NITRATE REMOVAL FROM WATER USING SURFACE-MODIFIED ADSORBENTS

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A Thesis submitted in fulfillment for the degree of

Doctoral of Philosophy

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Sydney, New South Wales, Australia. February 2017.

CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Mahatheva Kalaruban

June 2017.

ACKNOWLEDGEMENTS

This is a great time to thank all the people who helped, supported, motivated, and guided me throughout my Ph.D. study and made me to successfully complete my Ph.D. thesis. I will be thankful for them forever in my life.

First and foremost, I would like to say my sincere thanks to my principle supervisor Professor Saravanamuthu Vigneswaran for giving the chance to pursue my Ph.D. degree. I would not have completed my Ph.D degree successfully without his full support, guidance, suggestions, and encouragements all the time. Secondly, I would like to say thanks to Dr. Paripurnanda Loganathan for his great support and guidance throughout my whole Ph.D. He spent a lot of time for me to complete the each and every stage of my research successfully. I really appreciate for his great help and guidance. I also thank my co-supervisor Dr. Jaya Kandasamy who helped and supported me from the beginning to the end of my studies. I am grateful to him forever. Also I thank to Dr. Tien Vinh Nguyen for his guidance and suggestions at earlier stages. I would like to thank Senior Technical Officer Dr. Johir for his full support in carrying out my laboratory experiments and providing friendly suggestions at all stages. Much thanks to my university friends Danious, Muna, Tanjina, Gayathiri and Roobavannan for their great help, friendship and companionship.

I wish to acknowledge the University of Technology Sydney and CRC Care for their financial support during my study. I would like to give a special thanks to my lovely parents, my siblings, my dear wife Niranthary and her parents for their endless love, support, and encouragement all the time. Last, but not least, I would like to thank my relatives and my friends who provided a great support during this time.

DEDICATION

To My Lovely Parents

JOURNAL PAPERS

Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Naidu, G., Nguyen, T.V., Vigneswaran, S., 2016. Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies. Separation and Purification Technology. 158, 62-70.

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Johir, M.A.H., Nguyen, T.V., Kalaruban M., Prahan, M., Ngo, H., Shim, W., Vigneswaran , S., 2016. Removal of phosphorus by a high rate membrane adsorption hybrid system. Bio Resource Technology. 201, 365-369.

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Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Ngo, H., Vigneswaran, S., 2016. Enhanced removal of nitrate from water using surface modified agricultural wastes. International Conference on Water : From Pollution to Purification (ICW 2016), Kerala, India, 12th-15th December 2016.

AWARDS & SCHOLARSHIPS

Won the second prize of "Best Poster Presentation Award" in the 5th IWA regional conference on Membrane Technology, Kunming, China.

Higher Degree Research publication award

CRC Care postgraduate scholarship, Sydney, Australia (2014 – 2017)

International Research Scholarship – University of Technology Sydney (2013 -2017)

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NOMENCLATURE/ABBREVIATION

AG = amine grafted

Al^0 = Zero valent aluminium

Cl^- = chloride

ClO^- = hypochlorite

ClO_4^- = perchlorates

C_e = equilibrium concentration of nitrate-N (mg /L) equilibrium

COD = chemical oxygen demand

D_L = the axial dispersion coefficient (m^2/s)

Dm = aqueous phase diffusivity (m^2/s)

Ds = the surface diffusion coefficient (m^2/s)

Dowex 21K XLT = strong base anion exchange resin composed of Styrene-DVB

dS/m = desiSiemens per meter

Fe^0 = zero valent iron

Fe^{3+} = iron (III)

$FeCl_3.6\ H_2O$ = Iron(III) chloride hexahydrate

FTIR = Fourier transform infrared spectroscopy

H_2PO_4 = dihydrogen phosphate ion

HCl = hydrochloric acid

HCO_3^- = bicarbonate

HSDM = Homogeneous surface diffusion model

HNO_3 = Nitric acid

kf = the external mass transfer coefficient (m/s)

K_F = Freundlich constants (mg/g)

KNO_3 = Potassium nitrate

KH_2PO_4 = Monopotassium phosphate

KCl = Potassium chloride

K_L = Constant related to the affinity of the binding sites (L/mg)

LDHs = layered double hydroxides

M = mass of dry adsorbent (g)

MBR = membrane bioreactor

mg N/L = milligram nitrogen per litre

mg NO_3^- / L = mg nitrate per litre

mg N/g = milligram nitrogen per gram

mg P/L = milligram phosphorus per litre

mg PO_4^{3-} / g = mg phosphate per gram

mg P/g = milligram phosphorus per gram

mg SO_4^{2-} / g = mg sulphate per gram

mg S/g = milligram sulphur per gram

Mg^0 = zero-valent magnesium

N = nitrogen

N_2 = nitrogen gas

NaCl = sodium chloride

NaOH = sodium hydroxide

Na_2SO_4 = sodium sulphate

Na_2CO_3= sodium carbonate

$NaHCO_3$ = sodium bicarbonate

NH_3 = ammonia

NO = nitric oxide

N_2O = dinitrogen monoxide

NO_3^- = nitrate

NO_2^- = nitrite

$(NH_4)_2SO_4$ = ammonium sulphate

No = saturation adsorbate concentration (mg/L)

n = Freundlich constant

P = phosphorus

PE = population equivalent

pH = measure of the acidity or basicity of an aqueous solution

PZC = point of zero charge

Q = flow rate (cm^3/s)

Q_e = amount of nitrate adsorbed per unit mass of adsorbent (mg N/g)

Q_{max} = maximum amount of the nitrate-N adsorbed per unit weight of the adsorbent (mg/g)

r = radial distance from the centre of adsorbent particle (m)

RO = reverse osmosis

rpm = revolutions per minute

SEM = Scanning electron microscopy

SMAHS = submerged membrane adsorption hybrid system

SO_4^{2-} = sulphate

XRD = X-ray diffraction

ZVI = Zero-valent iron

ABSTRACT

Elevated concentrations of nitrate in surface and ground waters can cause eutrophication of natural water bodies, and in drinking water they can pose a threat to human health, especially to infants by causing 'blue baby' syndrome. Adsorption technology is an attractive method to remove nitrate from water compared to other technologies in terms of simplicity, cost, design, operation and maintenance, and effectiveness.

An anion exchange resin known as Dowex 21K XLT was surface modified by incorporating Fe (Dowex-Fe) to increase the surface positive charges and tested for removing nitrate. The batch adsorption data at pH 6.5 fitted well to the Langmuir model with maximum adsorption capacities of 27.6 mg N/g, and 75.3 mg N/g for Dowex and Dowex-Fe resins, respectively. The fluidised-bed adsorption capacities were 18.6 mg N/g and 31.4 mg N/g at a feed concentration of 20 mg N/L and filtration velocity of 5 m/h for Dowex and Dowex-Fe, respectively. Low-cost agricultural wastes, specifically corn cob and coconut copra were also surface modified but by amine-grafting to increase the surface positive charges. The Langmuir nitrate adsorption capacities (mg N/g) were 49.9 and 59.2 for the amine-grafted (AG) corn cob and AG coconut copra, respectively, at pH 6.5. Fixed-bed adsorption capacities were 15.3 mg N/g and 18.6 mg N/g at the same feed concentration and flow velocity as in the Dowex study for AG corn cob and AG coconut copra, respectively. In both batch and column experiments, nitrate adsorption declined in the presence of sulphate, phosphate and chloride, with sulphate being the most competitive anion. More than 95% of adsorbed nitrate was desorbed by 1 M KCl in all adsorption/desorption cycles and the adsorbents were successfully regenerated in each cycle with little reduction in adsorption capacity.

A submerged membrane (microfiltration) adsorption hybrid system (SMAHS) was utilised for the continuous removal of nitrate. The volume of water treated to maintain the nitrate concentration below the WHO limit of 11.3 mg N/L and the amount of nitrate adsorbed per gram of adsorbent for all four flux (2.5, 5, 10 and 15 L/m^{2}h) tested were in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob. A rise in flux increased the volume of water treated and the amount of nitrate adsorbed. The exhausted agricultural waste adsorbents in both the column and SMAHS trials can be directly applied to lands as nitrate fertilisers, while the desorbed nitrate solution containing K can be used in fertigation to supply nutrients (N and K) to plants.

An electrochemical-adsorption system was investigated to remove nitrate simultaneously using the adsorption and electrochemical methods. In this system four adsorbents were added inside an anode stainless steel box where the Cu plate served as the cathode. It was found that nitrate removal was higher in a short period of time and the cost was low. The optimum nitrate removal scenario for the integrated system was at pH 7, 1 A, and 31 V for a distance of 1 cm apart between the electrodes. Nitrate removal in the integrated system is approximately the sum of the removals derived from the individual processes. The innovative feature of this study is the integration of an electrochemical system with the adsorption process where the adsorbents are kept intact with the anode.

The different methods undertaken in the four nitrate removal studies can’t be compared and each method has advantages and disadvantages in terms of nitrate removal efficiency, cost, raw water quality and removal efficiency of other pollutants. However, if the raw water contains only nitrate the column method is best compared to other methods. It is recommended that the encouraging results obtained in our laboratory scale studies be tested in series of cells connected to each other for continuous removal of nitrate. It is also recommended that these experiments are conducted at pilot plant scale, which is closer to practical conditions.

CHAPTER 1

INTRODUCTION

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CHAPTER 1

Introduction

1.1. Research Background

Water is a basic need for all life forms on the planet Earth but increasingly, clean and safe drinking water in the world is becoming scarce. More than one billion people in developing countries do not have access to it (Gosling and Arnell, 2016). Local ground water supplies constitute the major source of drinking water in the world's rural areas and this mostly originates from private wells. Water in many areas is becoming more polluted with inorganic and organic chemical compounds and ions produced by synthetic compounds, and the result of industrial and agricultural activities. One of the major inorganic pollutants of waters is nitrate and it affects the quality of water at elevated concentrations. Nitrate enters water bodies as a result of excessive use of fertilisers and contamination from animal waste and urine, sewer leakage, and industrial discharge. Nitrate is the stable form of nitrogen in the nitrogen cycle and has an unreactive character. Once the nitrate enters the environment it is very difficult to remove it. The increasing level of nitrate contributes to potentially serious problems for people's health and the environment. It is therefore very important to prevent nitrate pollution by using cost-effective treatment methods that can remove large amounts of nitrate efficiently.

1.1.1. Nitrate effects

Nitrate at high concentration can cause methemoglobinemia in infants (Fewtrell, 2004) and fairly recent studies have suggested that it can also cause cancer in humans (Chiu et al., 2007; Kumar et al., 2009; Meenakshi and Viswanathan, 2007). High nitrate concentrations (> 300 mg/L) can also pose a threat to animals' health (Islam and Patel, 2010). Since nitrate is a plant nutrient, it enhances the growth of water plants such as algae which use dissolved oxygen and cover large areas of space in water bodies. Due to oxygen depletion, most aquatic plants and animals die and they in turn pollute the water even more (Jorgensen and Williams, 2001).

1.1.2. Nitrate removal technologies

There are several nitrate removal technologies used in water treatment such as reverse osmosis, chemical reduction methods, biological methods, electrodialysis, and adsorption. Compared to other methods, adsorption is a better choice because of its reduced operational cost and minimum waste disposal. Furthermore, adsorption methods do not need highly advanced technologies, design features or processes to operate effectively. Adsorption technology has been used for the removal of organics (Crittenden et al., 1993), heavy metals (Sounthararajah et al., 2014), dyes (Garg et al., 2003) and several inorganic anions such as fluoride (Wajima et al., 2009), bromate (Bao et al., 1999), phosphate (Blaney et al., 2007) and nitrate (Samatya et al., 2006; Zhan et al., 2011). The nitrate removal efficiency of the adsorbents depends on the adsorbent dosage, nitrate concentration, pH, temperature and co-ions present in the water (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a). Generally, ground and surface water contain several anions such as phosphate, sulphate and chloride. The nitrate adsorption will be affected by the anions and by their concentration. Almost all the studies reported in literature suggest that sulphate is the most competent anion that presents in the water. Almost all the studies reported in literature suggests that sulphate is the most competent anion presents in the water.

1.2. Research needs

Several adsorbents such as ion exchange resins, agricultural wastes, industrial wastes and natural materials have been tested for nitrate removal. To increase the adsorption capacity of the adsorbents, surface modification techniques have been investigated and applied during the last two decades. Surface modification techniques such as protonation, amine grafting, metal/ metal oxide impregnation, and surfactant incorporation have proved to be effective and increase the adsorption capacity of the material several times higher than unmodified material (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a).

Among the adsorbent types, ion exchange resins are promising adsorbents for nitrate removal with applicability over a wide pH range; they also have high adsorption capacities with reusable characteristics. The commercially ion exchange resin Langmuir adsorption capacities reported in literature were generally higher than other adsorbents and they were in the range of 14.8 - 39.2 mg N/g. Modification of the surface of the ion exchange resin can increase the nitrate adoption capacity. Several studies have been done on metal impregnated ion exchange resins for removing phosphate, fluoride and arsenic. However, only one study appears to have been published on nitrate removal using metal impregnated ion exchange resin (Jiang et al., 2011).

Another type of adsorbent used for nitrate removal is the low-cost agricultural wastes. The adsorption capacities of agricultural wastes are very low and therefore large amounts of adsorbents are required. This causes waste disposal problems and increases cost. To overcome this problem, agricultural wastes have been surface modified using amine-grafting and then employed for nitrate removal. Amine grafting of agricultural wastes such as rice hull, wheat straw, sugarcane bagasse, peanut hull, pine bark and coconut husk has proved to increase nitrate adsorption capacities (Orlando et al., 2002b; Xu et al., 2012). Amine-grafted agricultural wastes Langmuir adsorption capacities were higher (14.2-16.7 mg N/g) and this capacities were approximately equal to that of the commercial anion exchange resin Amberlite IRA 900 (16.7 mg N/g). To date, no studies have been reported for nitrate removal using the largely available agricultural wastes, corn cob and coconut copra, which are produced in large quantities in many parts of the world. Corn cob is a widely available agricultural waste and corn is one of the most ubiquitous grain crops cultivated globally, with an annual worldwide production of about 5.2 x 10^{11} kg (Ioannidou et al., 2009). Coconut is one of the main palm tree types cultivated throughout the tropical world and copra waste is derived from total annual coconut production, which amounts to approximately 50 million tons (Bhatnagar et al., 2010).

Most studies on the use of modified adsorbents for nitrate removal were tested in static batch adsorption experiments (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a), yet only a few have been tested using dynamic column adsorption experiment (Nur et al., 2015; Xu et al., 2012). Findings from column experiments are more relevant to real-operating systems in treatment plants. Furthermore, the previous column studies neither tried to model the adsorption behaviour nor considered complementary ions' effects on nitrate adsorption for surface modified agricultural wastes. Only a very few column mode experiments were conducted on repeated adsorption/desorption cycles (Xu et al., 2012; Hekmatzadeh et al., 2012). Studies on repeated adsorption/desorption cycles are important because they provide information on the regeneration potential of the adsorbent which - if successful - can cut down the material costs significantly.

The submerged membrane adsorption hybrid system (SMAHS) with adsorbent replacement at appropriate times is another dynamic adsorption method for long-term water treatment operation. In this system the adsorbents adsorb the metals/organics/anions and the membrane filters other pollutants such as microparticles, micro-organisms, suspended solids, colloids, and organics (partially). The membrane also separates adsorbents from the effluent stream (Guo et al., 2005). No SMAHS experiment under continuous operation with small amounts of adsorbent replacement has hitherto been reported for removing nitrate from water.

Another dynamic process used to remove nitrate is the electrochemical treatment system. Several nitrate removal studies have been reported using this particular system but mostly without integrating the adsorption process (Emamjomeh and Sivakumar, 2005; Paidar et al., 1999; Uğurlu, 2004). However, in one study, an adsorbent was incorporated in this system so that the adsorption process employed an integrated electrochemical process. In this study, a carbon electrode was coated with an ion exchange resin (BHP55) and tested for nitrate removal (Kim and Choi, 2012). However, the adsorbent was not tested without an electrochemical system to separate the effects of electrochemical treatment and adsorption. Also, in this study the effects of co-ions, pH and electrochemical factors such as distance between electrode and current influencing nitrate removal in water were not investigated. Information on these factors influencing nitrate removal is required to optimise the process. It is evident that similar experiments on other potential adsorbents are required.

