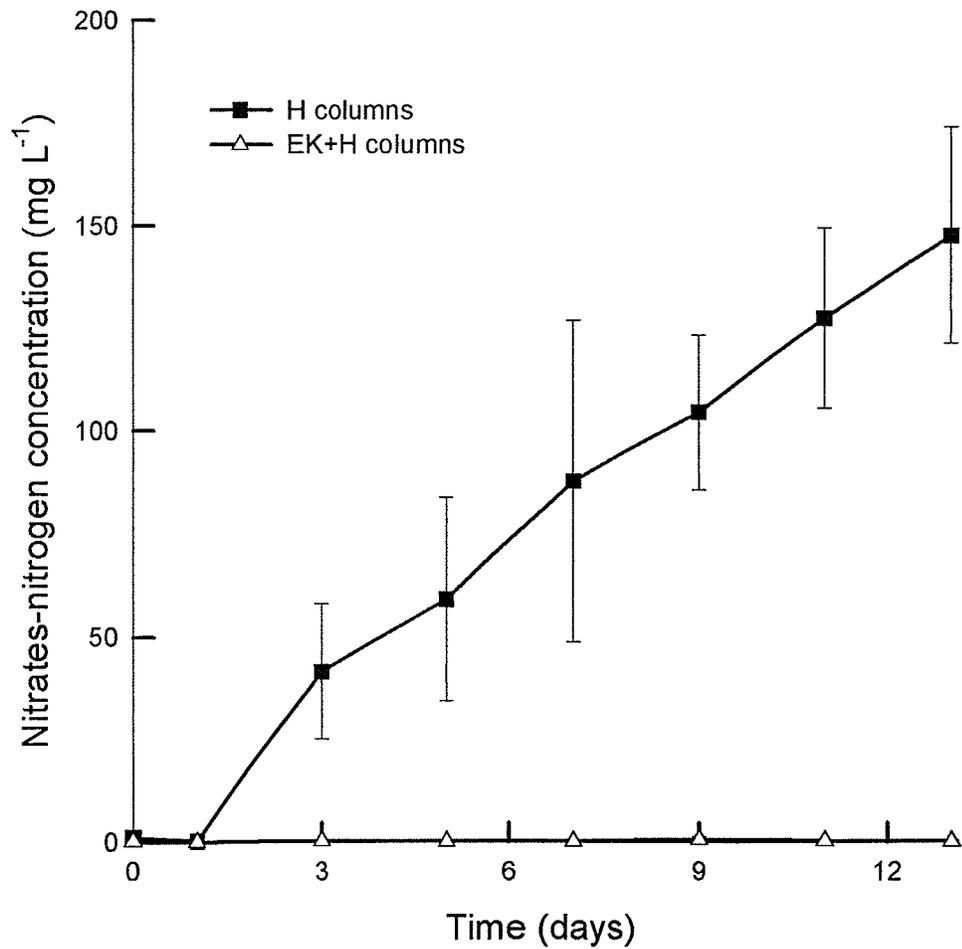


Fig 4.3

Nitrate-nitrogen concentration at a relative distance of 0.2 from inflow end as influenced by the electrokinetic treatment. The error bars represent the standard error among three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns. Relative distance of a port from the inflow end was the ratio of a port's distance from inflow end to the total length of the soil column.

The results showed that applying an electrical potential gradient to the soil caused the anode to attract and accumulate nitrates rapidly at the anode end. In a field situation, by having a timed-pumping operation, the concentrated nitrate can be evacuated to a confined, safer location for further treatment. Treatments like biological denitrification systems and catalytic systems can be used for such purpose. These systems convert nitrate to nitrogen gas.

The application of the electrical potential gradient retarded the nitrate ion movement. Despite having a steep nitrate gradient at the inflow end, the anode restricted the movement of nitrates further into the column. As demonstrated, such retardation effectively curtailed the movement of nitrates against an applied hydraulic gradient as high as 1.25 and formed a nitrate ion barrier around the anode. In the field, by appropriately locating the electrodes, an electrokinetic nitrate ion barrier may be created against existing natural hydraulic gradients.

4.4.2 Apparent electrical conductivity (EC_a)

Figure 4.4 illustrates the changes in EC_a along the columns during the experiment. Before the start of the experiment both types of columns showed similar EC_a values. The EC_a values showed a tendency to increase towards the outflow end as water flow tends to wash soil solutes and accumulate towards the outflow end. With the introduction of KNO_3 solution at the inflow end, the EC_a values at the inflow ends increased. By Day 5, the EC_a values at the cathode end decreased probably because of the OH^- ions build up there. Although there was accumulation of NO_3^- at the anode end, the EC_a values were yet to decrease as the H^+ ions are also produced at the anode.

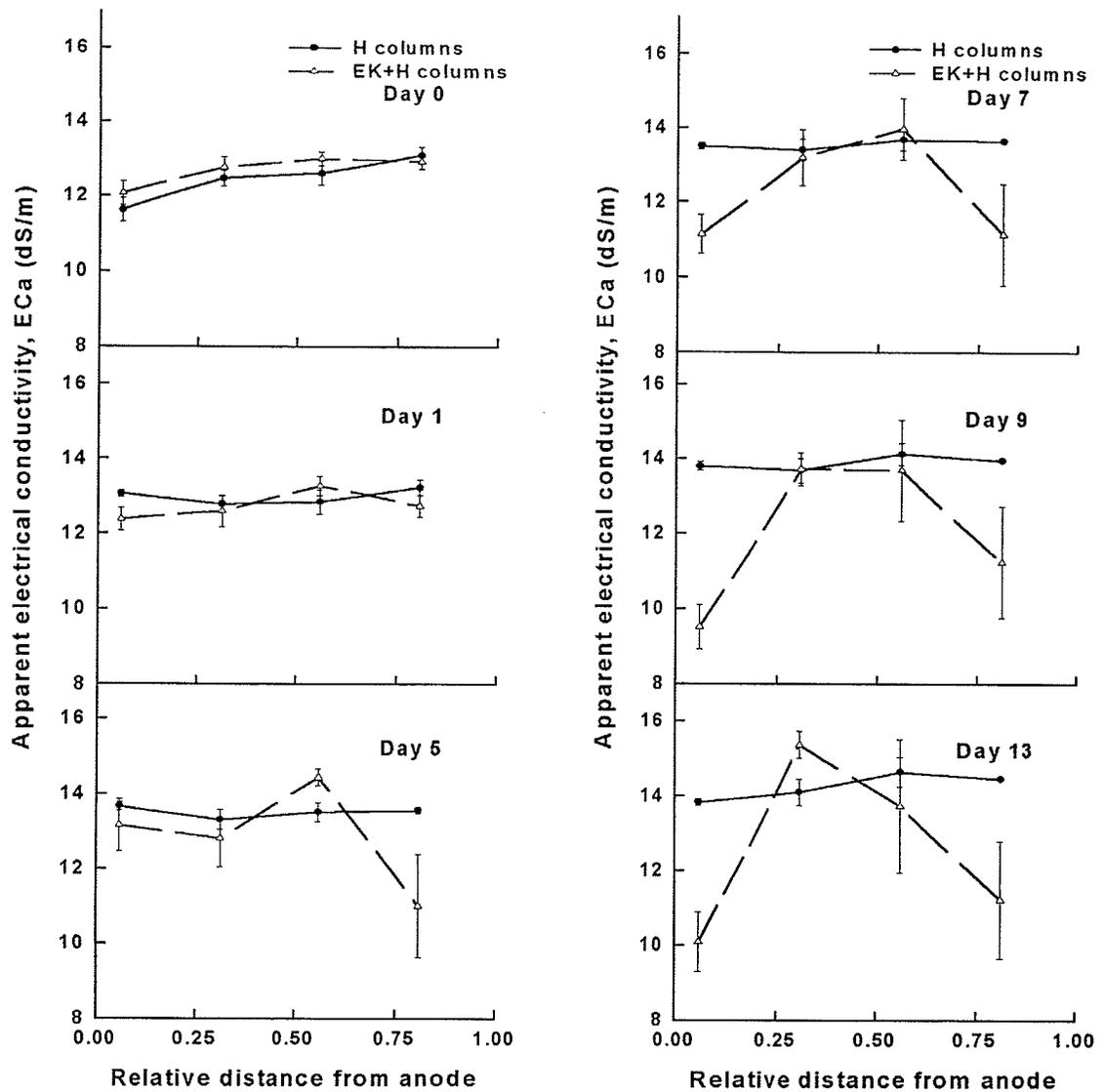


Fig. 4.4 Apparent electrical conductivity in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error among three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

On Day 7 EC_a values at the anode end started to decline as more and more nitrate ions accumulated at this end. For the remainder of the experiment the EC_a values at both ends decreased further because of continuous build up of nitrate and hydroxyl ions at the anode and cathode ends, respectively. Apparent electrical conductivity values in hydraulic column followed the nitrate movement. In electrokinetic columns TDR probes responded to NO_3^- and OH^- ions accumulation and movement.

4.4.3 Water content

The TDR probes monitored the changes in the water content in all columns. The volumetric water content values varied between 0.40-0.45 $m^3 m^{-3}$. Figure 4.6 shows the changes in water content during the electrokinetic treatment period. The water content slightly decreased towards the end of the column for both types of columns.

The water contents of the hydraulic columns were slightly higher than those from the electrokinetic columns. The changes within a group of columns or between columns were not significantly ($p < 0.05$) different. The porosity values varied between 0.44 - 0.47.

4.4.4 Hydraulic conductivity

The average hydraulic conductivity was about $1.00E-7 m s^{-1}$. After the application of voltage the hydraulic conductivity of the electrokinetic columns increased to $1.25E-7 m s^{-1}$. The increase may have been due to the cathode pulling water towards it. Because the columns are all saturated completely, this increase in hydraulic conductivity was not reflected on the TDR water content values.

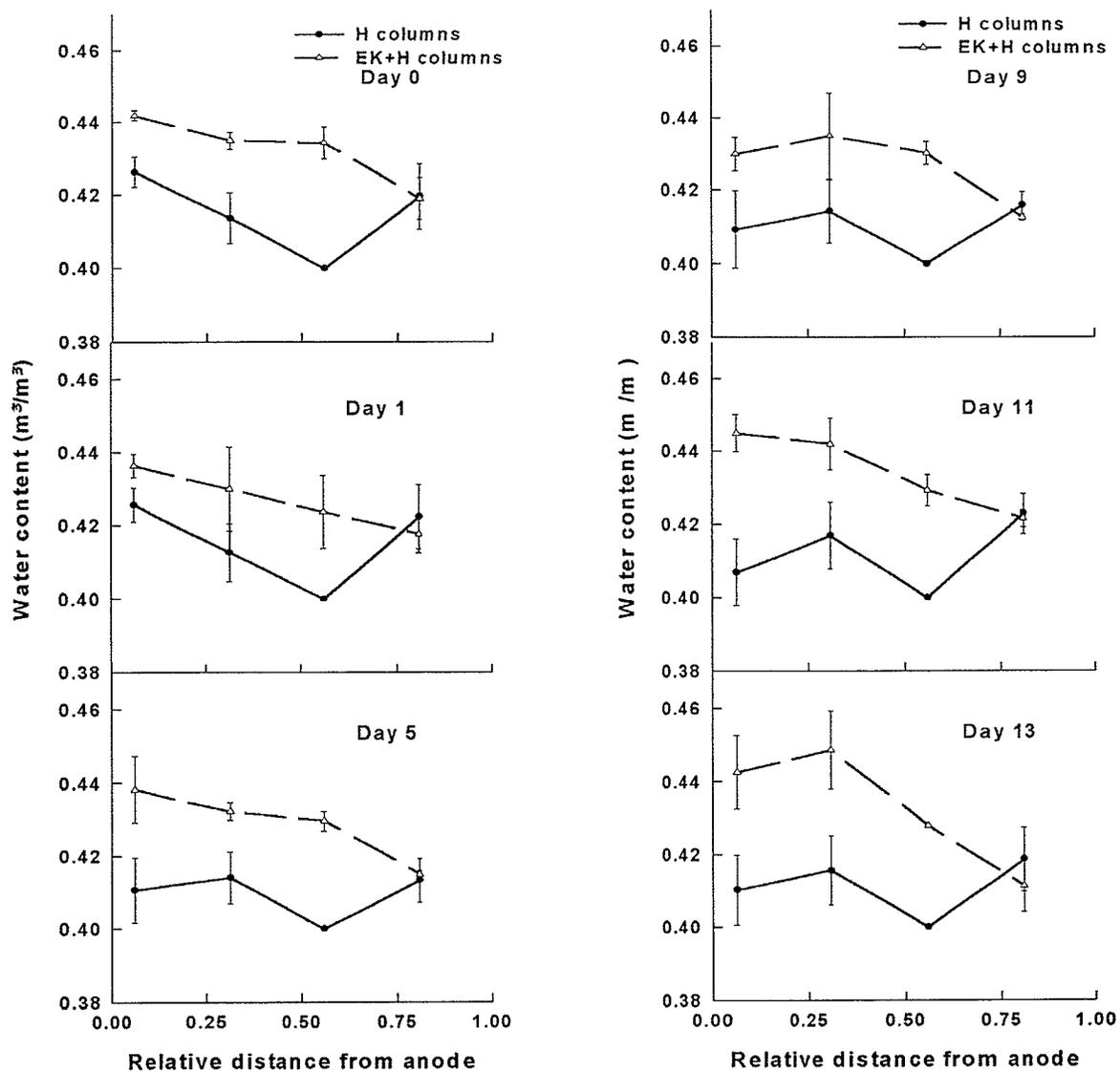


Fig. 4.5 Water content in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error among three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

4.4.5 pH

The pH in the hydraulic column was about 6.5 and did not change during the experiment. In contrast the pH in the electrokinetic columns decreased to about 4.0 near the anode, and increased to about 8.0 near the cathode and was attributed to the production of H^+ , and OH^- ions from the hydrolysis, respectively (Fig. 4.6).

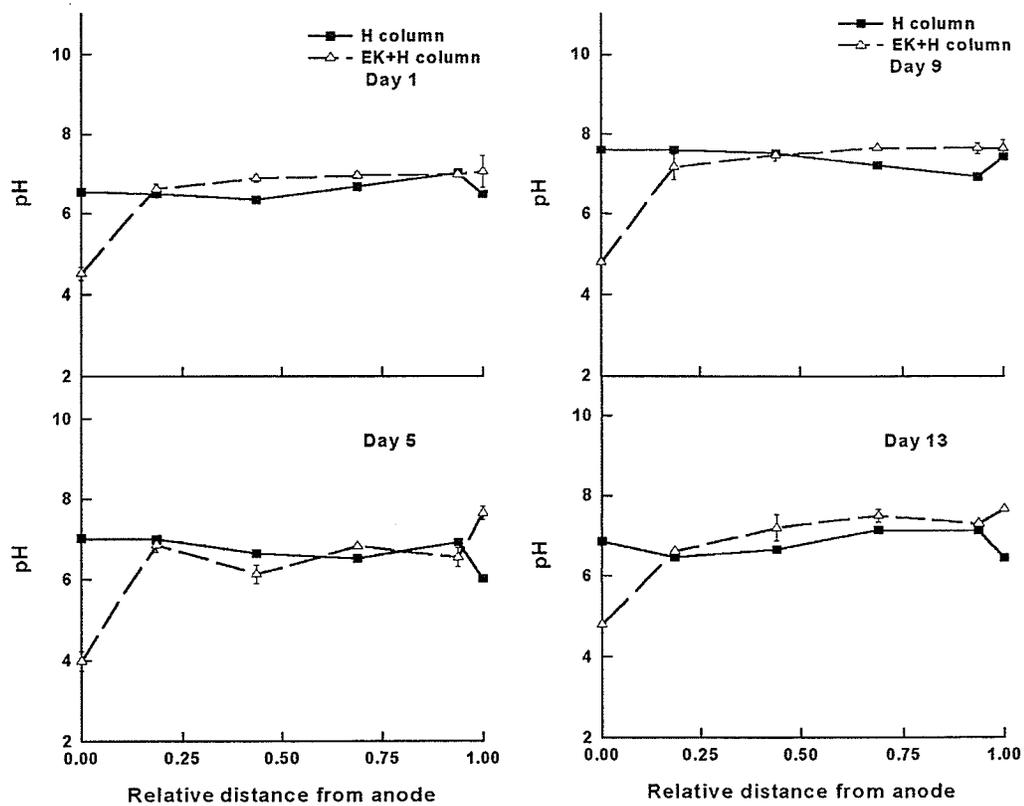


Fig. 4.6 pH in soil columns as affected by the electrokinetic treatment. Error bars represent the standard error among three replicates. H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns.