1.3. Research objectives

The objectives of the research were to:

(i) Study the efficiency of removing nitrate from water using a chemically modified ion exchange resin, Dowex and two agricultural wastes (corn cob and coconut copra) in experiments utilising batch, column and SMAHS and electrochemical-adsorption hybrid system.

(ii) Model the batch equilibrium adsorption data using Langmuir, Freundlich and Sips models.

(iii) Model the batch adsorption kinetics using pseudo-first order, pseudo-second order, Elovich and Homogeneous surface diffusion models (HSDM).

(iv) Model the column adsorption data using empirical models of Thomas, Adam-Bohart, Yoon-Nelson and the mathematical plug-flow model.

(v) Determine the effect of pH and co-existing anions on the adsorption of nitrate.

(vi) Investigate desorption of nitrate from the ion exchange resin and the regeneration potential of adsorbents for multiple reuse purposes.

(vii) Test SMAHS on all adsorbents under different flow rates to determine the amount of nitrate removal and volume of water that can be treated, to maintain the nitrate level below the recommended WHO level in a long-term treatment.

(viii) Determine the level of nitrate removal efficiency using electrochemical process combined with adsorption process at different pHs, electrode distance, current, voltage and in the presence of co-ions.

1.4. Thesis content

Chapter 1 – This chapter presents an introduction consisting of research background, research needs and research objectives.

Chapter 2 – This chapter presents a literature review providing a detailed review of (i) nitrate contamination and its effects; (ii) nitrate removal technologies; (iii) adsorption process and mechanism; (iv) application of adsorption processes; (v) technologies on surface modification of adsorbents; (vi) adsorbent regeneration; and (vii) submerged membrane hybrid system.

Chapter 3 – This chapter investigates the efficiency of removing nitrate from water using unmodified and iron-modified Dowex 21k XLT ion exchange resin. Modeling of batch and column adsorption data and regeneration of adsorbents used in column were also conducted.

Chapter 4 – This chapter describes the enhanced removal of nitrate from water using amine-grafted low-cost agricultural wastes such as corn cob and coconut copra. Nitrate removal capacities were investigated using batch and column experimental methods. Data on modelling of adsorption results and regeneration of adsorbents are also presented.

Chapter 5 – This chapter compares the nitrate removal efficiency and volume of water treated using four adsorbents (Dowex, Dowex-Fe, AG corn cob, and AG coconut copra) in a submerged membrane adsorption hybrid system at four flow rates of water.

Chapter 6 – This chapter investigates the enhanced removal of nitrate in an integrated electrochemical-adsorption system. Four adsorbents served to compare the nitrate removal efficiency under different experimental conditions, namely different current, electrode distance, voltage, and pH. The effects of co-ions such as phosphate, sulphate and chloride ions were also investigated.

Chapter 7 – This chapter presents the conclusions of the study, a summary of the main themes explored in the thesis, and provides recommendations for future studies.

CHAPTER 2

Literature Review

CHAPTER 2

Literature Review

2.1. Water demand

The crisis over water supplies is becoming a major problem worldwide. Though 3/4 of the area of the Earth is covered by water, only 2.5% is fresh water and only a small amount of water is easily accessible (Oki and Kanae, 2006). In the 2015 World economic forum's global risks report, survey participants ranked the water crisis as the biggest of all risks to humans, higher than weapons of mass destruction, conflicts between states and the spread of diseases. In the next 15 years, the global shortfall between the forecast water demand and available supply will increase to 40% (UNWWDR, 2015). The rapid increase in population from 2.5 to 6.1 billion occurred from 1950 to 2000 (Cleland, 2013), and this has implications for water supplies and other natural resources. Over 2 billion people are suffering from severe water stress (Gosling and Arnell, 2016). More people, expanding areas of irrigated agriculture, and rapid economic development are dramatically increasing demands for water. Figure 2.1 shows the projected global water stress in 2030.

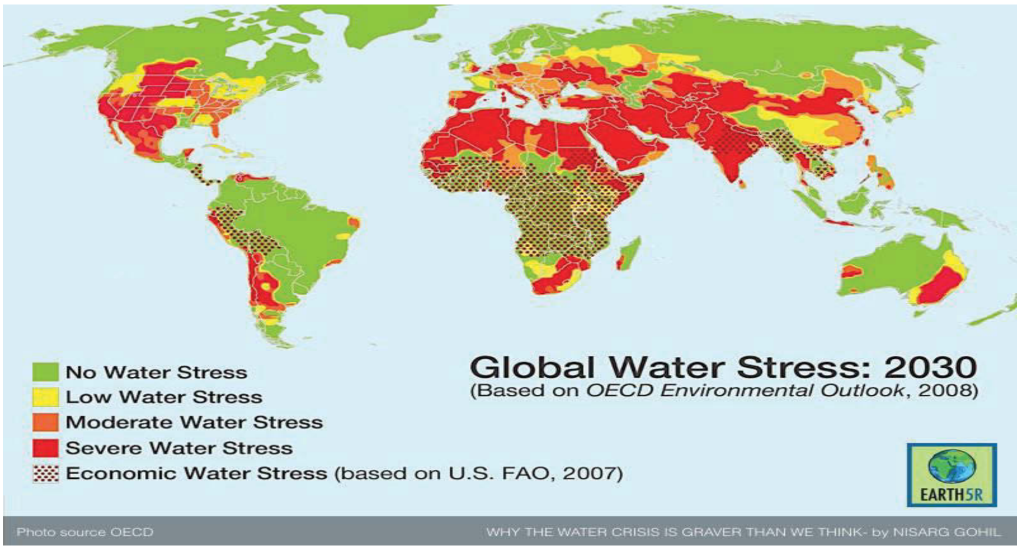

Figure 2.1. Global water stresses in 2030

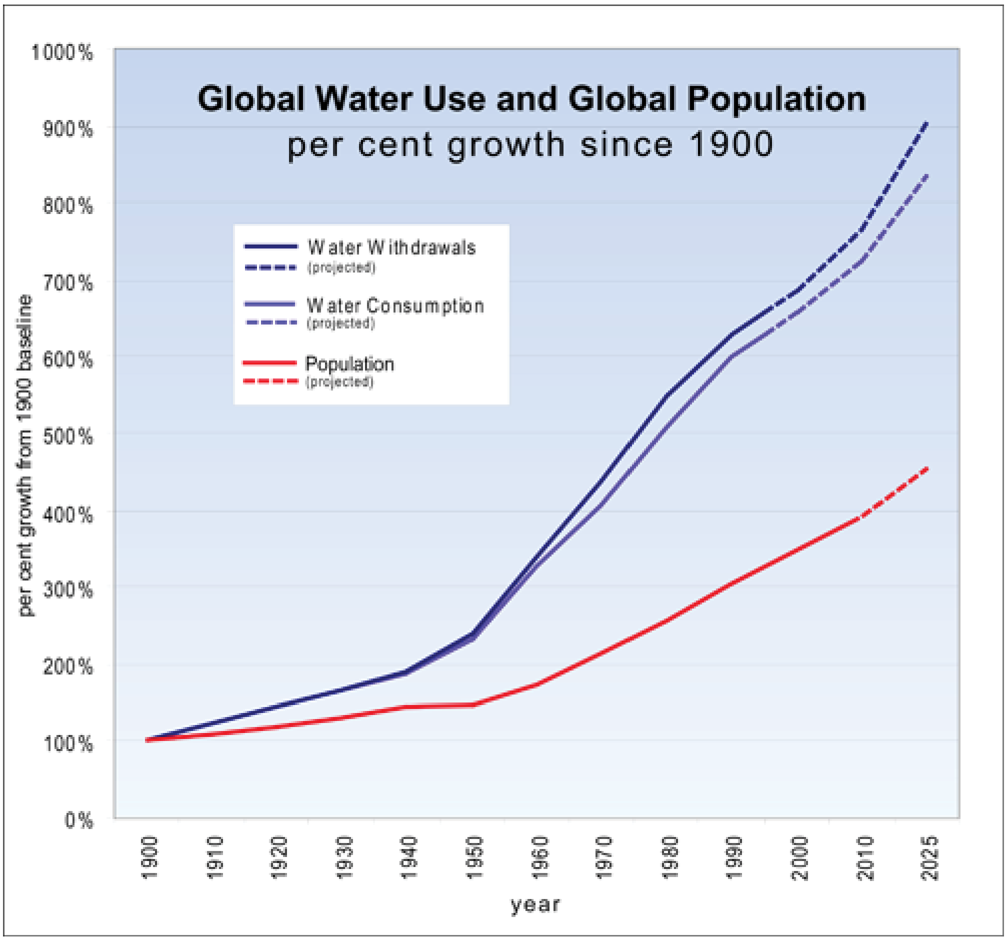

Figure 2.2. The rate of growth in fresh water withdrawal, water consumption and population (Sources: Shiklomanov, 1999; US Census Bureau, 2011).

Figure 2.2 shows that water withdrawal and water consumption rates have increased faster than population growth. Freshwater is distributed quite unevenly around the world. Furthermore, to supply water-demanding areas with much needed water from surplus areas is impractical. Therefore, the scarcity of water is becoming a serious problem in many parts of the world. Water withdrawal in the rapidly growing populated areas, larger areas set aside for agriculture, and industrial regions are being depleted of water and consequently becoming degraded.

Generally, agricultural water withdrawal is much higher than the other forms of water withdrawal. Nearly 70% of water is being used for agricultural purposes and about 18% and 13% are used for industrial and domestic usage, respectively (Wada et al., 2011). However, the percentage regarding industrial water usage is more than 50% for developed countries. Gleick, 2006 reported that the ratios of industrial to total water withdrawal in Finland, UK, France, Canada, and Russia were 84%, 75%, 74%, 69%, and 64%, respectively. On the global scale, ground water fulfills 40% of industrial water demand, 20% of irrigation water demand, and 50% of drinking water demand (Wada et al., 2010). This shows that the amount of ground water abstraction is high and increasing daily. If the ground water abstraction is higher than the ground water recharge this is known as nonrenewable ground water abstraction. The global nonrenewable ground water abstraction is 42% (309 km^3/yr) of the total ground water abstraction of 734 km^3/ yr (Wada et al., 2010). Nonrenewable ground water abstraction is high in northwest and southern India, northeast Pakistan, northeast China, central and western United States, Mexico, southern Spain and northern Iran. These places are currently experiencing water stress and in the future this water stress will increase and the levels of ground water will decline and subsequently be irreversible.

2.2. Water pollution by nutrients

As N and P are essential nutrients for plants, they serve to enhance the growth of unwanted plants such as algae in water bodies. They also cause eutrophication. N is the major nutrient that is more widespread than P in most estuaries and coastal areas, and is therefore more responsible for eutrophication (Howarth, 1988; Nixon et al., 1996; NRC, 1993). The nutrients are released to the water bodies by point sources and non-point sources. The amount and rate of release of the nutrients depends on the concentration and amounts in the effluent or leachates, climatic conditions (rainfall), soil type, ground water table and distance to the water bodies. Some examples of point and non-point sources are summarised below (Carpenter, 2008).

Point Sources

- Waste water effluent (municipal and industrial)
- Runoff and leachate from waste disposal sites
- Runoff and infiltration from animal feedlots
- Runoff from mines, oilfields, unsewered industrial sites
- Storm sewer outfalls from cities with a population
- Overflows of combined storm and sanitary sewers
- Runoff from construction sites

Non-point sources

- Runoff from agriculture (including return flow from irrigated agriculture)
- Runoff from pasture and range
- Urban runoff from unsewered areas and sewered areas with a population
- Septic tank leachate and runoff from failed septic systems
- Runoff from construction sites
- Runoff from abandoned mines
- Atmospheric deposition over a water surface
- Activities on land that generate contaminants, such as logging, wetland conversion, construction, and development of land or waterways.

Point sources can be measured, monitored and controlled at a single place while non-point sources cannot be measured or regulated easily. Most non-point sources are intermittent and can also be continuous. Generally, agricultural activities are the main non-point source for nutrient pollution and they occur through the use of fertilisers. For example, the global uses of fertiliser (involving N and P) and water for agriculture are illustrated in Figure 2.3. The graph shows that nitrate usage was higher and the N increment rate also was more than P from 1960 to 2000.

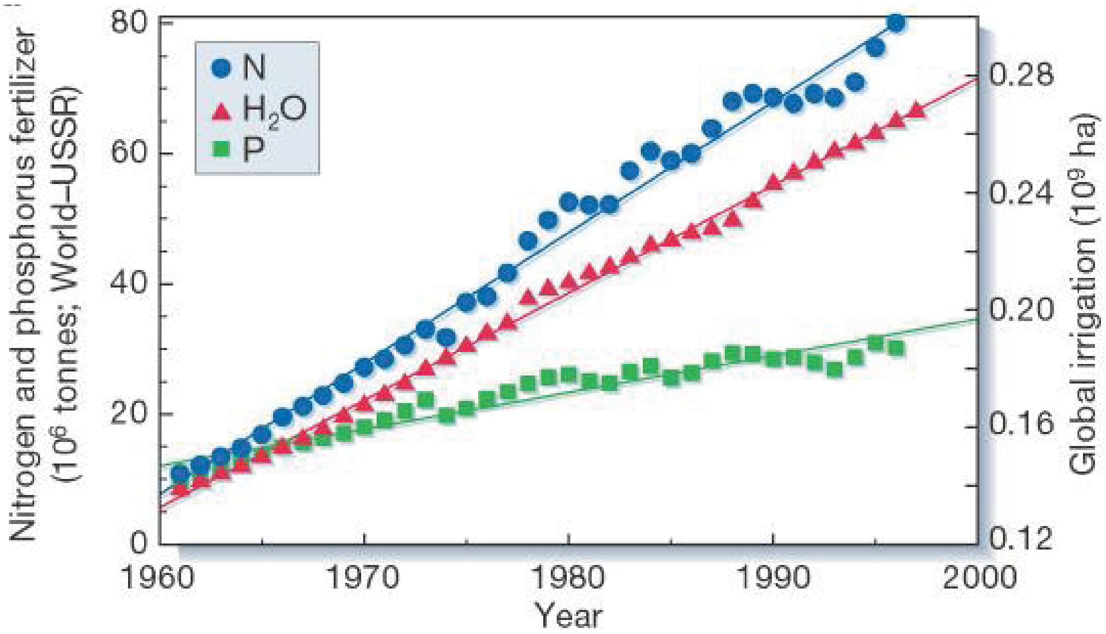

Figure 2.3. Total global use of N, P and water (former USSR not included (Tilman et al., 2002), based on FAO data)

2.3. Nitrate pollution

Nitrate is a pollutant that can contaminate sources of ground and surface water (Lerner, 1986; Yang et al., 1999). Once the nitrate enters the soil and ground water, it is very difficult to remove it. The nitrate level in ground water mainly increases due to the use of inorganic and organic fertilisers in agriculture (Ator and Ferrari, 1997; Hudak, 2000). Nitrate contamination of ground water depends on soil, crop type, fertiliser management system, climate and farming systems. Nitrate can seep into ground water by percolating through the soil or by runoff. The disposal of municipal sludge on fields, animal wastes, and urine, leaking sewerage systems, old and badly designed land fill are also reasons for nitrate contamination of water sources (Fetter et al., 1999; Hudak, 1999; Yu et al., 2007).

Nitrate may be formed in water bodies through oxidation from nitrite, ammonia, and organic nitrogen compounds such as amino acids. Animal wastes such as manure and urine contain ammonia and organic nitrogen and they can enter water through sewage effluent and runoff from land. Ammonia is converted into nitrite by bacteria such as Nitrosomonas and it can further oxidise to nitrate through the actions of bacteria such as Nitrobacter (Canfield et al., 2010), shown below in equation form:

$$2\ NH_3 + 3\ O_2 \xrightarrow{\text{Nitrosomonas}} 2\ NO_2^- + 2\ H^+ + 2\ H_2O \qquad (2.1)$$

$$2\ NO_2^- + O_2 \xrightarrow{\text{Nitrobacter}} 2\ NO_3^- \qquad (2.2)$$

These chemical equations express the oxygen demand in water bodies and consequently the deleterious effects that can seriously impact on the environment. Simultaneously in the absence of oxygen, the denitrifying bacteria converts the nitrate and nitrite into nitrogen gas and dinitrogen monoxide/Nitrous oxide (Canfield et al., 2010):

$$\begin{matrix} NO_2^- \\ NO_3^- \end{matrix} \xrightarrow[\text{Organic carbon}]{\text{Denitrifies}} N_2 + N_2O \qquad (2.3)$$

2.3.1. Ground water nitrate pollution

The world's ground water nitrate concentration distribution is shown in Figure 2.4 and it is based on the available data of some developed and developing countries' annual reports published by their environmental protection agencies (Zhou, 2015). Many studies have shown that fertiliser usage in agriculture is the main nitrate source in ground water and other sources are dairy and poultry operations, barnyards, and feedlots (Harter et al., 2002; Hudak, 2000; Wylie et al., 1995). The map shows that most regions in India are at high risk of nitrate pollution. India is still very much an agricultural country and the amount of fertiliser use is high. Many studies reported that the overuse of fertiliser is the main reason for ground water nitrate pollution in India (Majumdar and Gupta, 2000; Rao, 2006). A water quality assessment study conducted by the National Environmental Engineering Research Institute (NEERI) in 17 Indian states reported that out of 4696 water samples, 1290 (27%) were contaminated by nitrate. Furthermore, this finding exceeded the Indian drinking water nitrate concentration (Bulusu and Pande, 1990).