5. ELECTROKINETIC REMEDIATION OF NITRATE-CONTAMINATED SOIL

5.1 Chapter summary

Groundwater contamination due to the movement of nitrates from intensive livestock operations has become a major concern for surrounding communities that use groundwater as their water supply. The traditional pump-and-treat method is ineffective in medium to fine textured agricultural soils due to the low hydraulic conductivity. This study presents the results of a laboratory experiment investigating the feasibility of using electrokinetic treatment in retaining, accumulating, moving and converting nitrates in a medium-textured agricultural soil under moderate hydraulic gradients.

This study was aimed at remediating nitrate-contaminated soil by exploiting the processes of accumulation, migration, and conversion to other products using electrokinetics. Therefore, the objectives of this study were to conduct a laboratory scale experiment to determine the use of electrokinetics to retain, move, accumulate and convert nitrates to other forms so as to remediate a nitrate-contaminated soil.

In the first phase of the experiment, when the anode was located at the inflow end of the columns, nitrate movement due to a hydraulic gradient of 1.25 was slowed down by the electrokinetic treatment. After 15 days of flow, the effluent nitrate concentration in the control column rose to 90 mg L⁻¹ while no nitrates were detected in the effluent from columns subjected to electrokinetic treatment.

After 15 days, the polarity of the electrodes was switched by placing the cathode on the inflow end and the second phase of experiment was continued for another 20 days. The cathode near the inflow end promoted the reduction of nitrates entering the column to

other forms. The anode near the outflow end promoted the migration and accumulation of negatively charged nitrate ions towards the outflow end. Six days after the switch the nitrate concentration at a relative distance of 0.2 from cathode was significantly lower ($p < 0.05$) than that in the hydraulic column. The nitrate concentrations in the entire treatment columns were brought to $< 5 \text{ mg NO}_3\text{-N L}^{-1}$ and significantly lower ($p < 0.05$) than in the control by the 12th day. The $\text{NO}_2\text{-N}$ level remained below 1 mg L^{-1} throughout the experiment. The gas collected at the cathode showed presence of N_2O indicating some of the nitrates being converted to N_2O gas. There is no significant increase in $\text{NH}_3\text{-N}$ resulting from the electrokinetic treatment. The hydraulic conductivity varied between $1.0\text{E-}7 - 3.6\text{E-}7 \text{ m s}^{-1}$. The current requirement varied between 3 and 6 mA. The average current density was 3 A m^{-2} . The daily average energy consumption was 3.6 kWh m^{-3} .

Electrokinetic treatment retarded nitrate movement against a hydraulic gradient as high as 1.25, and effectively restored a medium textured soil contaminated with $\text{NO}_3\text{-N}$. To achieve optimum results in the field, the electrodes have to be located based on contamination location and the direction of hydraulic gradient. Field-scale studies have to be carried out to further understand the optimum electrode configuration, and frequency of polarity switching.

Keywords: Electromigration, Electrokinetic remediation, nitrate

5.2 Introduction

Groundwater contamination due to the movement of nitrates from intensive livestock operations has become a major concern for surrounding communities that use groundwater as their water supply. Nitrates play a vital part in plant growth as an

important nutrient. But when found in excess, nitrates can easily move within the soil and reach the groundwater. High nitrate levels in drinking water supplies represent a significant risk to human health as they are directly responsible for methaemoglobinaemia in infants and may play a role in the development of some forms of cancer. The Canadian Guidelines for Drinking Water Quality limits the Maximum Acceptable Concentration (MAC) of nitrates in drinking water to 10 mg L^{-1} as $\text{NO}_3\text{-N}$ and 1 mg L^{-1} as $\text{NO}_2\text{-N}$ (Health and Welfare Canada 1993). When over twenty six percent of the population in Canada depends on the groundwater as their source for drinking water, the problem of groundwater contamination becomes even more important (Hess 1986).

The set of experiments described in Section 3.1 on the effect of electrokinetics on nitrates showed that nitrate can be converted to other products at the cathode. But this conversion did not occur at a large scale so as to completely remediate a nitrate contaminated soil. Therefore, ways and means of increasing nitrate conversion need to be investigated. According to the half-equation provided by Segall and Bruell (1992) on electrokinetic nitrate reduction, adding H^+ at the cathode should enhance nitrate reduction. The hydrolysis reaction that invariably takes place in any electrokinetic application produces H^+ at the anode. Therefore, positioning the anode at the inflow end should increase nitrate reduction. The set of experiments described in Section 4.1 showed that nitrate can be accumulated and retained around anode forming a nitrate ion barrier. Conversely, positioning the anode at the outflow end should hasten the nitrate ion flow towards the outflow end. If we can combine the beneficial effects of these different processes, then we may be able to completely remediate a nitrate contaminated soil.

This study was aimed at remediating nitrate-contaminated soil by exploiting the processes of accumulation, migration, and conversion to other products using electrokinetics. Therefore, the objectives of this study were to conduct a set of laboratory experiments to determine the use of electrokinetics to retain, move, accumulate and convert nitrates to other forms so as to remediate a nitrate-contaminated soil. Soil columns were subjected to a hydraulic gradient of 1.25 to ensure extreme groundwater flow condition.

5.3 Materials and methods

The study was performed in two phases. In the first phase, nitrate retention potential of electrokinetics against an applied hydraulic gradient was evaluated. In the second phase, the remediation of the nitrate-contaminated soil by converting, moving and accumulating nitrates using electrokinetics was evaluated. The results were compared with those of the control where flow occurred due to applied hydraulic gradient only.

Soil columns were used to conduct the laboratory experiment. All of the six columns were subjected to a hydraulic gradient of 1.25 for the entire duration of the treatment that lasted 35 days. The three electrokinetic columns (EK+H) were subjected to electrokinetic treatment in two phases. In Phase 1, the anode was located on the inflow end during the first 15 days. In Phase 2, the polarity of the electrodes was switched on the 15th day and the treatment continued for an additional 20 days with the cathode located at the inflow end. Therefore, the Phase 1 had the anode at the inflow end from Day 0 to Day 15. The Phase 2 continued from Day 15 to Day 35 with the cathode at the inflow end.

The same apparatus that was used in Section 3.3 was used with necessary

modification. A detailed description of the materials and methods was given in Chapter 3. Only changes in the procedures or analyses are described below. The soil columns were filled with the same experimental soil as described in the Section 3.3.5. The bulk densities of the soil columns were in the range of $1.34\text{-}1.39 \times 10^3 \text{ kg m}^{-3}$. The bulk densities and the porosity of the hydraulic columns and the electrokinetic columns are given in Table 5.1.

The changes in analyses are as follows. Porewater samples were diluted using a Microlab[®] 500 Series Diluter (Hamilton Company, Reno, NV). Nitrate, nitrite, and ammonium content of the diluted samples were analysed using Technicon[®] Autoanalyzer II Colorimeter. The N₂O analysis was done using a Varian[®] CP-3800 gas chromatograph (Varian Inc., Palo Alto, CA). For this analysis a 15-mL cathodic gas sample was obtained using a 30 mL syringe and stored in airtight vials that were previously vacuumed. The pH of the solution was measured using a Accumet[®] Model 15 pH meter.

Nitrite content of the diluted samples were analysed with a Technicon[®] autoanalyzer II Colorimeter. The principle used in this method is that the nitrite ions form a reddish-purple azo dye at pH 2.0-2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride. The colour was measured at a wavelength of 520 nm. In this analysis a low calibration range of 0.5-10 mg NO₂-N with a detection limit of 0.2 mg N L⁻¹ was used. The procedure adopted is explained below:

Table 5.1 Bulk density and porosity of the soil columns for the third set of experiments

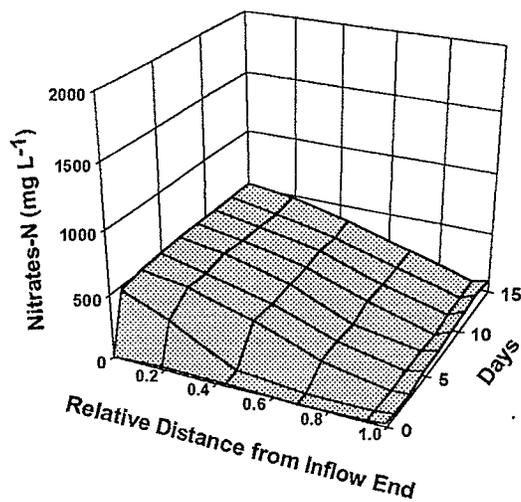
Sample No.	Bulk density ($\times 10^3 \text{ kg m}^{-3}$)	Porosity (%)
Hydraulic columns:		
H ₃₁	1.37	48.3
H ₃₂	1.34	49.4
H ₃₃	1.37	48.3
Electrokinetic columns:		
E ₃₁	1.35	49.0
E ₃₂	1.37	48.3
E ₃₃	1.39	47.6

1. A nitrite calibration stock solution of $1000 \text{ mg NaNO}_2\text{-N L}^{-1}$ was prepared by dissolving 0.4930 g NaNO_2 , (which was previously dried for 24 hours at 105°C and desiccated), in de-ionized water and the volume was brought to 100 mL .
2. Nitrite standards in the high range were prepared as $0.5, 1.0, 2.0, 5.0, \text{ and } 10.0 \text{ mg NaNO}_2 \text{ L}^{-1}$ from nitrate stock solution through appropriate dilution. These solutions were prepared ahead of time and stored in the refrigerator.
3. In the autoanalyzer the calibration standards were run first followed by quality control standards. A sample time of 35 s and total time of 80 s were used. Once the calibration is verified, thawed samples were placed on the autosampler and run. After every 25 samples blanks and standard 3 solution ($2.0 \text{ mg NaNO}_2 \text{ L}^{-1}$) were introduced to do a baseline correction.
4. Measured values were first multiplied by a constant to convert the values to $\text{NO}_2\text{-N mg L}^{-1}$ units. Then they were multiplied by appropriate dilution factor to obtain actual nitrate concentration in the porewater or soil section.

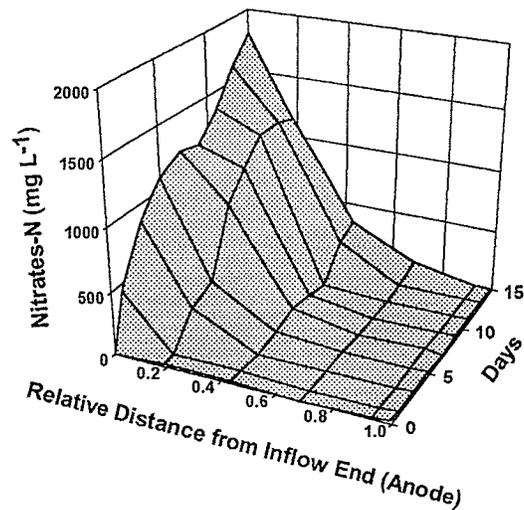
5.4 Results and discussion

5.4.1 Nitrate-N concentrations

Figure 5.1 shows the changes in nitrate concentrations as affected by the electrokinetic treatment in the first phase of the experiment. Figure 5.1a shows the gradual increase of nitrate concentration along the lengths of the control columns in the direction of applied hydraulic gradient. The influent nitrates concentration remained at 500 mg L^{-1} . The effluent nitrates concentration gradually rose to 90 mg L^{-1} in 15 days.



a)



b)

Fig. 5.1 Nitrates-N concentrations in the soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Anode is located at the inflow end (phase 1). Relative distance of a port from the inflow end was the ratio of a port's distance from inflow end to the total length of the soil column.

In the EK+H columns (Fig. 5.1b), nitrates quickly accumulated at the anode end indicating a migration of nitrates from the constant head source. The influent concentration of nitrates tripled in 15 days. Despite a high concentration of nitrates at the inflow end, the movement of nitrates through the EK+H columns was slow and nitrates never showed up in the effluent within 15 days. This showed that electrokinetic treatment can effectively retard nitrate movement against a hydraulic gradient of 1.25 which is much higher than that of normal field conditions. The presence of high nitrate concentration at the inflow end, however, creates a high concentration gradient and causes the nitrates to move into the columns due to chemical migration as shown in the Fig. 5.1b. Therefore, if pump-and-treat method is to be employed, the water high in nitrate concentration has to be quickly moved out for further treatment above ground.

The Phase 2 of the experiment began after 15 days when the polarities of the electrodes were switched by placing the cathode on the inflow end and the anode on the outflow end. This second phase of the experiment was continued for another 20 days. Figure 5.2 shows the changes in nitrates concentrations as affected by the electrokinetic treatment in the second phase of the experiment. Figure 5.2a shows further increase of nitrate concentration along the lengths of the control columns that were subjected to hydraulic gradients only. The influent nitrates concentration remained at 500 mg L^{-1} . When the electrodes were switched, the conversion of nitrates into other forms started near the cathode which is now located at the inflow end, while nitrates in the rest of the columns migrated quickly and accumulated at the outflow end (anode) (Fig. 5.2b).

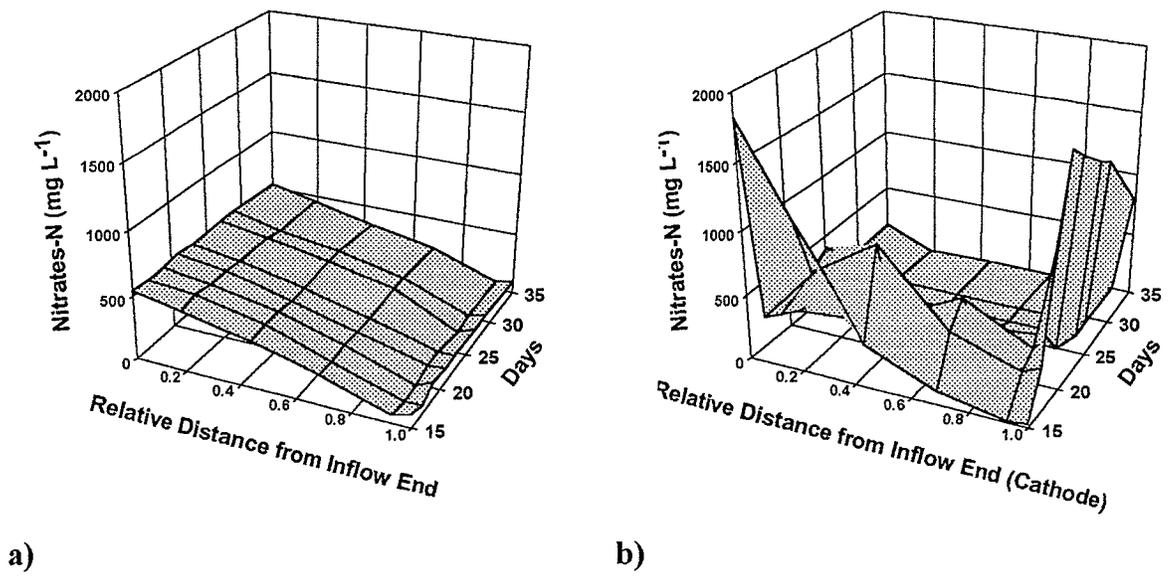


Fig. 5.2 Nitrate-N concentrations in the soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Cathode is located at the inflow end (phase 2). Relative distance of a port from the inflow end was the ratio of a port's distance from inflow end to the total length of the soil column.