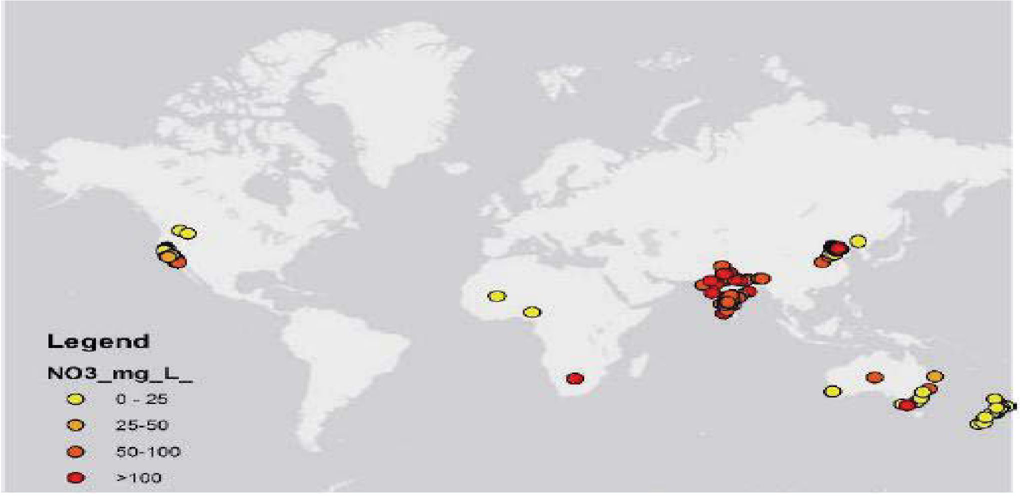

Figure 2.4. Nitrate concentration of ground water in different regions of the world (Zhou, 2015).

Ground water nitrate contamination (> 2.26 mg N/L nitrate) in Australia is shown in Figure 2.5. The red points on this map signify areas where nitrate concentration is greater than 2.26 mg N/L. Most areas exceed the nitrate drinking water standard level of 11.3 mg N/L and some areas are in excess of 22.6 mg N/L (LWRRDC, 1999), The major explanations for nitrate pollution in Australia are the high levels of fertiliser application, soil cultivation and grazing. These are augmented by the disposal of wastes from manufactured and processed agricultural products, and effluent disposal. Keating et al. (1996) analysed the ground water of inland areas of northeastern Australia and discovered that Darling Downs and Callide Valley had nitrate concentrations higher than 11.3 mg N/L due to cereal cropping, pasture, and cotton and grain production. Also, nitrate concentrations higher than 11.3 mg N/L were found in irrigated areas of northern Victoria (Bauld, 1994; Bolger and Stevens, 1999), horticulture areas of Perth (Pionke et al., 1990) and under irrigated and dryland pastures and vineyards of the southeastern region of South Australia (Bauld, 1994; Bolger and Stevens, 1999; Dillon et al., 1999). The excessive levels of nitrate usage have percolated through the soil and reached underlying aquifers. The shallow unconfined aquifers are most vulnerable to contamination by the higher level of nitrate concentrations.

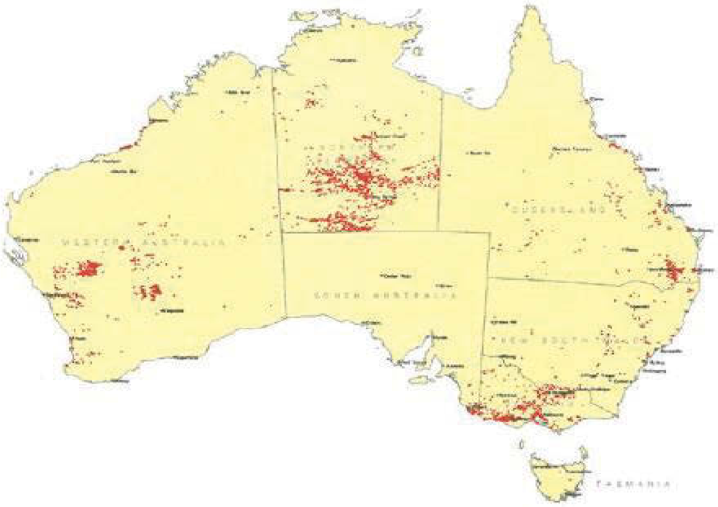

Figure 2.5. The distribution of bores across Australia with nitrate levels greater than 2.26 mg N/L (Source: LWRRDC, 1999)

2.3.2. Surface water nitrate pollution

For several decades, surface water pollution has been a major issue, especially in developing countries due to urbanisation. Urban storm water runoff is contaminated by fertilisers, spillage of chemicals, organic and inorganic liquids on the roads, parking or docking areas and construction areas, animal urine and wastes. Contaminants may include high concentrations of nitrate and when the runoff water reaches rivers, lakes, ponds and other aquifers it can contaminate the surface water.

In India, Bangladesh, and Nepal, surface waters have been polluted severely and critically near urban areas due to the continuous discharge of large qualities of pollutants (Karn and Harada, 2001). Rao (1998) reported that in India, the Vamsadhara and Godavari river basins reached a maximum nitrate concentration of 101.6 mg N/L. One of the non-point pollution sources of surface water is fossil fuel combustion products. Jaworski et al. (1997) analysed the data of 33 river waters from the early 1900s in the northeastern United States and found that increase in nitrate concentration in rivers was correlated with rising fossil fuel emissions of N.

2.4. Nitrate pollution effects

2.4.1. Health effects

High nitrate levels can cause blue baby syndrome or methemoglobinemia, especially in infants. The nitrate is converted into nitrite by the baby's digestive system and then nitrite reacts with the oxyhemoglobin, which is the protein in the baby's blood that carries oxygen. In this reaction the methemoglobin forms and it is deprived of the ability to carry oxygen. As a result, the baby's tissues may not get enough oxygen and the mucus membrane becomes blue in colour. The baby's digestive system and respiratory system are also affected by the high nitrate levels. Severe methemoglobinemia can result in brain damage and death (Kross et al., 1992; Majumdar and Gupta, 2000).

Healthy adults can consume fairly large amounts of nitrate with few known health effects and it is absorbed and excreted in urine. However, the prolonged intake of high levels of nitrate may cause gastric problems due to the formation of nitrosamines.

Studies have revealed that excess nitrate level in drinking water causes diarrhea, abdominal pains, hypertension, central nervous system birth defects, spontaneous abortions, respiratory tract infections, diabetes, and various kinds of cancers (Chiu et al., 2007; Fewtrell, 2004; Lohumi et al., 2004; Tate and Arnold, 1990). In animals, the high nitrate concentration (> 300 mg/L) can result in animal death and at lower concentrations it also increases the incidence of still-born calves, abortions, lower milk production and cystic ovaries (Islam and Patel, 2010).

2.4.2. Environmental effects

One of the more serious environmental problems caused by nitrate is eutrophication. An excessive amount of nitrate in water leads to the proliferation of algal bloom (Camargo and Alonso, 2006). This is a scenario where dissolved oxygen concentration in the water decreases, resulting in the death of desirable plants and species (Smith et al., 1998). Eutrophication by the nutrients has been identified in coastal lagoons, lakes, estuaries and embayments in South Australia (Brodie, 1995), Victoria (Morris et al., 2003) and Northern Australia (Bormans et al., 2004).

2.5. Nitrate standard limits

Many governments in developed and developing countries have major concerns about the excess levels of nitrate in drinking water and have taken action to control the nitrate concentration through legislation and the imposition of regulations. The recommended nitrate concentration limit for Australia is 50 mg/L for infants up to 3 months old and 100 mg/L for adults and children over the age of 3 months (NHMRC, 2011). Table 2.1 shows the standard limit of nitrate in drinking water for some countries. Most countries follow the World Health Organization (WHO) drinking water standard limits. Table 2.2 shows the nitrate discharge limit discharge to natural water bodies for different countries.

Table 2.1. Nitrate standard limits in drinking water for different countries

Country/Organisation	Nitrate limit (mg N/L)	Reference
WHO	11.3	WHO, 2011
Australia	11.3	NHMRC 2011
USA	10	USEPA, 2009
Canada	10	Health Canada, 2012
India	10	BIS, 1992

Table 2.2. Nitrate limit for discharge to natural water bodies for different countries

Country/Organisation	Nitrate limit (mg N/L)	Reference
Australia	15	DPIWE, 2001
European Union	15 mg N/L (10000-100,000 PE) 10 mg N/L (> 100,000 PE) (PE-Population Equivalent)	EU (EuropeanUnion), 1991
USA	15 mg N/L	USEPA, 2009
Canada	Un-ionised ammonia 1.25 mg N/L	Environment Canada, 1991
India	10 mg N/L	CPHEEO, 2012

2.6. Nitrate removal Technologies

Action has been taken to prevent the nitrate pollution of water in many countries. Governments have begun implementing laws and fertiliser management policies strictly to prevent the contamination of water by nitrate. However, once the nitrate is released into the environment, it is very difficult to remove it. Nitrate percolates through the soil and reaches the ground water or reaches the surface water by runoff. Nitrate is a highly soluble ion and stable in water. Thus, traditional water treatment methods such as lime softening and filtration are difficult to use for the removal of nitrate from water (Kapoor and Viraraghavan, 1997). Several technologies such as electro-dialysis, reverse osmosis, adsorption and chemical and biological methods have been developed to eradicate nitrate (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a). Every technology has its advantages and disadvantages in terms of ease of operation, operational and maintenance costs, waste disposal, removal efficiency, pre-treatment, and post-treatment.

2.6.1. Reverse osmosis

Reverse osmosis (RO) is an advanced technology that has been used in water treatment to remove most pollutants including nitrate. Reverse osmosis is a pressure-driven membrane filtration process in which a semi-permeable membrane is used to filter the feed water by having different pressures on opposite sides of the membrane (Darbi et al., 2003). Figure 2.6 illustrates the basic principle of the RO process. Water with a high concentration of pollutants that do not pass through the RO membrane is called the reject water or concentrate. The RO membrane was developed for desalination of seawater and brackish water, and the first RO desalination plant was installed in Goalinga, California in 1965 (Crittenden et al., 2005). Though the RO requires a lot of capital investment and in terms of operation and treatment is expensive, it can remove most pollutants such as anions (nitrate, phosphate, fluoride), cations (copper, iron, lead, barium), other inorganic contaminants, microorganisms natural organic matter and hardness. It enjoys high removal efficiencies (Darbi et al., 2003; Malaeb and Ayoub, 2011).

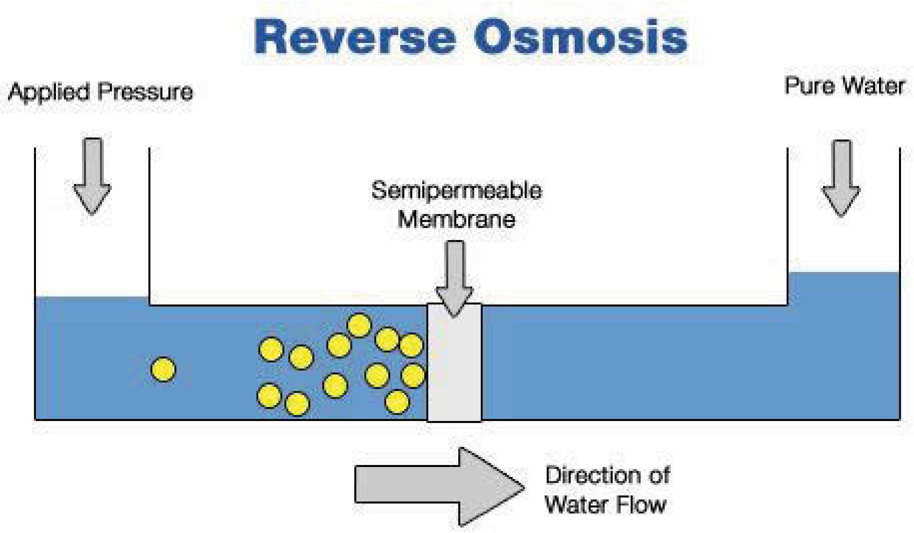

Figure 2.6. Reverse osmosis process

2.6.1.1. RO membrane

One of the problems with RO, however, is the feed water needs pretreatment to reduce the scaling or fouling on the membrane due to the high concentration of pollutants such as organic matter, solutes and biological contaminants (Kapoor and Viraraghavan, 1997). Pretreatment methods such as granular filtration, coagulation, flocculation, sedimentation and micro and ultra filtration are used to reduce the scaling problem. The pH adjustment and addition of anti-scalant (polyacrylic acid) helps to reduce scaling on the membranes. Biofouling can be prevented by disinfection using chlorination. The RO process needs post-treatment to readjust the water quality. The most common post-treatment strategies are pH and alkalinity adjustment, degasification, disinfection and corrosion inhibitor addition or blending feed and product water (Bergman, 2007; Crittenden et al., 2005). The reject water and chemical cleaning residuals which are produced during the pre- and post-treatment phases have to be disposed of properly and this cost must be added to the operational cost.

Bohdziewicz et al. (1999) tested nitrate removal using reverse osmosis and nanofiltration on several flat membranes of 36.6 cm^2 surface area with dead-end mode operating condition. The maximum nitrate removal documented in this study was 76.3% with 2.76×10^6 Pa transmembrane pressure for the initial nitrate concentration of 100 mg/L. Schoeman and Steyn (2003) reported that the nitrate concentration fell from 42.5 mg N/L to 0.9 mg N/L when they used the 4040-LHA-CPA2 membrane with an area of 79 m^2. The flow rate was approximately 85 L/min with a transmembrane pressure development of 230 kPa pressure.

2.6.2. Chemical denitrification

The zero-valent metals such as iron and aluminium are effective for chemical denitrification in the removal of nitrate from drinking water (Shrimali and Singh, 2001). They have a high electron-donating tendency and can reduce nitrate to N_2 and NH_3 and the iron or aluminium are oxidised to Fe^{2+} /Fe^{3+} or Al^{3+}. However, the disadvantages of this method are long reaction time, pH control and the post-treatment needed for the removal of ammonia (Kumar and Chakraborty, 2006). Chemical denitrification has been conducted using zero-valent Fe (Huang and Zhang, 2004), zero-valent Al (Luk and Au-Yeung, 2002) and zero-valent Mg (Kumar and Chakraborty, 2006) and Al-Fe alloy (Xu et al., 2017). The reactions of the chemical denitrification are given below in Tables 2.3 and 2.4. The disadvantages of this method are higher waste disposal, inconsistent nitrate reduction and risk of nitrite formation.

Table 2.3. Nitrate reduction by zero-valent iron

Reaction with Fe	Reference
$6\ NO_3^- + 10\ Fe^0 + 3\ H_2O \rightarrow 5\ Fe_2O_3 + 3\ N_2 + 6\ OH^-$	Siantar et al., 1996
$NO_3^- + Fe^0 + 2\ H^+ \rightarrow Fe^{2+} + NO_2^- + H_2O$	
$6\ NO_3^- + 4\ Fe^0 + 10\ H^+ \rightarrow Fe^{2+} + 3\ NH_4^+ + 3\ H_2O$	Cheng et al., 1997
$NO_3^- + Fe^0 + 2\ H_3O^+ \rightarrow Fe^{2+} + NO_2^- + 3\ H_2O$	Huang and Zhang, 2004
$2\ NO_3^- + 5\ Fe^0 + 6\ H_2O \rightarrow 5\ Fe^{2+} + N_2 + 12\ OH^-$	Choe et al., 2000

Table 2.4. Nitrate reduction by zero-valent aluminium

Reaction with Al	Reference
$3\ NO_3^- + 2\ Al^0 + 3\ H_2O \rightarrow 3\ NO_2^- + 2\ Al(OH)_3 \downarrow$	Luk and Au-Yeung, 2002
$6\ NO_3^- + 8\ Al^0 + 18\ H_2O \rightarrow Al(OH)_3 \downarrow + 3\ NH_3(g) + 3\ OH^-$	Murphy, 1991
$6\ NO_3^- + 10\ Al^0 + 18\ H_2O \rightarrow 10\ Al(OH)_3 \downarrow + 3\ N_2 + 6\ OH^-$	Luk and Au-Yeung, 2002
$2\ NO_2^- + 2\ Al^0 + 4\ H_2O \rightarrow N_{2\ (g)} + 2\ Al(OH)_3 \downarrow + 2\ OH^-$	Kapoor and Viraraghavan, 1997

2.6.3. Biological Denitrification

Biological denitrification is an effective method used to treat drinking water, ground water and waste water using microbes where the nitrate is reduced to nitrogen gas, ammonia and nitrite. In this method, the concentration of ions other than nitrate does not change. Through microbial activity the nitrate is reduced to nitrogen gas, ammonia, and nitrite. The ammonia formed can combine with chlorine and form chloramine and nitrogen trichloride, which change the taste and odour of drinking water (Shrimali and Singh, 2001). This is a disadvantage of the biological denitrification method. The other disadvantages are: slowness of the process (period lasting 2-3 weeks), carbon addition, need to adjust pH and temperature and post-treatment to disinfect the micro-organisms (Kapoor and Viraraghavan, 1997). The addition of carbon is necessary for biological respiration and to provide an electron donor for dissimilatory nitrate reduction. The denitrification rates increase with rising temperature and the maximum temperature is mostly about 75 ^{0}C (Bremner and Shaw, 1958). Generally the best pH is that ranging from 6-8 (Firestone, 1982).

The biological denitrification process occurs through anaerobic bacteria which respire by using nitrate as opposed to oxygen as their electron acceptor (Hiscock et al., 1991; Kapoor and Viraraghavan, 1997):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

2.6.4. Electrodialysis (ED)

Electrodialysis is an ions separation process using cation transfer membranes and anion transfer membranes by applying an electrical potential difference between oppositely charged electrodes. The transfer of ions occurs from the low concentrated to a high concentrated solution due to the electric current and ion charges. Although electrodialysis has several advantages such as higher nitrate removal efficiency, it does not require extensive pre-treatment, requires lower acid dosages compared to the RO method (Rautenbach et al., 1987). It has some disadvantages such as it needing a more complex electrical and membrane system, capital investment and energy. Also, highly concentrated wastes generated in this system need to be disposed of (Kapoor and Viraraghavan, 1997). Some studies on nitrate removal using electrodialysis are shown in Table 2.5.

Table 2.5. Studies on removal of nitrate using ED

Water type	Electrodes	Voltage	Current	Membranes conditions	Duration	Initial NO_3^- con (mg N /L)	Final NO_3^- con (mg N /L)	Reference
Well water	-	0.6 V	8.1 A	CMV/AMV type membrane, 50 m^2	-	12	1.8	Kneifel et al., 1988
Ground water	Pt coated Ti	15 V	10 mA/cm^2	Surface area 200 cm^2	10 min	30	20.5	Elmidaoui et al., 2001
Ground water	Pt coated electrode	-	3.3 mA/cm^2	Surface area 36 cm^2	250 min	56	4.7	Sahli et al., 2008
Saline water	TiO_2/RuO_2, Cu	9 V	-	IONAC,MC-3470 typemembrane,16 cm^2	24 h	82	24.8	Bosko et al., 2014
Ground water	DSE electrode	1.5 V/cell	9 A	CMX, ACS membranes, 200 cm^2	10 min	22	3.6	El Midaoui et al., 2002

2.6.5. Electrochemical (EC)

The electrochemical method is a widely used process for water and waste water treatment. This technology is easy to operate and produces less sludge, and there is no need to handle chemicals (Chen, 2004; Rajeshwar and Ibanez, 1997). The advantages and disadvantages of electrochemical technology are summarised in Table 2.6. The EC process has been used in several sites for ground water treatment (Joffe and Knieper, 2000). Processes such as electrocoagulation, electro-flotation, electro-oxidation, and electro-reduction are examples of the electrochemical technology method. Several pollutants such as dissolved solids, suspended matter, anions, cations, dyes, and organics can be removed through these processes. Two or multiple electrodes can be used as anodes and cathodes to provide electric charge coupled with DC voltage. In the electrocoagulation process sacrificial electrodes (Al, Fe) are employed. While applying the electrical current, they dissolve and generate the coagulating agent (metal hydroxides) and gas bubbles. This is an advantage of sacrificial electrode in that it provides the coagulating metal ions which form the metal hydroxide complexes. Therefore, the nitrate is adsorbed on the surface of the metal hydroxide complexes. In this process nitrate reduction also occurs and it is in fact converted into other forms of nitrogen (NH_3 and N_2). While the stable anodes (Ti/RuO_2, Ti/Pt-Ir, Pt and etc) use, the nitrate is removed only by the electro-reduction. Nitrate removal has been studied over the last few decades using electrode metals such as Ni, Fe, Al, Zn, Au, Pt, Pd, Ag, Cu, Ru, and Rh (Bouzek et al., 2001; Da Cunha et al., 1996; Dima et al., 2003; Li et al., 1988b; Reyter et al., 2008). Cu was found to be the best cathode for the reduction of nitrate to ammonia at alkaline solutions (Bouzek et al., 2001; Reyter et al., 2008).

2.6.5.1. Nitrate, nitrite and ammonia removal

Nitrate is reduced to harmless nitrogen gas as the main product in this technology (Pressley et al., 1972). During the process, low concentrations of some by-products such as ammonia and nitrite may be produced in the solution (Kim et al., 2006; Paidar et al., 1999). Consequently, the nitrite is reduced to nitrogen gas and ammonia (Li et al., 2009). In their investigation (Marinčić and Leitz, 1978) found that direct oxidation from ammonia to nitrogen gas occurred well on platinum anode than titanium platinised anode. While the chloride ions are present in the water, the indirect oxidation occurs for ammonia. The Cl^- ions are oxidised at the anode and immediately react with water and produce hypochlorite, which is a strong oxidant which reacts with the ammonia and produces nitrogen gas (Pressley et al., 1972). Li et al. (2009) reported that they did not find any nitrite or ammonia in the final solution in the presence of chloride ion when they utilised Fe as cathode and Ti/IrO_2 as anode. The other reactions occurring in the anode and cathode are oxygen evolution and hydrogen evolution, respectively. Several electrochemical studies have been conducted on the removal of nitrate, ammonia and nitrite and these analyses are listed in Table 2.7.

2.6.5.2 Advantages and disadvantages of the electrochemical process

Table 2.6. Advantages and disadvantages of electrochemical technology

No.	Advantages	Disadvantages
1	Simple method, easy to operate and low maintenance	Cannot be used in some places/countries where electricity is too expensive
2	Able to produce palatable, clear, colourless, and odourless water	High conductivity of water is required to achieve high performance
3	Produces low sludge which is readily settable and easy to de-water	The efficiency may be compromised due to the formation of impermeable oxide film on the cathode
4	Produces effluent with less total dissolved solid (TDS) compared to chemical treatment	If sacrificial electrodes are used, they can be dissolved in water and need to be replaced regularly
5	Removes the smallest colloidal particles	
6	No need to use chemicals	
7	The produced gas bubbles carry the pollutants to the top and can be easily removed	
8	Renewable energy can be used to operate the system in rural areas and reduce energy costs	

Table 2.7. Summary of nitrate removal using the electrochemical process

Pollutant	Current/Current density	Cell voltage (V)	Electrodes and conditions	Initial and final concentration (mg N/L)	Remarks	Reference
Nitrate	28-76 A/m^2	-	Ti/Pt, Cu	Ci-135.4, Co- 123.2	Highest nitrate removal occurred at 28 A/m^2	Paidar et al., 1999
Nitrite	0.05-2 A	-	Stainless steel	Ci- 2.25, Co- 0	Highest removal was at high current of 2 A and at low pH of 2	Abuzaid et al., 1998
Nitrate	0.5-2.5 A	6-25	Al	Ci-10.4 Co- 4.5	Higher removal at pH range of 9-11	Emamjomeh and Sivakumar, 2005
Nitrite, Nitrate, Ammonia	77 mA	12	Al,Fe	Ci- 0.05, Co- 0.0.04	Removal increased with increasing current intensity	Uğurlu, 2004
Nitrite and Ammonia	1-2.5 A	-	Graphite, TiO_2	13.5-22.3 (NO_2^-Ci- 5mg/L, 10 mg/L NH_4^+)	Removal increased with increasing current density	Lin and Wu, 1996
Ammonia	500-1200 A/m^2	-	Ti/IrO_2, SS	NH_3 Oxi.rate 225 g/h.m^2	High and stable oxidation rate was in the pH range 5.5-10	Vanlangendonck et al., 2005
Nitrate	10- 60 mA/cm^2	0-50	Ti/IrO_2, Fe (40 cm^2)	Ci-22.5, Co- 21	High current and high temperature favoured nitrate reduction	Li et al. (2010)
Ammonia	30 mA/cm^2	-	Boron doped diamond, Pt wire	Ci- 0.05 M, C_O- 0.03	Active chlorine in the solution effectively removed ammonia	Kapałka et al. (2010)
Nitrate,	30 mA/cm^2	-	Diamond, IrO_2-Ta_2O_5, Stainless steel	Ci- 5.6, Co- 5.2	High sulphate concentration (1000 ppm) removed more nitrate by forming perxosulphates	Lacasa et al., 2011
Nitrate	-	2.9 80	Graphite, Carbon cloth, Iron rashing rings	Ci- 67.7, C_O- 52.8 C_i – 67.7, C_O-62.3	Higher removal occurred at low pH for graphite. Optimum pH was 9-11 for iron rings. Higher nitrate removal occurred at high voltage	Koparal and Öğütveren, 2002
Nitrate, Arsenic	-	10-25	Mild steel	Ci- 67.7, C_O- 56.9	Maximum removal achieved at high voltage of 25 V	Kumar and Goel, 2010

2.6.6. Adsorption

The adsorption process is a simple water treatment technology with reduced operational costs and minimal waste disposal problems (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a). The efficiency required for removing pollutants depends on the adsorbent dosage, adsorbate concentration, pH, temperature and co-ions concentration. The disadvantages are as follows: the presence of complementary ions and problems associated with the disposal of exhausted adsorbents. To overcome the disposal problems, the adsorbents can be regenerated by desorption of nitrate and re-use it several times. As long as the adsorbent is not eco-toxic, it can be directly applied to agricultural lands to supply the adsorbed nitrate to plants.

Adsorption can be broadly divided into two groups: (i) chemical adsorption and (ii) physical adsorption (McKay, 1996). Physical adsorption characteristics are as follows: attraction of ions to the adsorbent surface is by Van der Waal's and electrostatic force; heat of adsorption is low; not very specific; activation energy is not required; and it is reversible. Meanwhile the chemical adsorption characteristics are: occurs at low or high temperature; heat of adsorption is high; not reversible; highly specific to the adsorbate; and activation energy is required.

2.6.6.1. Adsorption mechanism

Generally, adsorption takes place in three steps: (i) external mass transfer of adsorbate from bulk solution to the surface of the adsorbent by diffusion or turbulent movement; (ii) adsorbates transfer to internal structure of the adsorbent and reaches the available adsorption site; and (iii) rapid uptake (McKay, 1996). The adsorption process takes place until it reaches the equilibrium state and it depends on temperature, physical and chemical characteristics, concentration of adsorbate and subsequent interaction between adsorbate and adsorbent (Chaudhari et al., 2003; McKay, 1996). The surface area and pore size of the adsorbents also influence the adsorption process. Higher surface area is favourable for adsorption and it increases when the pore size declines. However, if the pore size is very small compared to the adsorbate, the adsorbate cannot enter through the pore and this is referred to as steric effects.

There are seven adsorption mechanisms (Faust and Aly, 2013; Loganathan et al., 2013b) and these are as follows: (i) Van der Waals forces (outer-sphere surface complexation), (ii) ion exchange (outer-sphere surface complexation), (iii) hydrogen bonding (H- bonding), (iv) ligand exchange (inner-sphere surface complexation), (v) surface precipitation, (vi) diffusion, and (vii) chemical modification of the adsorbent surface. Nitrate adsorption occurs via the first two mechanisms which are weak physical and non-specific adsorption mechanisms. The next two mechanisms - chemical and specific adsorption - operate for other anions such as phosphate and fluoride.

2.6.6.1.1. Van der Waals force

Van der Waals force is a weak and short range force acting between atoms. This adsorption is a physical adsorption process and the attraction increases with increasing polarisability and adsorbate size. Van der Waals forces are stronger for larger organic molecules and adsorbents and weaker for smaller sized inorganic adsorbates such as nitrate, phosphate, and fluoride (Gupta et al., 2009).

2.6.6.1.2. Ion exchange

The ion exchange process is a stoichiometric one where the adsorbent takes up the ions from the solution and releases equivalent moles of counter ion to maintain the adsorbent's electro-neutrality (Eq 2.4 - $\blacksquare^{+}$ -represents positive charged adsorbent). The ion exchangers consist of a matrix with negative or positive charge functional groups which are compensated with a freely mobile positive or negative counter ion. The positively charged ion exchange resins attract negatively charged anions and the adsorption process is governed by electrostatic attraction or columbic forces. This is a physical adsorption process which is rapid and reversible. The ion exchangers prefer to adsorb ions of higher valency, at higher concentration, and ions of smaller hydrated equivalent volume (Helfferich, 1995).

$$\blacksquare^{+}\,..Cl^{-} + NO3^{-} \longrightarrow \blacksquare^{+}\,..NO3^{-} + Cl^{-} \qquad (2.4)$$

Ion exchange resins can be divided into acrylic or styrenic types. The acrylic type has an aliphatic matrix whereas the styrenic type consists of an aromatic matrix. Anion exchange resins can be classified as shown in Table 2.8, based on the structure and functional groups.

Table 2.8. Anion exchange resin classification (Crittenden et al., 2005)

Type of resin	Functional group	Structure
Weak-base	Secondary amine	$[R(CH_3)_2N)HOH$
Strong-base anionic type I	Trimethyl- amine	$[R(CH_3)_3N^{+}]\ Cl^{-}$
Strong base anionic type II	Dimethyl ethanol-amine	$[R(CH_3)_2(CH_2CH_2OH)N^{+}]\ Cl^{-}$

Several studies have been done on nitrate removal using anion exchange resins. The Langmuir adsorption capacities of ion exchange resins are in the 10 – 50 mg N/g range (Table 2.9). The advantage of ion exchange resin is, it can be regenerated easily by desorbing the adsorbed nitrate using NaCl, KCl, NaOH solutions. The regenerated ion exchange resin can also be reused.

The ion exchange resin's nitrate removal efficiency declines in the presence of other anions such as phosphate, sulphate, bicarbonate and chloride. The affinity order towards the anion exchange resins is generally as follows (Crittenden et al., 2005):

$SO_4^{2-} > ClO_4^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > OH^-$

To overcome this problem of other anions competing with nitrate for adsorption, nitrate selective anion exchange resins are produced. One type of nitrate selective resin is that made-up of macroporous styrene strong-base anion (SBA) with N-tributylamine functional groups. This type of resin is commercially produced and known by the name Purolite A 520E.