The influent nitrate concentration in the electrokinetic column decreased from 1200 to 200 mg NO₃-N L⁻¹ in two days and was significantly lower than control (p<0.05) (Table 5.2) compared to that in the hydraulic column. The influent nitrate concentration in the EK+H columns, despite being in constant contact with the 500 mg NO₃-N L⁻¹ solution, was brought down to 30 mg nitrates-N L⁻¹ by the eighth day after switching (Day 23). Six days after switching polarity the nitrate concentration at a relative distance of 0.2 from cathode was significantly lower (p<0.05) than that in the hydraulic column.

The nitrate concentrations in the entire treatment columns were brought to <5 mg NO₃-N L⁻¹ and significantly lower (p<0.05) by the 12th day since Phase 2 began. Based on evidence presented in the literature on the nature of the chemical conversions, the H⁺ produced during the Phase 1 of the experiment may have played a vital role in enhancing the reduction of nitrates during Phase 2. This is in agreement with the chemical reactions given by Segall and Bruell (1992). Therefore, switching the polarity can be of benefit as it not only concentrated nitrates at a location but also produced H⁺ that resulted in a faster reduction of nitrates during Phase 2. When the electrodes were switched, the nitrate concentration in the effluent increased from zero to about 330 mg nitrates-N L⁻¹ in two days and reached 1700 mg nitrates-N L⁻¹ in six days. The second phase demonstrated the beneficial use of three different processes, such as cathodic conversion of nitrates and moving and accumulating nitrates at the anode, in eliminating nitrates from the contaminated soil.

Table 5.2 Nitrate-N concentrations in soil columns as affected by the electrokinetic treatment (cathode at the inflow end).

Day	Relative distance (from cathode)	Mean nitrate-N (mg L ⁻¹)		CV	R ²
		H Column	EK+H Column		
15	0.0	532.3	1202.5	29.0	0.80
	0.2	465.0	1521.0	103.0	0.65
	0.4	352.8	332.4	113.0	0.50
	0.6	213.2	96.7	80.4	0.61
	0.9	57.3	0.0	115.0	0.71
	1.0	89.6	0.0	106.5	0.78
17	0.0	514.0	215.0*	11.3	0.97
	0.2	490.0	654.0	125.0	0.50
	0.4	375.0	994.0	121.0	0.60
	0.6	223.0	443.0	127.0	0.65
	0.9	46.0	280.0	112.0	0.74
	1.0	49.0	330.0	96.0	0.77
19	0.0	520.0	122.0*	30.0	0.93
	0.2	473.0	762.0	130.0	0.52
	0.4	350.0	380.0	101.0	0.42
	0.6	228.0	601.0	155.0	0.60
	0.9	58.5	348.0	139.0	0.72
	1.0	96.1	1091.0	106.0	0.76
21	0.0	532.0	58.2**	16.0	0.98
	0.2	472.5	105.2*	27.0	0.94
	0.4	352.0	276.1	112.0	0.34
	0.6	237.1	285.5	69.3	0.37
	0.9	79.5	329.8	83.3	0.78
	1.0	96.0	1723.0	165.4	0.66

Mean comparison * significantly different (p<0.05), **significantly different (p<0.01), ***significantly different (p<0.001). All the other mean comparisons are not significantly different (SAS version 8.02). H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns. CV = Coefficient of variation. R² = Coefficient of determination.

Table 5.2 Nitrate-N concentrations in soil columns as affected by the electrokinetic treatment (cathode at the inflow end) (continued).

Day	Relative distance (from cathode)	Mean nitrate-N (mg L ⁻¹)		CV	R ²
		H Column	EK+H Column		
23	0.0	523.0	29.0***	5.9	0.99
	0.2	458.0	25.8**	17.2	0.98
	0.4	359.0	77.0	64.0	0.76
	0.6	242.0	112.0	102.0	0.38
	0.9	-	-	-	-
	1.0	88.1	1599.0	110.8	0.76
27	0.0	532.0	66.0**	8.9	0.99
	0.2	460.5	0.9***	6.6	0.99
	0.4	371.4	0.9*	10.0	0.99
	0.6	265.0	0.7*	23.9	0.98
	0.9	-	-	-	-
	1.0	109.2	1403.0	109.2	0.76
29	0.0	533.0	111.5*	3.5	0.99
	0.2	438.0	1.8**	15.9	0.99
	0.4	377.8	1.3**	11.6	0.99
	0.6	249.5	0.9*	134.5	0.97
	0.9	72.4	0.7	112.3	0.83
	1.0	89.4	1321.3	106.0	0.75
35	0.0	518.6	165.0**	8.6	0.99
	0.2	453.5	0.4***	4.3	0.99
	0.4	335.5	0.9**	20.0	0.98
	0.6	226.0	3.0*	38.5	0.95
	0.9	-	-	-	-
	1.0	91.7	797.0	91.7	0.77

Mean comparison * significantly different (p<0.05), **significantly different (p<0.01), ***significantly different (p<0.001). All the other mean comparisons are not significantly different (SAS version 8.02). H = Hydraulic (control) columns. EK+H = Electrokinetic (treatment) columns. CV = Coefficient of variation. R² = Coefficient of determination.

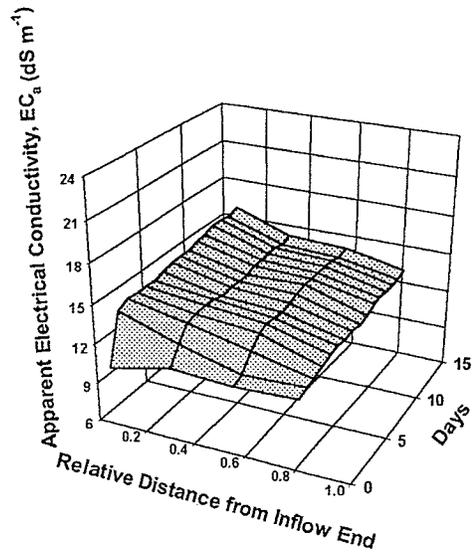
The extracted samples were also tested for other forms of nitrogen. The $\text{NO}_2\text{-N}$ level remained below 1 mg L^{-1} throughout the experiment. There is no significant increase in $\text{NH}_3\text{-N}$ resulting from the electrokinetic treatment. No ammonia gas was detected during remediation. The gas collected at the cathode showed the presence of N_2O indicating some of the nitrates being converted to N_2O gas. The current requirement varied between 3 and 6 mA. The average current density was 3 A m^{-2} . The daily average energy consumption was 3.6 kWh m^{-3} .

5.4.2 Apparent electrical conductivity (EC_a)

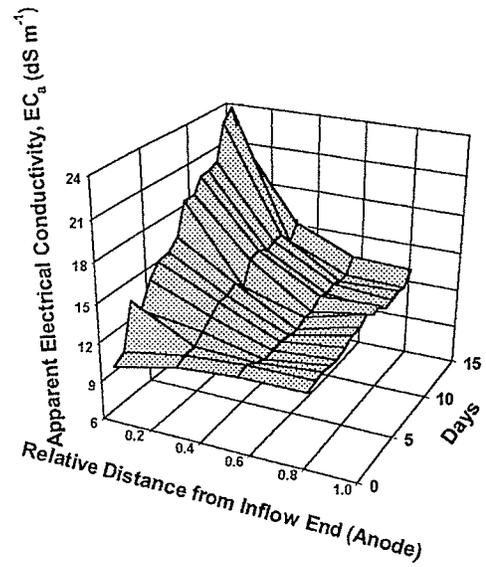
The changes in apparent electrical conductivity (EC_a) as measured by mini-TDR Probes is shown in Fig. 5.3. Figure 5.3a shows the changes of EC_a in the control columns during the first phase. The EC_a follows the KNO_3 solution movement into the column.