Table 2.9. List of anion exchange resins used for nitrate removal and their adsorption capacities

Resins*	Conditions of adsorption	Langmuir adsorption capacity (mg N/g)	Reference
Purolite A 520E	20 mg N/L, 0.1-10 g/L adsorbent, 120 rpm, 24 ^{0}C	33.1	Nur et al., 2015
Amberlite IRA 400	pH -6.8, 0.45- 4.5 mg N/L, 2.5 g/L adsorbent, 26 ^{0}C	14.8	Chabani et al., 2007
Dowex D 201	pH- 6.28-9.2, 11.2-135.5 mg N/L, 2 g/L adsorbent, 140 rpm, 20 ^{0}C	39.2	Song et al., 2012)
Amberlite IRN 9766	pH- 6.5-6.8, mg N/L, 1 g/L adsorbent, 150 rpm, 25 ^{0}C	43.5	Dron and Dodi, 2011
Indion NSSR	pH- 2, 14.2 mg N/L, 0.125 - 4 g/L adsorbent, 20 ^{0}C	26.9	Milmile et al., 2011
NDP-2	pH- 6.28-9.2, 11.2-135.2 mg N/L, 2 g/L adsorbent, 140 rpm, 20 ^{0}C	39.3	Song et al., 2012
Purolite A 300	pH- 6.28-9.2, 11.2-135.2 mg N/L, 2 g/L adsorbent, 140 rpm, 20 ^{0}C	33.3	Song et al., 2012
Duolite A 171	pH-5 - 5.5, 22.6-112.9 mg N/L, 0.1 g adsorbent, 120 rpm, 30 ^{0}C	27.9	Sowmya and Meenakshi, 2013

*All the resins are made of Quaternary ammonium functional groups

2.6.6.1.3. Hydrogen bonding

Hydrogen bonding is a chemical adsorption process and it occurs by a strong dipole-dipole attractive force between a strong electro positive H atom in a molecule and a strong electro negative molecule (Helfferich, 1995). The energy of adsorption of H-bonding is greater than that of Van der Waals forces and electrostatic attraction but lower than that involved in ligand exchange. The H-bonding adsorption does not occur for nitrate but it does for some anions such as phosphate and fluoride on ion exchange resins (Maheshwari, 2006; Solangi et al., 2010). The fluoride is a highly electro negative element and a smaller sized ion, and therefore fluoride can be adsorbed by H-bond.

2.6.6.1.4. Ligand exchange

Adsorption as executed by the ligand exchange process occurs by forming a covalent bond between the anion and atoms on the adsorbent surface. Here an anion such as phosphate/fluoride replaces the previously bonded OH^- ions on the adsorbent (Loganathan et al., 2003). This is a highly selective specific adsorption process which can occur even if the solution contains higher concentrations of other anions.

2.6.6.1.5. Precipitation/Surface precipitation

Precipitation occurs for the phosphate and sulphate anions when they form metal phosphate and metal sulphate in the solution phase according to the thermodynamic solubility product principle (Loganathan et al., 2014; Sparks, 2001). This precipitation occurs while the solution phase concentration of the product's constituents exceeds the solubility product. Surface precipitation can happen even when the constituents of the product concentrations in the solution phase fail to exceed the solubility product principle. These anions may be removed from the solution by adsorption and/or precipitation at the surface of the adsorbents. Precipitation or surface precipitation does not occur in the case of nitrate adsorption.

2.6.6.1.6. Diffusion

Adsorption occurs through a 2-step process on microporous sorbents such as hydrous metal oxides and zeolites. In the first step the adsorbates are adsorbed on the outer surface of the adsorbents and reach a pseudo-equilibrium at solid-solution interface within an hour and in the second step adsorbate moves into the interior pores and channels of the adsorbent by diffusion at a longer period of time (days and months) (Trivedi and Axe, 2006).

2.6.6.1.7. Surface modification

Chemical modification of the adsorbents is an effective technique to enhance the adsorption capacity of adsorbents. In this method, surface modification is done by incorporating metals, amine groups, and cationic polymers on the adsorbents to increase their surface positive charge (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a). By executing this modification, more nitrate ions are electrostatically attracted by the modified adsorbents compared to the unmodified adsorbents and removed from the water. One of the common physical modifications is by heat treatment, which has been applied to several adsorbents and proved to increase the adsorption capacity of various adsorbents (Gupta et al., 2009; Yin et al., 2007). With heat treatment, the surface area and porosity increase due to the loss of volatile and/or decomposable compounds from the adsorbent. Therefore, more adsorption sites are exposed and adsorption increases after heat treatment. More detailed studies concerning surface modification are outlined in section 2.6.8.

2.6.6.2. Factors influencing adsorption

2.6.6.2.1. pH

The changes in solution pH affect nitrate adsorption on most of adsorbents. Generally, nitrate adsorption is low at very high pH (>8). At high pH, negative surface charges increase and repel the negatively charged nitrate ions. Sowmya and Meenakshi (2013) reported that the sorption capacity of ion exchange resin Duolite A 171 remained the same in the pH range of 3-9 and started to decrease after pH 9. Most of the adsorbents show higher nitrate removal efficiency at low pH (pH < 4), due to the increased number of positive charges on the surface of the adsorbent caused by protonation (Ohe et al., 2003). Chatterjee and Woo (2009) reported that the removal of nitrate on chitosan beads increased when a decrease in pH (8 to 3) occurred due to protonation. Protonation increased the surface positive charges of the adsorbent, resulting in increased electrostatic attraction of nitrate and therefore more nitrates were removed. In some adsorbents the decrease in pH led to a decrease in the adsorption because at low pH, the solution contained a high concentration of Cl^- (HCl) ions (which are added in the form of HCl to adjust the pH) which competed with nitrate ions causing a decrease in nitrate adsorption. For example, in the study by Bhatnagar et al. (2008b), the percentage of nitrate removal by $ZnCl_2$ modified GAC was almost constant at the pH range 4-11. However, it decreased at pH 3 due to competition with Cl^- ions which were added as HCl to adjust pH.

2.6.6.2.2. Co-ions

The co-ions effect is an important factor in nitrate removal. If the co-ions concentrations are much higher than nitrate concentration in the solution, the nitrate removal is significantly reduced. Another factor that reduces nitrate adsorption is the valency or charge of the co-ions. If the valency is more than one as in sulphate and phosphate, nitrate adsorption falls because the higher the valency or charge the higher the tendency for adsorption. Generally, sulphate ion is the most competent anion of all other anions such as phosphate, chloride, fluoride and carbonate ions (Crittenden et al., 2005). In some adsorbents such as layered double hydroxide (Zn-Al-Cl and Mg-Al-Cl) and hydroxyapatite (HAP), however, the affinity order towards the adsorbents were reported to be $CO_3^{2-} > PO_4^{3-} > Cl^- > SO_4^{2-}$ and $Cl^- > CO_3^{2-} > SO_4^{2-} > PO_4^3$, respectively (Islam and Patel, 2009; Islam and Patel, 2010). However, the concentration of these ions should also be considered in evaluating their competitive behaviour in the adsorption process. For example, the concentration of phosphate ions is usually much lower than that of nitrate ions and therefore even with the higher charge on phosphate, the competition from this ion is low**.** For example, Keränen et al. (2015) conducted a study on the co-ions effect utilising different ratios of nitrate and phosphate on amine grafted pine saw dust. The nitrate removal efficiencies for the N: P concentration ratios of 30:0, 30: 1, 30:5, 30: 10, 30:30, and 30:50 were 73, 72, 72, 66, 49 and 26%, respectively. When evaluating the charge effect of phosphate ions the pH of the solution should be considered because the charge on the phosphate ions increases with pH ($H_2PO_4^- \rightarrow HPO_4^{2-} \rightarrow PO_4^{3-}$)

Purolite A 520E is a nitrate selective anion exchange resin, which was used in the co-ions effect study in column experiments conducted by Samatya et al. (2006). In their study, sulphate and chloride concentrations were 10 times higher than the nitrate concentration (100 mg/L) and these ions were tested with nitrate individually and together. The breakthrough point bed volumes were observed to be 451, 209, 165, and 120 for the influent concentration of NO_3^- alone, NO_3^-: 10 SO_4^{2-}, NO_3^-: 10 Cl^-, and NO_3^- : 10 Cl^- : 10 SO_4^{2-} , respectively. These results revealed that chloride ions competed more with nitrate ions than sulphate. The chloride ions competed more here due to the high concentration of chloride ions than nitrate. Sulphate ions had less affinity towards the ion exchange resin due to the long-chain carbon structure of the resin which preferred Cl^- and NO_3^- than SO_4^{2-}. Purolite A520 E is functionalised with trimethylamine exchange sites (Gu et al., 2004; Sengupta, 1995). The hydrophobic trait of the resin increases when the carbon chain length also increases. Thus, the resin easily adsorbs ions with less hydration energy required. Here the nitrate and sulphate hydration energies are -314 kj/mol and -1103 kj/mol (Song et al., 2012). Thus, the Purolite resin A520E adsorbed more nitrate ions than sulphate and proved to be a nitrate-selective resin.

2.6.6.2.3. Temperature

Temperature is another factor affecting adsorption. The adsorption capacity of adsorbents increases (endothermic reaction) or decreases (exothermic reaction) or does not change when the temperature increases in the solution. The type of behaviour depends on the characteristics of the adsorbent and adsorbate interaction. The thermodynamic constants obtained from adsorption data at different temperatures such as standard Gibb's free energy change ΔG^0, standard enthalpy change ΔH^0 and standard entropy change ΔS^0 reveal the nature of the adsorption process. The Langmuir model constant b (Samatya et al., 2006) is used to calculate these theromodynamic constants using the following equations (Aydın and Baysal, 2006; Bhatnagar et al., 2008b; Bulut and Aydın, 2006):

$$\Delta \mathrm{G}^0 = -\mathrm{RT}\ln(\mathrm{b}) \tag{2.5}$$

$$\ln\frac{\mathrm{b}_2}{\mathrm{b}_1} = -\frac{\Delta \mathrm{H}^0}{\mathrm{R}}\left(\frac{1}{\mathrm{T}_2} - \frac{1}{\mathrm{T}_1}\right) \tag{2.6}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{2.7}$$

Where, b is a Langmuir constant (L/mol) at temperature T (K); R is an ideal gas constant (8.314 J/mol.K). The parameters b_2 and b_1 are Langmuir constants at temperatures T_2 and T_1, respectively. The ΔG^0 and ΔH^0 are in J/mol and ΔS^0 is in J/mol.K.

If the free energy changes are negative the nature of the adsorption is spontaneous. The positive or negative value of enthalpy change indicates that the adsorption process is endothermic or exothermic, respectively. The positive and negative value of the entropy change suggests there is an increase and decrease in randomness, respectively, in the solid/solution interface during the adsorption process.

Bhatnagar et al., 2008b, reported that, when the temperature increased from 10 ^{0}C to 45 ^{0}C, the adsorption of nitrate by a $ZnCl_2$ modified GAC adsorption decreased. ΔG^0 and ΔH^0 were calculated using thermodynamic equations (Eq 2.5, 2.6) and ΔG^0 was found to be in the range -4.01 to -2.75 kJ/mol and ΔH^0 was -13.16 kJ/mol. Physical adsorption occurs between -20 – 0 kJ/mol value of ΔG^0 and the chemical adsorption range is -80 to -400 kJ/mol (Özcan and Özcan, 2004; Yu et al., 2001). If the ΔH^0 value is less than 40 kJ/mol, it can be considered an example of physical adsorption. Consequently, the nitrate adsorption by $ZnCl_2$ modified GAC adsorption was exothermic in nature and it occurred through physical adsorption. The standard entropy change was negative and it revealed the (Aydın and Baysal, 2006; Bhatnagar et al., 2008b; Bulut and Aydın, 2006) degrees of freedom of the adsorbed species actually decreased. Demiral and Gündüzoğlu (2010) reported that Langmuir nitrate adsorption capacity of $ZnCl_2$ modified sugar beet bagasse increased from 9.1 to 27.6 mg/g when the temperature rose from 25 ^{0}C to 45 ^{0}C. They obtained negative ΔG^0 values for the adsorption and this suggested that the adsorption was spontaneous in nature. The positive ΔS^0 indicated there was an increase in the randomness of the nitrate in the solid/surface interface. The negative ΔH^0 revealed that the adsorption process was endothermic in nature.

2.6.7. Adsorbents

Several adsorbents have been investigated for nitrate removal and they are summarised in Figure 2.7. Generally, the removal of nitrate by ion exchange resins is more effective compared to other adsorbents. Yet the costs of the ion exchange resins are higher than those of other adsorbents such as agricultural wastes, industrial wastes and natural adsorbents. Despite the absorbents' higher cost the nitrate removal by ion exchange is cost-effective because it is much more efficient.

Though agricultural wastes, industrial wastes, carbon-based adsorbents, natural adsorbents and bio sorbents have demonstrated poorer adsorption capacities, they can be used in larger amounts per unit cost of adsorbent to remove more nitrate. However, the problem is large amounts of exhausted adsorbents have to be disposed of at specific sites without contaminating the environment. During the last decade, these low-cost adsorbents have been surface modified to increase adsorption capacity. Modified adsorbents have shown 4-11 times greater adsorption capacity than unmodified adsorbents (Loganathan et al., 2013a). The unmodified adsorbents' Langmuir nitrate Langmuir adsorption capacities were in the range of 1.7-92.1 mg /g and after modification the Langmuir adsorption capacities were in the 125–363 mg /g range (Bhatnagar and Sillanpää, 2011). Table 2.10 presents a comparison of the adsorption capacities of adsorbents before and after modification and the type of modification.

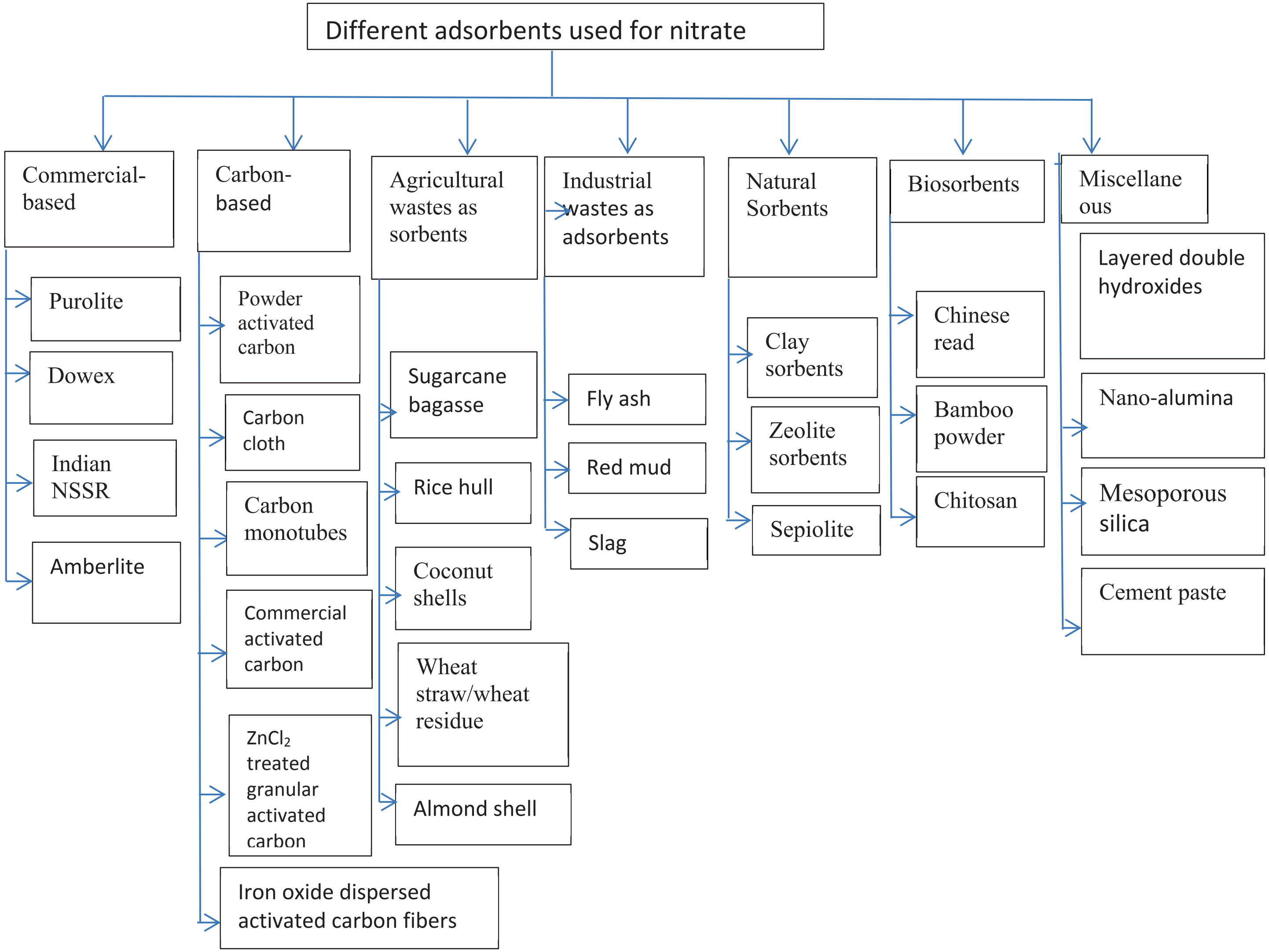

Figure 2.7. List of different adsorbents used to remove nitrate from water (Bhatnagar and Sillanpää, 2011)

2.6.8. Adsorbent modification

Adsorbents are being surface modified by several chemical and physical methods to increase their adsorption capacity (Figure 2.8, Figure 2.9). In physical modification, adsorbents are treated with heat to remove volatile matter and other impurities, so that the surface area and porosity of the adsorbents increase and the functional groups, which are favour for the nitrate adsorption is exposed on the surface. Chemical surface modification techniques are protonation, amine grafting, metal or metal oxide impregnation, and surfactant modification. Chemical surface modification increases the surface positive charges by providing new functional groups which favour nitrate adsorption.

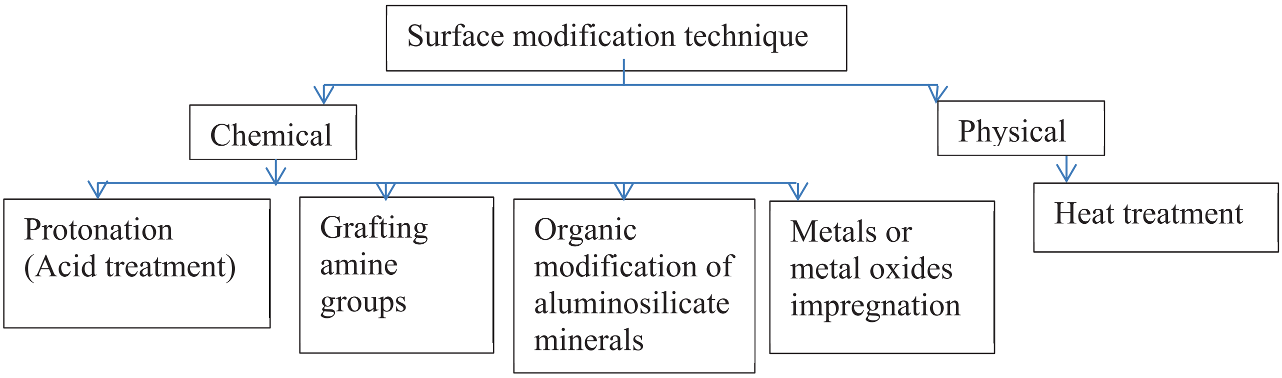

Figure 2.8. Surface modification techniques used to enhance nitrate removal by adsorbents (Loganathan et al., 2013a)

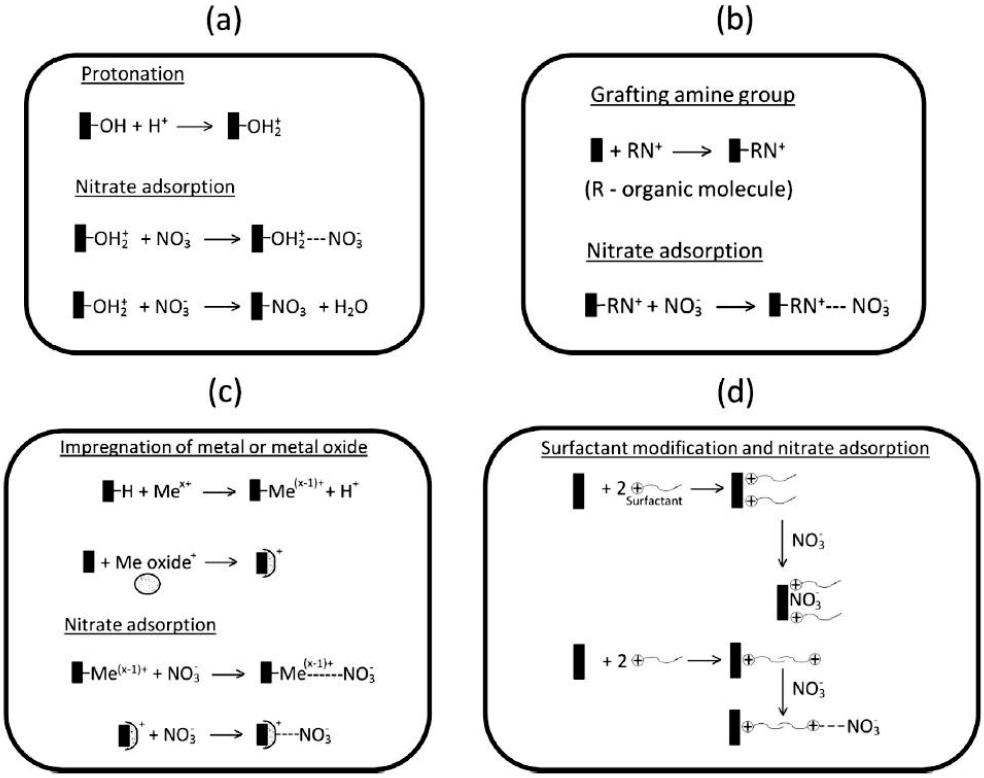

Figure 2.9. Schematic illustration of surface-modified adsorbents (█ represents unmodified adsorbents) (a) surface protonation, (b) surface impregnation of metal or metal oxide, (c) surface grafting of amine group, (d) cationic surfactant modification (Loganathan et al., 2013a)

2.6.8.1. Protonation

Protonation is a cost-effective and simple technique that enhances the adsorption of nitrate by treating the adsorbents with acid. In protonation, the number of positive charges (H^+) on the adsorbent surface is increased and in this way the electrostatic attraction of the nitrate increases. Several adsorbents such as sepiolite, red mud, activated carbon cloth and chitosan were modified by protonation and tested for nitrate removal. Results revealed that the modified adsorbents were more efficient in removing larger amounts of nitrate compared to unmodified adsorbents (Loganathan et al., 2013a).

2.6.8.2. Metal and metal oxides impregnation

Metal or metal oxide impregnation on the surface of the adsorbent increases the surface positive charges because metals exist in solutions as cations and some metal oxides have positive charges (Demiral and Gündüzoğlu, 2010; Namasivayam and Sangeetha, 2005). Heavy metals have the ability to adsorb on the surface of the adsorbents through electrostatic attraction and/or the ligand exchange mechanism (Loganathan et al., 2013a). The positive charges of the adsorbed metallic ions attract the negatively charged nitrate ions from water by electrostatic attraction forces. In some studies, the adsorbents' surface area and pore volume increased following metal impregnation, which in turn increased their adsorption capacity (Demiral and Gündüzoğlu, 2010; Namasivayam and Sangeetha, 2005).

Several adsorbents were surface modified with metals and examined for their ability to remove anions. Examples of this are as follows: copper (II) loaded on Dowex M4195 for phosphate removal (Sengupta and Pandit, 2011); zirconium (lV) loaded on polypropylene fiber for phosphate removal, and iron (III) loaded on Amberlite IRA 900 for phosphate removal (Blaney et al., 2007); titanium (IV) metal ions and examined for phosphate, arsenic removal (Cumbal and SenGupta, 2005); and aluminium (III) loaded zeolite for arsenate, phosphate and fluoride removal (Xu et al., 1998) from water. Nitrate removal was tested using metal/metal oxide loaded chitosan, zeolites, polymer resin, agricultural wastes such as coconut coirpith, sugar beet tailing, sugarcane bagasse and peanut shell (Bhatnagar et al., 2008b; Hassan et al., 2010; Namasivayam and Sangeetha, 2005, 2008; Sepehri et al., 2014; Sowmya and Meenakshi, 2013; Zhan et al., 2011). In all these studies the adsorption capacity increased when metals were incorporated into the absorbents.

2.6.8.3. Amine grafting

Amine grafting is a suitable method for producing weak-base anion exchangers from agricultural wastes to remove nitrate. Though mesoporous silica, clays, and carbon nanotube were modified using this method and shown to have higher adsorption capacity, the material cost is higher compared to agricultural waste (Orlando et al., 2002b; Saad et al., 2008; Xu et al., 2012; Yu et al., 2007). In the agricultural wastes modification method, first an epoxy group is introduced into the lignocellulosic structure of agricultural wastes and then it is grafted by amine groups. The amine grafted adsorbents contain Cl^- as counter ions and when the nitrate adsorption occurs, the Cl^- ions exchanged with NO_3^- ions:

$$R\text{-}N^+(CH_2CH_3)_3.Cl^- + NO_3^- \longrightarrow R\text{-}N^+(CH_2CH_3)_3 \ldots NO_3^- + Cl^- \qquad (2.8)$$

Most of the studies on amine grafting of biological materials followed the method employed by Orlando et al. (2002a). Agricultural wastes such as rice husk, sugarcane bagasse, coconut husk, pine bark, persimmon tea leaf, moringa oleifera and laun sawdust were amine modified by this method to produce anion exchangers and tested for their ability to remove nitrate. The Langmuir nitrate adsorption capacity for the amine grafted materials was in the range of 14.2-16.7 mg N/g and this capacity was reported to be approximately equal to that of the commercial anion exchange resin Amberlite IRA 900 (16.7 mg N/g). Orlando et al. (2002a) asserted that the affinity order of amine grafted sugar cane bagasse for nitrate was as follows: $SO_4^{2-} > Br^- > NO_3^- > NO_2^- > F^- > PO_4^{3-}$. The adsorbed nitrate can be desorbed from these amine grafted adsorbents and the adsorbent can be reused several times to remove nitrate (Katal et al., 2012).

2.6.8.4. Organically modified aluminosilicate minerals and carbon electrodes

Alumino silicate minerals such as zeolites, smectites, hallosites, and kaolinites are cheap, negatively charged materials, but negligible adsorption capacities for anions. Therefore these materials were surface modified by using cationic organic loading and tested for nitrate removal in several studies. Zeolites are surface modified and have been used to remove pollutants in water treatment. While zeolite materials were surface modified by surfactants, a monolayer or ‘hemimicelle’ formed at the solid-solution interface (Haggerty and Bowman, 1994; Zhan et al., 2011). The negatively charged hydrophobic tails of the surfactant attached with the zeolite material (hydrophobic bonding by Van der Waals forces) and the positively charged hydrophilic heads of the surfactant attract anions such as nitrate. Subsequently these are removed from the solution (Guan et al., 2010; Haggerty and Bowman, 1994; Schick et al., 2010).

In most studies, zeolite, halloysite and smectite were surface modified by Hexadecyltrimethylammonium (HDTMA) and used for nitrate removal (Haggerty and Bowman, 1994; Li and Bowman, 2001; Xi et al., 2010). HDTMA is a major cationic surfactant with tetrasubstituted ammonium cation, permanently charged pentavalent nitrogen and a long straight alkyl chain. Cetylpyridinium bromide (CPB) is another cationic surfactant that has been used and tested for nitrate removal (Zhan et al., 2011). Eq 2.9 shows the nitrate adsorption on CPB modified zeolite:

$$\text{Zeolite-CP-CP}^{+}\ldots\text{Br}^{-} + \text{NO}_3^{-} \rightarrow \text{Zeolite-CP-CP}^{+}\ldots..\text{NO}_3^{-} + \text{Br}^{-} \qquad (2.9)$$

2.6.8.5. Heat treatment

Heat treatment is a physical treatment used to increase the adsorption capacity by increasing the adsorbents’ surface area and porosity. By heating, the surface area and porosity increase due to the release of volatile matter and/or decomposable compounds occupied in the adsorbent as gasses. In this way more adsorption sites are exposed to more adsorbates from the solution. For example, heat treatment of carbon increased the removal of dissolved organic compounds (Gupta et al., 2009; Yin et al., 2007). Socías-Viciana et al. (2008) concluded that the nitrate adsorption by LDH increased from 62 to 105 mg/g when temperature rose from 550 ^{0}C to 850 ^{0}C. However, the specific surface area decreased while the temperature increased from 650 ^{0}C to 850 ^{0}C due to the formation of spinal-like crystalline oxides. They concluded that the increase in adsorption capacity observed above 550 ^{0}C was due to the CO_3^{2-} decomposed into CO_2 and nitrate adsorbed on the sites of CO_3^{2-} occupied earlier. Unfortunately, heat treatment is not a cost-effective method and the adsorption capacity increment is not high compared to chemical modification methods.

Table 2.10. Comparison of nitrate adsorption capacities of surface modified and unmodified adsorbents

Adsorbent	Modification	Experimental conditions (Nitrate concentration -mg N/L)	Unmodified adsorbent Langmuir adsorption capacity (mg N/g)	Modified adsorbent Langmuir adsorption capacity (mg N/g)	Remarks	Reference
Activated carbon cloth	Protonation (H_2SO_4, HCl)	Batch, pH 7, 25 ^{0}C, 26 mg/L	5.4	28.4	Adsorption capacity increased due to the acid treatment, which created additional positive charges on the surface of the adsorbent. By this, more nitrate ions removed by strong electrostatic attraction.	Afkhami et al., 2007
Red mud	Protonation (HCl)	Batch pH 6, Room temp, 1.1-56.4 mg /L, 4 g adsorbent /L,	26	82	Specific surface area was increased from 14.2 m^2/g to 20.7 m^2/g. ZPC increased from pH 8.2 to 8.5 indicates the increment of surface positive charges	Cengeloglu et al., 2006
Chitosan beads	Protonation ($NaHSO_4$), cross-linked (CL), non CL	Batch, pH 5, 30 ^{0}C, 5.6-226 mg/L, 20 g adsorbent /L	CL 20, non -CL 18	CL 21, non -CL-18	Zeta potential increased from 30.1 mV to 38.5 mV at pH 5. Protonation increased the surface positive charges and more nitrate adsorbed by the electrostatic attraction.	Chatterjee et al., 2009

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir ad. capacity	Modified Langmuir ad. Capacity	Remarks	Reference
Wheat straw	Amine grafting	Batch, pH 6.8, 23 ^{0}C, 11.3 -113 mg/L, 4 g adsorbent/L	2	28.2	Zeta potential value increased from -35 mV to + 40 mV This indicates that, surface positive charges increased after amine grafting thereby more nitrate removed by electrostatic attraction	Yu et al., 2007
Polypropylene	Amine grafting	Batch, pH 7.2, Room temp, 45.2 mg/L	Amount adsorbed 2.9	Amount adsorbed 5-5.2	The adsorption increased due to the increase in polarity of the film as a result of quaternerisation.	Taleb et al., 2008
Sugarcane baggase-Biochar	Amine grafting	Batch, pH 3, 22^{0}C, 0.2-22.6 mg/L, 2 g adsorbent/L,	0.5	6.4	Surface area of bio char - 41.67 m^2/g ZPC of biochar - pH 5.35 Nitrate adsorption increased due to the increment of net positive charges on the surface of the adsorbent after amine grafting and at low pH (3) the positive charges were higher.	Hafshejani et al., 2016

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir ad. capacity	Modified Langmuir ad. Capacity	Remarks	Reference
Sugarcane bagasse (BG), Rice hull (RH)	Amine grafting	Batch, 30 ^{0}C, 0.2-6.8 mg/L, 2 g adsorbent/L	-	19.6 (BG), 18.3 (RH)	Amine grafting increased the surface positive charges of the materials and nitrate removed by the electrostatic attraction	Orlando et al., 2002a
Wheat straw	Amine grafting	Column, pH 5.1, room temp, 45.2 mg/L, Bed height -1 cm, 5 ml/min	negligible	Column adsorption- 19.6 mg/g	Zeta potential at pH range 2-12 -WS 2.2 mV to -46.3 mV, AG WS- +35.3 mV to -7 mV. This indicates that the nitrate adsorption increased by the additional positive charges of the adsorbent after amine grafting and higher nitrate removal achieved by the electrostatic attraction.	Xing et al., 2011
Coconut shell powder (CSP)	Ammonium quaternary salt	Batch, pH 2.5, 25 ^{0}C, 4.5-225.8 mg/L, 10 g adsorbent/L,	negligible	7.7	BET surface area increased from 218 m^2/g to 221 m^2/g ZPC of the modified CSP was around pH 4.7 and this indicates a sufficient positive charge on adsorbent surface for the nitrate adsorption	De Lima et al., 2012