In Fig. 5.3b the EC_a increase correlated well with the accumulation of nitrates. In overall the shapes of the EC_a graphs were similar to those of the nitrate concentration graphs. As these EC_a measurements were non-destructive, their continuous measurement were useful in predicting nitrate concentration at a location well before doing the costly nitrate analysis.

Fig. 5.4 shows the changes in EC_a during the second phase of the experiment. The EC_a of the control columns continued to gradually increase as the nitrate concentration increase in the columns. In the EK+H columns the EC_a values rapidly declined and decreased below the original values. Because the TDR mini-probe measured the bulk soil water conductivity the presence of other ions such as H^+ and OH^- produced during the hydrolysis had affected the EC_a readings.

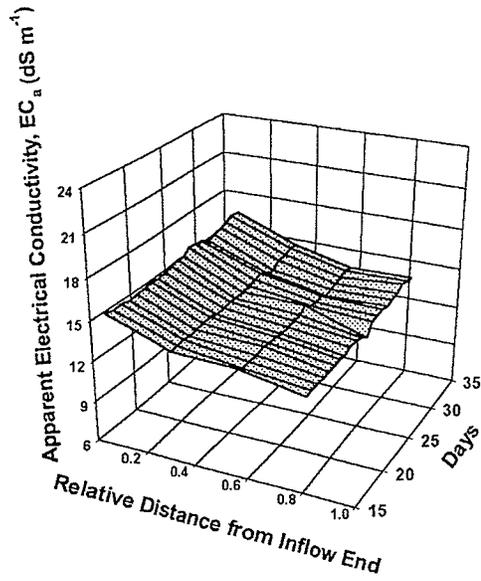


a)

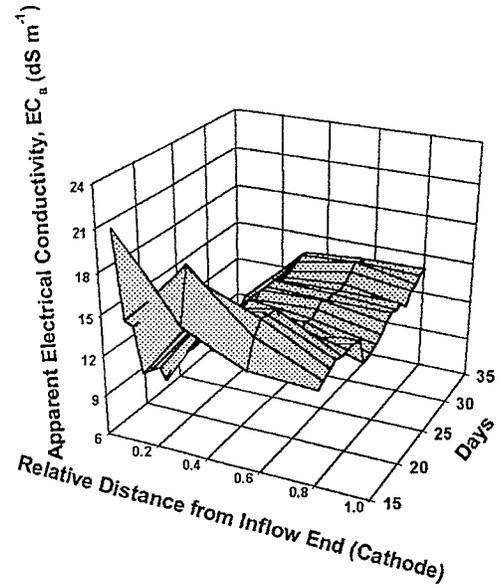


b)

Fig. 5.3 Apparent electrical conductivity (EC_a) of soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Anode is located at the inflow end (phase 1). Relative distance of a point from the inflow end was the ratio of a point's distance from inflow end to the total length of the soil column.



a)



b)

Fig. 5.4 Apparent electrical conductivity (EC_a) of soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Cathode is located at the inflow end (phase 2). Relative distance of a point from the inflow end was the ratio of a point's distance from inflow end to the total length of the soil column.

5.4.3 Nitrous oxide content

Nitrous oxide content of the cathodic gas was measured from Day 6 to Day 20 after cathode was positioned at the inflow end. The N_2O content of the cathodic gas varied between 37.2-352.8 ppm with an average value of 152.7 ppm. Figure 5.5 shows the relationship between the N_2O content of the cathodic gas and the NO_3-N content of the solution in the cathode chamber. It showed an inverse relationship between these two parameters with a low correlation ($R=0.60$) between them. A low NO_3-N concentration solution means more conversion of NO_3-N , and we can expect a higher production of N_2O . From the environmental point of view, these N_2O contents are high and therefore the cathodic gas cannot be released directly to the environment without further processing. In a field situation, however, the expected presence of NO_3-N in a locality is not expected in hundreds of $mg L^{-1}$ but may be in tens of $mg L^{-1}$. Therefore, a high N_2O concentration in the cathodic gas is not expected. But this possibility needs to be confirmed before employing electrokinetic treatment for nitrate remediation.

5.4.4 Water content

The TDR probes also monitored the changes in the water content in all columns. The changes in water content as measured by TDR mini-probes are shown in Fig. 5.6 and Fig. 5.7. The water content varied between 0.40-0.47 $m^3 m^{-3}$. In the EK+H columns the flow seemed to increase during the first phase of the experiment and decrease during the second phase of the experiment. These were reflected in the times taken to extract samples from sampling ports. As all the columns were completely saturated, these changes were not detected by the TDR mini-probes.

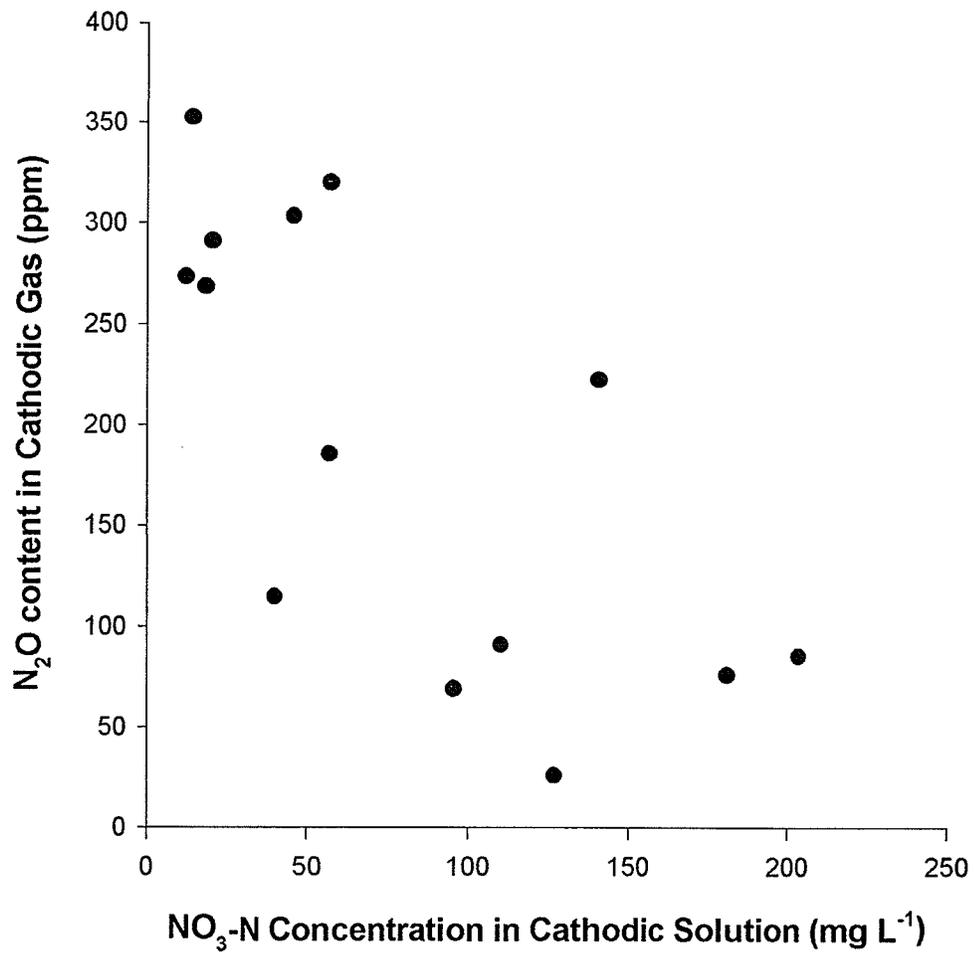
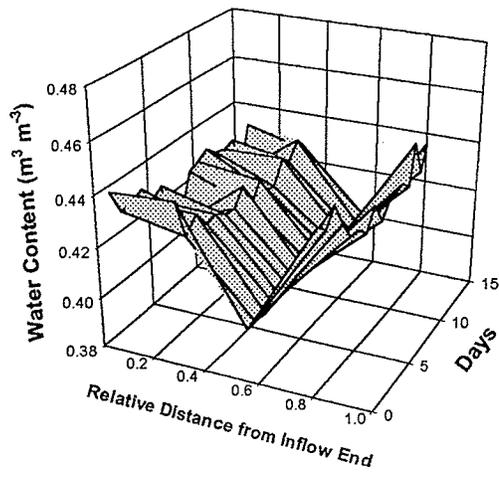
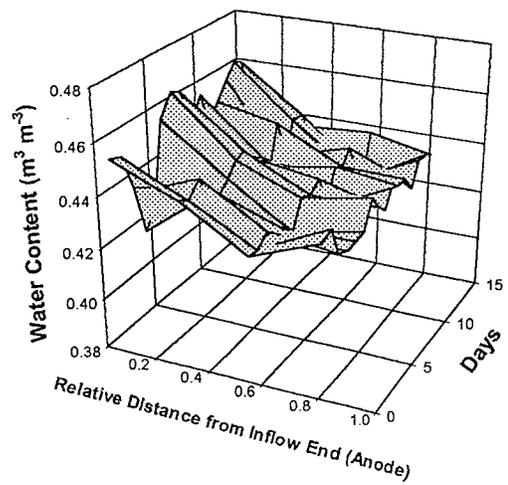


Fig. 5.5 The relationship between the N_2O content of the cathodic gas and the $\text{NO}_3\text{-N}$ content of the solution in the cathode chamber.

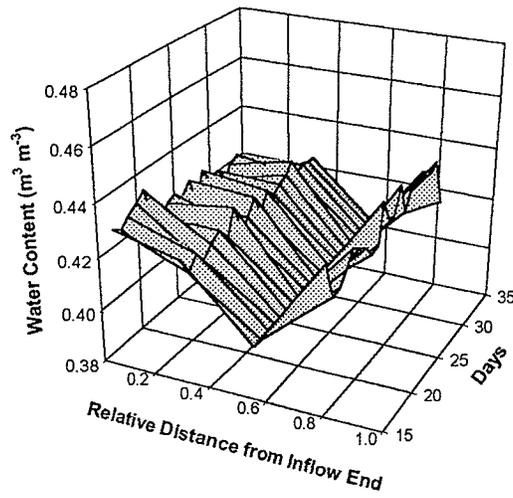


a)

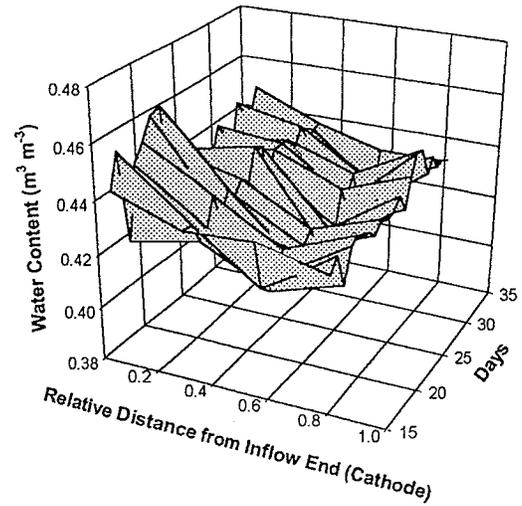


b)

Fig. 5.6 Water content of soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Anode is located at the inflow end (phase 1). Relative distance of a point from the inflow end was the ratio of a point's distance from inflow end to the total length of the soil column.



a)



b)

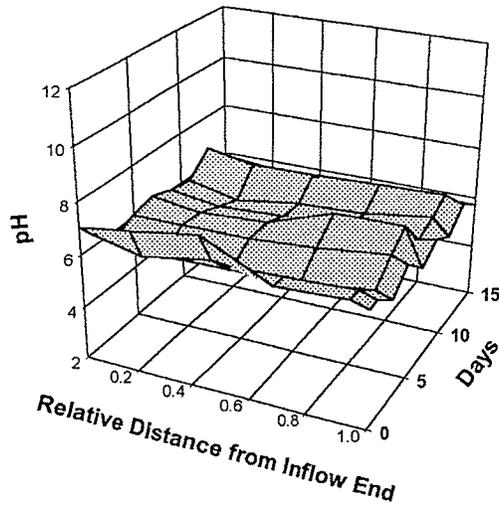
Fig. 5.7 Water content of soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Cathode is located at the inflow end (phase 2). Relative distance of a point from the inflow end was the ratio of a point's distance from inflow end to the total length of the soil column.

5.4.5 Hydraulic conductivity

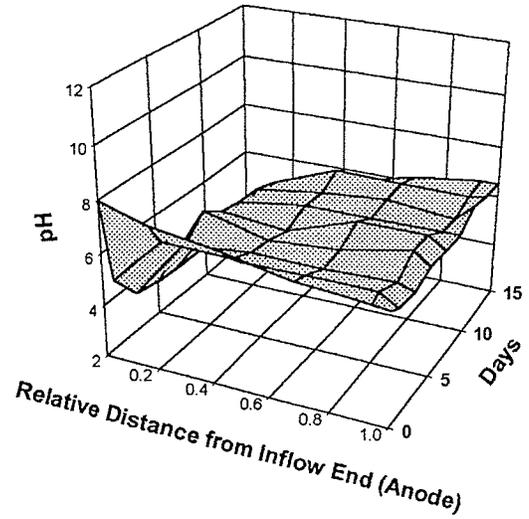
The average hydraulic conductivity was $2.5\text{E-}7 \text{ m s}^{-1}$ with a range from $1.0\text{E-}7$ to $3.6\text{E-}7 \text{ m s}^{-1}$. With the application of voltage the hydraulic conductivities in the EK+H columns changed. But the hydraulic conductivity values calculated for the EK+H columns were not reliable as the pressure from the gas produced in the outflow compartment frequently affected flow measurement.

5.4.6 pH

The changes in pH are shown in Fig. 5.8 and Fig. 5.9. The pH in the hydraulic column was about 6.5 and did not change during the experiment. In the EK+H columns, during the first phase of the experiment, the inflow end became acidic and the outflow end became basic because of the hydrolysis taking place at the anode and the cathode, respectively. When the electrodes were switched, the pH at the inflow end rose and became basic whereas the pH of the outflow end decreased and became acidic.