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir ad. capacity	Modified Langmuir ad. Capacity	Remarks	Reference
Rice hull, Saw dust, coconut husk, moringa hull, rice hull, pine bark, sugar cane baggasse	Amine grafting	Batch, 30 ^{0}C, 0.2-0.23 mg/L, 2 g adsorbent/L	-	10.6-16.7	Amine grafting increased the surface positive charges of the materials and nitrate removed by the electrostatic attraction	Orlando et al., 2002b
Zeolite	Metal impregnation (Fe)	Batch, pH 5.5, 25 ^{0}C, 26 mg/l, 2- 10 g adsorbent/L,	0.45	5.2	BET surface area of zero-valent iron modified zeolite (Ze-nZVI) and unmodified zeolite (Ze) were 49.7 m^2/g and 17.8 m^2/g. Nitrate removal occurred by the adsorption on the zero valent iron nano particles' surface and by redox reaction	Sepehri et al., 2014

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir ad. capacity	Modified Langmuir ad. Capacity	Remarks	Reference
Activated carbon	Metal impregnation (Fe^{3+})	Batch, pH 5.5, 25 ^{0}C, 35 ^{0}C, 45 ^{0}C, 33.9 mg/L, 6.5 g adsorbent/L	2.2-2.5	3.9-4.0	Fe_2O_3 nanoparticles coated on activated carbon and improved nitrate removal BET surface area increased from 922 m^2/g to 1012 m^2/g after metal impregnation	Mehrabi et al., 2015
Granular AC (Lignite)	Metal impregnation $ZnCl_2$	Batch, 25 ^{0}C, 1.1-33.9 mg /L, 2 g adsorbent/L	2.25	2.7-3.4	Surface area, pore volume reduced due to blockage of pores by Zn surface complex. However the Zn^{2+} ions increased the surface positive charges and removed the nitrate by electrostatic attraction.	Khan et al., 2011
Clinoptiloli	Metal impregnation (Fe^{3+}, Mn^{4+}, Mg^{2+})	Batch, 25 ^{0}C, 23 mg/L, 10-40 g adsorbent/L	Normal adsorption - 0.6	Norma adsorption - FeZ- 1.3 MnZ ~ 0.9 Mg Z ~ 0.8	Specific surface areas were 30.9, 24.4, 17.5, and 28.1 m^2/g for Zeolite, MgZ, MnZ, and FeZ, respectively. BET surface area reduced due to the formation of oxide particles at the surface and blocked the pores. However the metal ions increased the nitrate adsorption.	Pavlovic et al., 2014

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir ad. capacity	Modified Langmuir ad. Capacity	Remarks	Reference
Activated carbon (coconut coir pith)	Metal impregnation $ZnCl_2$	Batch, pH 3, 35 ^{0}C, 1.1-45.2 mg N/L	Negligible	2.3	Surface area increased from 167 m^2/g to 910 m^2/g Pore volume increased from 0.122 mL/g to 0.363 mL/g, ZPC 3.2 . Hence adsorption can occur due to chemisorption such as surface complex formation of nitrate with Zn^{2+} ion.	Namasivayam and Sangeetha, 2005,2008
Granular AC (Coconut)	Metal impregnation $ZnCl_2$	Batch, pH 5.5, 25 ^{0}C, 1.1-45.2 mg N /L, 2 g adsorbent/L	0.4	2.3	Surface area reduced from 1144 to 893 m^2/g due to the formation of zinc oxide, which significantly covered the pore openings. However adsorption increased due to the formation of micropores by ZnO and the ZnO acted as adsorbent. The adsorption incresed due to the increment of surafce positive charges.	Bhatnagar et al., 2008b

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir Ad. capacity	Modified Langmuir ads. capacity	Remarks	Reference
Kaolinite	Surfactant modification HDTMA-Br	Batch, 25 ^{0}C, 0-10 mM N, 40 g adsorbent/L	0.002	0.34	Nitrate adsorption increased due to the surfactant loading which increased the surface positive charges	Li and Bowman, 2001
Carbon electrode	Anion exchange resin (BHP55)	Continuous flow, room temp, 2 mM N, 50 ml/min	116 mg/m^2	266 mg/m^2	Nitrate removal increased by the coating of ion exchange resin on the surface of the electrode.	Kim and Choi, 2012)
Zeolite	Surfactant modification (HDTMA-Br)	Batch, 25 ^{0}C, 2-20 mM N, 100 g adsorbent/L,	< 0.02	CEC 100%- 0.9; 150%- 1.5; 200%- 1.3	Nitrate adsorption increased due to the surfactant loading which increased the surface positive charges	Li, 2003

Adsorbent	Modification	Exp. conditions	Unmod. Langmuir Ad. capacity	Modified Langmuir ads. capacity	Remarks	Reference
LDH (Zn-Al-Cl)	Heat treatment (Calcinattion temperature- 100, 150, 200, 300, 400 for 8h)	Batch, 25 ^{0}C, 2.26-22.6 mg N/L, 1-8 g adsorbent/L,	% removal 67.8	% removal 100-200 ^{0}C - 71-76, 300-400 ^{0}C - 42-62 Langmuir 200 ^{0}C- 40	Specific surface area 200 ^{0}C- 187, 600 ^{0}C- 202 and 800 ^{0}C - 212 m^2/g. Though specific surface area increased with increase in temperature, the nitrate removal reduced after 200 ^{0}C due to the structural deformation.	Islam and Patel, 2010
LDH (Ca-Al-Cl)	Heat treatment (100, 150, 200, 300, 400 for 8h)	Batch, 25 ^{0}C, 2.26-22.6 mg N/L, 1-8 g adsorbent/ L	% removal 67.8	% removal 100-200 ^{0}C - 71-76, 300-400 ^{0}C - 42-62	Adsorption increased due to the increment of specific surface area, which increased with increase in calcination temperature. Though the nitrate removal reduced after 200 ^{0}C due to the structural deformation. -	Islam and Patel, 2011

2.7. Types of adsorption experiments

Generally, there are two types of adsorption experiments that can be conducted to understand the adsorption process: firstly, static batch adsorption experiment; and secondly, dynamic column or submerged membrane hybrid system adsorption experiments. Batch adsorption experiments are easy to conduct and the results can be obtained in a short period of time. Batch adsorption is a closed system and can be generally divided into equilibrium isotherm and kinetics. The equilibrium adsorption experiment is conducted in a set of containers with different adsorbent dosages and known nitrate concentration in water for a period of time until equilibrium is attained (Nur et al., 2012). Alternatively, instead of different doses of adsorbent, one dose of adsorbent and different concentration of nitrate can be utilised (Yu et al., 2007). The adsorption kinetics is tested with a desired amount of adsorbent and a known concentration of nitrate at increasing time intervals. In all the above experiments the supernatant solution after the adsorption process is tested to determine the amount of nitrate adsorbed.

The equilibrium adsorption data is commonly examined using Langmuir, Freundlich, Temkin, Redlich Peterson and Langmuir-Freundlich models. The maximum adsorption capacity of the adsorbent can be obtained from the model which best fits the data. The values obtained can be compared with other adsorbents to determine the most efficient adsorbent. The pseudo-first order, pseudo-second order, Elovich and diffusion models have been used to explain adsorption kinetics. The models and their description are presented in section 2.8.

The column/dynamic adsorption process is used for treating large volumes of water. In the column, the adsorbents are fixed at a desired bed height and it is operated with the desired flow rate of waste water in the up-flow mode or down- flow mode. The removal of nitrate in the column adsorption process is highly efficient compared to batch adsorption and the results are directly applicable to real treatment conditions (Akratanakul et al., 1983; Faust and Aly, 1987; Tor et al., 2009). The effluent solution in the column experiment is collected at increasing times. When the effluent water concentration from the column reaches the influent concentration, the adsorbent is assumed to be saturated with nitrate.

In the down flow mode column adsorption process, the top layer of the adsorbent starts to adsorb the adsorbate first until it reaches saturation level and then the next layer which is called mass transfer zone adsorbs the solute. With time the mass transfer zone moves down to the bottom and this period is called the break through time. Subsequently, the effluent concentration starts to increase and reaches the concentration of the influent. The graph of C_t/C_0 Vs Time (C_t- concentration of effluent at time t, C_0 –influent concentration) produces an S-shaped curve whose characteristics depend on the influent flow rate, concentration of adsorbate and the volume capacity of the adsorbent (column height * internal area).

Nur et al. (2015) conducted a nitrate removal experiment using Purolite A520E in batch and fixed-bed column with a nitrate concentration of 20 mg N/L. Fixed-bed column experiments were conducted with 12 cm resin bed height and the influent filtration velocities were 2.5 and 5 m/h. The resin saturation occurred at 23 h (958 bed volume) and 52 h (1083 bed volume) for the 5 and 2.5 m/h filtration velocities, respectively. Shorter saturation time for the higher filtration velocity is probably because a large amount of nitrate entered the column in a short period of time (higher loading rate) and was adsorbed by the resin in that retention time. Hence it was saturated quickly. The manually calculated adsorption capacities from the breakthrough curves were 13.5 and 12.0 mg N/g for 2.5 and 5m/h filtration velocities, respectively.

Hekmatzadeh et al. (2012) carried out a fixed-bed column experiment using IND NSSR resin with different initial nitrate concentrations of 30, 20.2 and 13.6 mg N/L with the flow rate of 2.1 L/h and 20.5 cm bed height. The break brthrough time and the treated volume of water decreased with the increase in influent concentration. The breakthrough time was 36.2, 53.1 and 82.9 h and breakthrough bed volumes were 76.7, 111.6 and 173.5 for the initial nitrate concentrations of 30, 20.2 and 13.6 mg N/L, respectively. However, the adsorption capacity was virtually the same for all nitrate concentrations.

2.7.1. Submerged Membrane Adsorption Hybrid System (SMAHS)

Another dynamic adsorption system is known as the submerged membrane adsorption hybrid system and – as in the column studies - it is used to remove nitrate from water continuously. The membrane adsorption hybrid system is a developing technology which has been used to obtain high quality water. Microfiltration (MF) or ultrafiltration (UF) membranes are used to treat the water coupled with adsorption technology. Though the MF or UF does not remove the nitrate, they can both remove suspended solids, colloids, micro-organisms and micro-particles from the water and retain the adsorbents in the reactor (Guo et al., 2005). Here the adsorbents are kept continuously in suspension via aeration and when the adsorbent reaches saturation with the adsorbate, a percentage of the adsorbent is replaced to provide new adsorption sites, enabling the quality of effluent water to be maintained. The percentages of adsorbent and frequency of replacement are determined by measuring the effluent quality.

The MF membrane used in SMAHS has a pore size ranging from 0.01 μm to 20 μm and serves to separate the particle diameter greater than 0.01 μm. The ultra-filtration membrane has a pore size in the 5 nm to 50 nm range and is used to separate macromolecules with a molecular weight ranging from 10^4 to 10^6 Daltons. The membrane resistance to filtration in the UF is higher than the MF membrane, and therefore higher pressure is required in the UF.

2.7.2. Membrane fouling

The main concern of membrane filtration is the problem of fouling. This issue has several causes, such as water condition, membrane characteristics, and operating conditions. The main cause of fouling is the condition of the water and it occurs due to inorganic precipitates (i.e. metal hydroxides), colloids (i.e. clay minerals, colloidal silica, Fe, Al, Mn oxides, organic colloids) and micro-organisms (i.e. bacteria, algae). These foulants accumulate on the surface and in the pores of the membrane and cause reversible and irreversible fouling. Transmembrane pressure reveals the membrane fouling behaviour that occurs while an operation is underway. Transmembrane pressure increases due to the fouling that is produced by continuous membrane use (Vigneswaran et al., 2003).

When adsorption and membrane filtration are integrated into a single system this has several advantages. In this integrated system, the adsorbents are in suspension due to the process of aeration and this reduces membrane fouling through abrasion and membrane scouring. Consequently, the membrane's operation time and total usable life increase, which in turn helps to minimise operation and maintenance costs. Another advantage is that the frequency of membrane cleaning decreases and the membrane can be cleaned with less chemicals. It is evident that membrane fouling strongly depends on water conditions, adsorbent dosages, adsorption capacity, and solution chemistry (Gao et al., 2011).

2.7.3. Aeration

Aeration is one strategy to reduce membrane fouling and provide a hydraulic distribution. Aeration helps to keep the adsorbents in suspension, thereby the adsorbents move to all parts of the solution and adsorb the nitrate at all adsorption sites. The energy costs required for the aeration process are high and to use aeration efficiently it must operate close to the membrane (Meng et al., 2008; Wicaksana et al., 2006).

2.7.4. Membrane cleaning

The membrane is cleaned by physical or chemical methods. Physical cleaning is a common practice in submerged membrane systems and it serves to periodically backflush the membrane. Here, the permeate flux is pumped back through the membrane into the feed tank to remove any solid deposits (Bouhabila et al., 2001). However, if the pores are blocked by inorganic materials deposited on the membrane surface, the back flush practice is ineffective (Yoon et al., 1999). Chemical cleaning is also important to retain the high performance of the membrane and may include the following steps: (i) chemically enhanced back wash; (ii) maintenance cleaning with higher chemical concentration; and (iii) intensive/ recovery chemical cleaning (Le-Clech et al., 2006).

2.7.5. Applications of SMAHS

Most SMAHS studies have mainly focused on the removal of organic carbon and metals (Bryjak et al., 2008), phosphate (Johir et al., 2016), colour, and reactive dyes (Lee et al., 2006), and organic micropollutants (Shanmuganathan et al., 2015b). It appears that no studies have yet been reported on nitrate removal using SMAHS. The length of treatment time varied in these SMAHS studies with some experiments conducted on a short-term (6 h) (Shanmuganathan et al., 2015b) and some on long-term

(14 days) basis with partial replacement of adsorbents (Shanmuganathan et al., 2015a). The partial replacement of adsorbent helps to prevent cake formation on the membrane surface, resulting in reduced transmembrane pressure (Smith and Vigneswaran, 2009) as well as providing fresh adsorption sites for the removal of additional nitrate.

2.8. Modelling adsorption data

2.8.1. Batch adsorption models

The data obtained from the batch equilibrium adsorption experiments are generally investigated using the Langmuir, Freundlich, Temkin, and Sips (Langmuir-Freundlich) models. Of these, the Langmuir and Freundlich models are the most common ones used. The pseudo-first order, pseudo-second order, Elovich, and diffusion models have also been commonly employed to describe batch adsorption kinetics data.

2.8.1.1. Equilibrium adsorption models

2.8.1.1.1. Langmuir model

The model was developed by Langmuir (1918) to evaluate the absorption of gas and now it is widely used for ion adsorption from solution (Faust and Aly, 1987). The Langmuir adsorption model was developed with the assumption that one molecule is adsorbed at each adsorbent's surface site and the modules do not interact with each other. In other words, all the adsorption sites have the same affinity for the adsorbate, and thus the adsorption sites are homogeneous. The molecules or ions continue to adsorb until they form a monolayer to saturate the homogeneous adsorption sites. The Langmuir model equation for nitrate adsorption is:

$$Q_e = \frac{Q_{max}.K_L.C_e}{(1+K_L.C_e)} \tag{2.10}$$

Where, Q_{max} is the maximum amount of the nitrate-N adsorbed per unit weight of the adsorbent (mg/g), K_L is a constant related to the affinity of the binding sites (L/mg), Q_e (mg N/g) and C_e (mg /L) are the amount of nitrate adsorbed per unit mass of adsorbent and the nitrate concentration in solution at equilibrium, respectively.

Equation 2.11 can be rearranged into a linear form as shown below,

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}.K_L} + \frac{C_e}{Q_{max}} \qquad (2.11)$$

Or $$\frac{1}{Q_e} = \frac{1}{Q_{max}.K_L}.\frac{1}{C_e} + \frac{1}{Q_{max}} \qquad (2.12)$$

From the slope of a plot of C_e/Q_e Vs C_e, Q_{max} can be calculated using Eq 2.11. Alternatively, from the intercept of the plot $1/Q_e$ Vs $1/C_e$, Q_{max} can be calculated using Eq 2.12. Studies using this model determine the adsorption capacity of nitrate on several adsorbents are listed in Table 2.10.

2.8.1.1.2. Freundlich model

This model is an empirical model used to explain the heterogeneous adsorption system. That is the adsorption sites have different affinities towards the adsorbate. It can be expressed as (Namasivayam and Sangeetha, 2005),

$$Q_e = K_f.{C_e}^{1/n} \qquad (2.13)$$

Equation 2.13 can be rearranged to a linear form shown below,

$$\ln Q_e = \ln K_f + \frac{1}{n}\ln C_e \qquad (2.14)$$

Where Q_e is the equilibrium amount of adsorbed nitrate-N (mg/g) and C_e is the equilibrium concentration of nitrate (mg/L). K_f (mg/g)(L/mg)$^{1/n}$ and n are the Freundlich constants. K_f is related to the adsorption capacity of the adsorbent. The Freundlich model is widely used for nitrate adsorption and in some experiments this particular model fitted better than the Langmuir model (Yu et al., 2007).