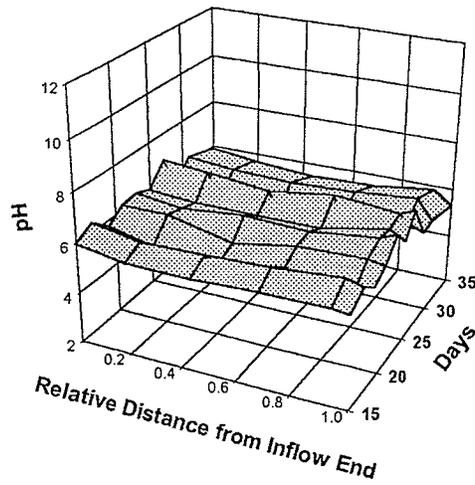


a)

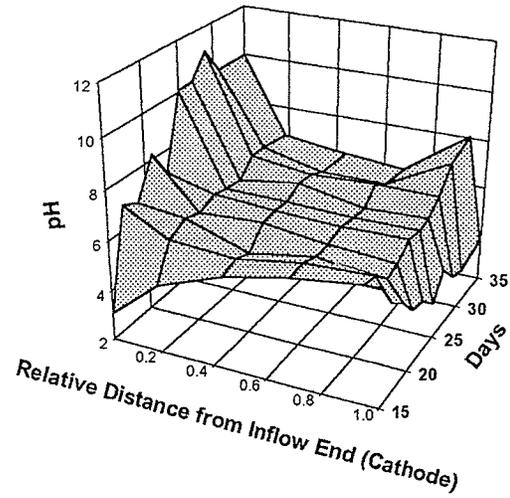


b)

Fig. 5.8 pH of soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Anode is located at the inflow end (phase 1). Relative distance of a port from the inflow end was the ratio of a port's distance from inflow end to the total length of the soil column.



a)



b)

Fig. 5.9 pH of soil columns as affected by the electrokinetic treatment (a) Control (H columns) (b) Electrokinetic treatment (EK+H columns). Cathode is located at the inflow end (phase 2). Relative distance of a port from the inflow end was the ratio of a port's distance from inflow end to the total length of the soil column.

6. CONCLUSIONS

The aim of this study was to employ electrokinetics to lower the nitrate levels in a contaminated site below the Maximum Acceptable Concentration (MAC) for nitrates in drinking water. To achieve this aim a series of laboratory experiments were conducted to come up with a procedure for remediating a nitrate-contaminated soil. Conclusions are as follows:

1. The first series of experiments conducted in the laboratory showed that the nitrates in soil can be converted to other forms using electrokinetic treatment. The conversion occurred at the cathode (a negative electrode) and in the surrounding soil. After nine days of electrokinetic treatment the nitrate concentrations at the inflow end and at a relative distance of 0.2 were significantly ($p < 0.05$) lower than those from hydraulic columns, showing a successful reduction near the cathode end.
2. The electrokinetic treatment did not affect natural ammonia nitrogen present in the soil nor did it convert nitrates into ammonia nitrogen. The soil pH near the electrodes changed by more than 30% because of the invariable hydrolysis taking place at the electrodes. The application of the electrical gradient potential also caused water to accumulate near the cathode.
3. The second series of experiments showed that applying electrical potential gradient to soil caused the anode (a positive electrode) to attract and accumulate nitrates rapidly at the anode end. The application of the electrical potential gradient retarded the nitrate ion movement. After 13 days, nitrate concentrations

at a relative distance of 0.2 from the anode in electrical column was significantly lower ($p < 0.05$) than in control showing that anode effectively retarded nitrate movement against a hydraulic gradient of 1.25. The anode acted like a trap in retaining nitrates against the hydraulic gradient. As demonstrated, such retardation effectively stopped the movement of nitrates against an applied hydraulic gradient and formed a nitrate ion barrier around the anode.

4. The third series of experiments showed that by changing the polarity of the electrodes, the nitrate levels in a contaminated soil can be brought below Maximum Acceptable Concentration for nitrates in drinking water. In these experiments the electrokinetic treatment retarded nitrate movement against a hydraulic gradient. After the polarity of the electrodes were switched, the influent nitrate concentration in the electrokinetic column was reduced from 1200 ± 284.0 to 200 ± 35.4 mg $\text{NO}_3\text{-N L}^{-1}$ in two days and was significantly lower ($p < 0.05$) compared to that in the hydraulic column. The influent nitrate concentration in the electrokinetic columns, despite being in constant contact with the 500 mg $\text{NO}_3\text{-N L}^{-1}$ solution, was brought down to 30 ± 20.0 mg nitrates-N L^{-1} by the eighth day after switching polarity. Six days after switching polarity, the nitrate concentration at a relative distance of 0.2 from cathode was significantly lower ($p < 0.05$) than that in the hydraulic column. The nitrate concentrations in the entire treatment columns were brought to < 5 mg $\text{NO}_3\text{-N L}^{-1}$ and significantly lower ($p < 0.05$) by the 12th day since phase 2 began. In the second phase, the beneficial use of three different processes, such as cathodic conversion of nitrates and moving and

accumulation of nitrates at the anode, effectively restored the medium textured soil contaminated with $\text{NO}_3\text{-N}$. To achieve optimum results in the field, the electrodes have to be located based on contamination location and the direction of hydraulic gradient.

5. The $\text{NO}_2\text{-N}$ level remained below 1 mg L^{-1} throughout the experiment. There is no significant increase in $\text{NH}_3\text{-N}$ resulting from the electrokinetic treatment. No ammonia gas was detected during remediation. The gas collected at the cathode showed the presence of N_2O indicating some of the nitrates being converted to N_2O gas. The current requirement varied between 3 and 6 mA. The average current density was 3 A m^{-2} . The daily average energy consumption was 3.6 kWh m^{-3} with intermittent treatment.

7. RECOMMENDATIONS FOR FUTURE RESEARCH

1. Laboratory experiments showed that electrokinetic treatment technique can be successfully used to remediate a nitrate-contaminated soil. To further reduce adverse environmental impact, experiments should be conducted to reduce the amount of N_2O gas generated during the process.
2. Experiments need to be conducted to find if a three row electrode configuration anode-cathode-anode will be more effective in preventing the spread of contaminant while converting contaminant nitrates.
3. Pilot scale studies should be conducted to verify the effectiveness of this remediation process in a field situation.
4. The effectiveness of electrokinetic remediation of nitrates under unsaturated conditions has to be investigated.
5. Economics of the application of electrokinetic treatment in the field and the best electrode and buffering material for field applications have to be studied.

8. CONTRIBUTION TO KNOWLEDGE

Nitrate contamination from agricultural and livestock fields has become a major concern for the communities surrounding them. All of the current technologies available for nitrate removal are for removing nitrates from drinking water supply. These *ex situ* methods generate waste solution that are high in nitrates and difficult to dispose. Therefore, there is a need to develop a new technology to address this issue at the field level. Electrokinetic remediation is an emerging technology for remediating contaminated soils. In the recent past, there have been attempts to combine electrokinetic technique with other technologies to remediate nitrate-contaminated soil. This study was aimed at developing a procedure to completely remediate a nitrate contaminated soil solely by using electrokinetic treatment.

A series of laboratory experiments were conducted to develop a procedure for remediating a nitrate-contaminated soil. Initially, the experiments were designed to understand the various processes that occur in a nitrate-contaminated soil under application of an electrical potential gradient. To simulate natural conditions a hydraulic gradient also was applied. Controls were setup to confirm the treatment effects of electrokinetics.

The results from these experiments gave an insight into the different processes that occur due to the application of an electrical potential gradient. First two studies demonstrated that not only nitrates can be denitrified using electrokinetics but can also be effectively retained at a location against a hydraulic gradient. Processes such as retardation and enhancement of nitrate movement, accumulation of nitrates at one location

and conversion of nitrates can be exploited to completely remediate a nitrate-contaminated soil. Production of acid because of the invariable hydrolysis, taking place at the electrodes, and considered as nuisance in many electrokinetic applications, can be put into beneficial use for converting nitrates. The final experiment was designed to exploit these different processes. It was demonstrated that, in fact, the electrokinetic treatment *per se* can be used to remediate a nitrate-contaminated soil.

Electrical conductivity of the soil media is one of the factors that could determine the success or failure of electrokinetic treatment. A high electrical conductivity means more current flow that results in more remediation. On the other hand, a low electrical conductivity means less remediation and eventual stalling of the electrokinetic process. During the electrokinetic process the acidity and the alkalinity produced at the electrodes profoundly changes the electrical conductivity of the soil media and need to be constantly monitored. In the laboratory experiments reported in the literature, the limited space in the columns makes it difficult to install electrical conductivity probes for continuous monitoring of electrical conductivity. Therefore the changes in electrical conductivity in such experiments were measured by destructive analysis. In the present study, TDR-mini probes were successfully introduced with minimum obstruction to flow and the changes in the apparent electrical conductivity were continuously monitored non-destructively.

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