2.8.1.1.3. Tempkin model

The Tempkin model is another empirical model used to describe the adsorption data (Aharoni and Ungarish, 1977). It assumes that the heat of adsorption of all molecules in the adsorbent layer will decrease linearly rather than in a logarithmic pattern with coverage (Aharoni and Ungarish, 1977). The model equation applied to nitrate is as follows:

$$Q_e = \frac{RT}{b}\ln(A_T C_e) \tag{2.15}$$

$$Q_e = \frac{RT}{b}\ln(A_T) + \frac{RT}{b}\ln(C_e) \tag{2.16}$$

$$\frac{RT}{b} = B \tag{2.17}$$

Where, Q_e is the equilibrium amount of nitrate-N (mg/g); C_e = equilibrium concentration of nitrate-N (mg/L); A_T = Tempkin isotherm equilibrium binding constant (L/g); b = Tempkin isotherm constant; R= universal gas constant (8.314 J/mol/K); T = Temperature at 298 K; and B = Constant related to heat of adsorption (J/mol).

This model can be linearised as follows,

$$Q_e = B\ln(A_T) + B\ln(C_e) \tag{2.18}$$

In several nitrate removal studies the Tempkin model was used to explain the batch experimental data. For example, Mehrabi et al., 2015 carried out a nitrate removal study with activated carbon (AC) and Fe_2O_3 nanoparticles modified activated carbon

(Fe-AC). The Tempkin model fitted well with high R^2 values (0.9802- 0.9960) for all the temperatures better than the Freundlich model (R^2 = 0.9422- 0.9778) for both AC and Fe-AC. Furthermore, the Tempkin model suggests that if the nitrate concentration in the solution was not very high or low, the adsorption heat of the entire nitrate in the layer will decrease linearly rather than logarithmic with (Mehrabi et al., 2015).

2.8.1.1.4. Sips model

The Sips model (Sips, 1948) is another empirical model developed by combining the Langmuir and Freundlich isotherm models. This model reduces to Freundlich isotherm model at low concentration of adsorbate and reduces to the Langmuir adsorption at high concentration of adsorbate. The equation of the model applied to nitrate is given below,

$$q = \frac{q_m b C_e^{1/n}}{1 + b C_e^{1/n}} \qquad (2.19)$$

Where C_e = equilibrium concentration of nitrate-N (mg /L); q = amount of nitrate-N adsorbed per unit mass of adsorbent (mg/g); q_m = maximum amount of nitrate-N adsorbed per unit mass of adsorbent (mg/g); b = Langmuir and Sips affinity constant (L/mg) and n = Freundlich and Sips constant.

The Sips model showed a better fit than the other isotherm models in some nitrate removal studies. For example, batch equilibrium adsorption data for nitrate adsorption on chitosan hydrogel beads (Chatterjee et al., 2009) fitted to the Langmuir, Freundlich and Sips models. However, the Sips model showed greater R^2 (0.999) values than the Langmuir (R^2 = 0.972-0.980) and Freundlich (R^2 = 0.941-0.949) models for all different temperature conditions of 20, 30, 40, and 50 ^{0}C studied. In this experiment, the Sips model constant n was quite close to 1 and this indicated that the Sips model reduced to the Langmuir model. This implies that the adsorption occurred on the chitosan gel beads surface due to the monolayer coverage.

2.8.1.2. Kinetic adsorption models

2.6.1.2.1. Pseudo-first order kinetics model

The equation for the pseudo-first order kinetic model is expressed below (Nur et al., 2014b):

$$\frac{dq_t}{dt} = k_1(\,q_e - q_t) \qquad (2.20)$$

Where, q_e = amount of nitrate-N adsorbed at equilibrium (mg /g); q_t = amount of nitrate-N adsorbed at time; t (min) (mg /g); and k_1 = rate constant of pseudo-first order adsorption (1/min). In most of the nitrate adsorption kinetics experiments the pseudo-first order model was one of the kinetic models used and the model's q_e values perfectly matched the experimental q_e values. For, example Hekmatzadeh et al. (2012) conducted a nitrate adsorption study using IND NSSR anion exchange resin and reported that the pseudo-first order model fitted well to the data with R^2 values greater than 0.98 and the q_e values were almost equal to the experimental q_e values.

2.8.1.2.2. Pseudo-second order kinetics model

The pseudo-second order kinetic model is described by the following equation (Nur et al., 2014b). The good fit of the data to this model suggests that the adsorption may occur through the process of chemisorption (Tor et al., 2009; Yan et al., 2010):

$$\frac{dq_t}{dt} = k_2.(q_e - q_t)^2 \qquad (2.21)$$

where, k_2 = equilibrium rate constant of pseudo-second order adsorption (g /mg.min). The integrated form of the equation is given below after applying the boundary conditions as $q_t = 0$ at $t = 0$ and $q_t = qt$ at $t = t$,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2.22}$$

The pseudo-second order model also fitted well with the experimental data in many nitrate removal studies. In some analyses this model fitted better than the pseudo-first order model. For example, in the study by Öztürk and Bektaş (2004) concerning activated carbon (AC) and sepiolite, activated sepiolite adsorption kinetics results fitted well to the pseudo-second order model with R^2 value of 0.999 for all 3 adsorbents whereas the pseudo-first order did not fit well ($R^2 = 0.2651$). The model's q_e values (4.0, 3.32, and 9.81 for AC, sepiolite, and activated sepiolite, respectively) were also approximately equal to the experimental q_e values (4.14, 3.46, and 9.8 for AC, sepiolite, and activated sepiolite, respectively) for the pseudo-second order model.

2.8.1.2.3. Elovich model

The Elovich model is used to express the adsorption process when the adsorbate ions and adsorbent surface sites interact chemically through a second order mechanism (Zhang and Stanforth, 2005). This model is suitable for the kinetics concerning adsorption of adsorbates on heterogeneous surfaces with variation in adsorption energies (Özacar and Şengil, 2005; Riahi et al., 2013):

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{2.23}$$

This equation can be linearised as follows,

$$q_t = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln(t) \qquad (2.24)$$

Where, α = initial adsorption rate (mg/g min), β = related to extent of surface coverage and activation energy for chemisorption (g/mg).

Chabani et al. (2007) conducted a nitrate adsorption experiment using IRA 400 resin with different conditions of agitation speed, temperature, and pH. In most of the experimental conditions the pseudo-first order and pseudo-second order models fitted better than the Elovich model. However, in some conditions such as at low pH (pH 3.17), and at high agitation speed (800 and 1000 rpm), the Elovich model fitted better than the other models.

2.8.1.2.4. Homogeneous Surface Diffusion Model (HSDM)

HSDM is used to study the adsorption kinetics process which comprises 3 steps: (i) the adsorbate diffuses through a stagnant liquid film layer surrounding the adsorbent particle; (ii) the adsorbate adsorbs from the liquid phase onto the outer surface of the adsorbent; and (iii) the adsorbate diffuses along the inner surface of the adsorbent particles until it reaches its adsorption site. The model equation is as follows:

$$\frac{\partial q_{td}}{\partial t} = D_s\left(\frac{\partial^2 q_{td}}{\partial r^2} + \frac{2}{r}\frac{\partial q_{td}}{\partial r}\right) \qquad (2.25)$$

Initial and boundary conditions for the process are shown here:

$t = 0; \quad q_{td} = 0$

$r = 0; \quad \frac{\partial q_{td}}{\partial r} = 0$

$r = r_p; \quad D_s\rho_p\frac{\partial q_{td}}{\partial r} = k_f(C - C_s)$

where, D_s = surface diffusion coefficient (m^2/s), q_{td} = nitrate-N concentration in the solid phase (mg /L), C = nitrate-N concentration in the liquid phase (mg /L), C_s = liquid phase concentration at adsorbent surface (mg N/L), r = radial distance from the centre of adsorbent particle (m), k_f = external mass transfer coefficient (m/s), and ρ_p = particle density (kg/m^3).

The orthogonal collocation method (OCM), the variable coefficient ordinary differential equation solver (VODE) and the Nelder–Mead simplex methods are used to calculate D_s and k_f in Eq 2.25 (Brown et al., 1989; Matulionytė et al., 2007; Villadsen and Stewart, 1967). Furthermore, the Langmuir isotherm model was employed to represent the adsorbate's equilibrium relationship at the adsorbent–adsorbate interface. The D_s parameter depends on the concentration of adsorbate and the k_f relied on the agitation speed of the batch system (Ahmad et al., 2012).

Nur et al. (2015) carried out a batch experiment on nitrate adsorption using Purolite A520E with an initial nitrate concentration of 20 mg N/L at 120 rpm shaking speed. They reported that the HSDM fitted well to the adsorption kinetics with the R^2 value of 0.99. In this experiment, surface diffusion coefficient D_s was higher for a smaller resin concentration than for a larger resin concentration. This confirmed that D_s greatly depends on the equilibrium concentration.

2.8.2. Column adsorption models

2.8.2.1. Thomas model

The Thomas (1944) is a frequently used adsorption model to study the adsorption capacity in column adsorption experiments and predict the breakthrough curve. This model assumes the Langmuir isotherm for equilibrium and second order reversible reaction for kinetics (Aksu and Gönen, 2004). This model is theoretically suitable for adsorption processes where the external and internal diffusion limitations are absent (Aksu and Gönen, 2004; Padmesh et al., 2005). The model when applied to nitrate is depicted in the following equation:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_T.q_0.m_c}{Q} - k_T.c_0.t \qquad (2.26)$$

where, k_T is the Thomas rate constant (L/min.mg), q_0 is the maximum solid-phase concentration of the nitrate-N (mg/g), m_c is the mass of adsorbent in the column (g), and Q is the volumetric flow rate (L/min). The values for k_T and q_o are determined from the slope and intercept, respectively, of a linear plot of ln (C_o/C_t – 1) vs t.

Nur et al. (2015) conducted a column experiment for nitrate removal using Purolite A520E with two filtration velocities (2.5 and 5 m/h). They found that the Thomas model adsorption capacities were 9.69 and 8.22 mg N/g for the velocities 2.5 m/h and 5 m/h, respectively. These values were not too different from the calculated values obtained from the breakthrough curves (13.5 and 12.0 mg N/g for 2.5 and 5 m/h, respectively).

2.8.2.2. Bohart- Adams model

The Bohart and Adams (1920) describes the relationship between C_t / C_o and time and used to describe the initial part of the breakthrough curve. This model is well suited to the initial part of the breakthrough curve. The equation of the model is presented below:

$$\ln\frac{C_t}{C_0} = k_{AB}C_0.t - k_{AB}.N_0.\frac{Z}{F} \qquad (2.27)$$

where, C_0 and C_t (mg/L) are the influent and effluent nitrate-N concentrations, respectively. k_{AB} (L /mg .min) is the kinetic constant, F (cm/min) is the linear velocity calculated by dividing the flow rate by the column section area, Z (cm) is the bed depth of column and N_0 (mg/L) is the saturation concentration. The values of N_0 and k_{AB} can be obtained from the intercept and slope of the linear plot of ln (C_t /C_0) against time (t).

Xu et al. (2013) did a fixed-bed column experiment on nitrate removal using an amine grafted wheat straw sample and fitted data to the Adam-Bohart model. This model fitted well to the data with R^2 values of 0.935 to 0.972. The N_0 value decreased when the bed depth increased. The k_{AB} increased with increasing flow rate, which indicated that the overall system kinetics was controlled by external mass transfer in the initial part of the column adsorption.

2.8.2.3. Yoon- Nelson model

Yoon and Nelson (1984) developed a model based on the assumption that the rate of decrease in the probability of adsorption of adsorbate is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The linearised Yoon-Nelson model for a single component system is expressed as,

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}\,.\,t - \tau.\,k_{YN} \qquad (2.28)$$

where k_{YN} (L min^{-1}) is the rate velocity constant, and τ (min) is the time required for 50% nitrate-N breakthrough. From the intercept and slope of the plot of a linear plot of ln [C_t/ (C_0 −C_t)] against sampling time (t) the values for τ and k_{YN} can be determined.

No studies have been reported on this model’s application to nitrate removal but the model was used to assess other pollutants’ removal. For example, Ahmad and Hameed (2010) used it for azo dye removal in fixed-bed column and found that - with increasing flow rate and increasing inlet concentration - the value of k_{YN} increased and τ decreased. However, with increasing bed height, k_{YN} decreased and τ increased.

2.8.2.4. Plug-flow model

The plug flow model is a dynamic model used to study the behaviour of fixed-bed and fluidised-bed adsorbers (Nahm et al., 2012; Shanmuganathan et al., 2014). This model was developed using the non-linear adsorption isotherm, mass balance in the solid and liquid phases, and mass transfer resistance through the adsorbent. To simplify the calculations of diffusional mass transfer inside the adsorbent, linear driving force (LDF) model, HSDM and Langmuir isotherm equations are used.

The plug-flow model for fluidised bed (Eq 2.29) is derived using the following assumptions: (i) the system followed plug-flow conditions without axial dispersion and (ii) the adsorbents in the bed are uniformly distributed. Here HSDM model is used to solve the equation. The surface diffusion coefficient D_s is determined from the batch kinetics and the mass transfer coefficient k_f is determined using the Nelder-Mead simplex method. The fixed-bed plug-flow model (Eq 2.30) parameters, axial dispersion coefficient, D_L and film mass transfer coefficient, k_f can be calculated using empirical correlations given by Eq 2.31 (Chung and Wen, 1968) and Eq 2.32 (Luna et al., 2011; Wakao and Funazkri, 1978). Additionally, the diffusion coefficient (D_s) of the homogeneous surface diffusion model (HSDM) can be determined by matching the simulation results with the data obtained in experimental adsorption breakthrough curve. In order to numerically solve the axially dispersed plug-flow and HSDM equations, the Nelder-Mead simplex method (Nelder and Mead, 1965), orthogonal collocation method (OCM) (Villadsen and Stewart, 1967) and double variable ordinary equation (DVODE) program are used.

Fluidised bed model for nitrate removal is as follows (Shanmuganathan et al., 2014):

$$\frac{\partial c}{\partial t} = -\frac{v}{\varepsilon_r}\frac{\partial c}{\partial z} - \frac{1-\varepsilon_r}{\varepsilon_r}\rho_p\frac{\partial q}{\partial t} \qquad (2.29)$$

$$\varepsilon_r = 1 - (1-\varepsilon_{mf})\cdot\left(\frac{L_{mf}}{L_f}\right)$$

Initial and boundary conditions

$t = 0; \quad c = 0$

$z = 0; \quad c = c_0$

where D_s = surface diffusion coefficient (m^2/s), c = nitrate concentration in the liquid phase (mg/L), q = nitrate concentration in the solid phase (mg N/L), L_{mf} = height of the initial fluidised-bed (m), L_f = height of the fluidised-bed (m), ε_r = fluidised-bed porosity, ε_{mf} = fixed bed porosity, ρ_p = bulk density (kg/m^3), v = fluid velocity (m/s), and z = bed depth (m).

Fixed bed model for nitrate removal (Nahm et al., 2012):

$$\frac{\partial c}{\partial t} = D_L\frac{\partial^2 c}{\partial z^2} - v\frac{\partial c}{\partial z} - \frac{1-\varepsilon_b}{\varepsilon_b}\rho_p\frac{\partial q}{\partial t} \qquad (2.30)$$

Initial and boundary conditions

$0 < z < L; \quad t = 0; \quad c = 0$

$$z = 0;\ t > 0\ \ D_L\left.\frac{\partial c}{\partial z}\right|_{z=0} = -v\left(c|_{z=0^-} - c|_{z=0^+}\right)$$

$$z = L;\ t > 0\ \ \left.\frac{\partial c}{\partial z}\right|_{z=L} = 0$$

D_L = axial dispersion coefficient (m^2/s), c = nitrate concentration in the liquid phase (mg N/L), q = nitrate concentration in the solid phase (mg N/L), ϵ_B= bed porosity, ρ_p = bulk density (kg/m^3), v = fluid velocity (m/s) and z = bed depth (m)

$$\frac{D_L\rho}{\mu} = \frac{R_e}{0.2+0.11\, R_e^{0.48}} \qquad (2.31)$$

$$Sh = 2.0 + 1.1\, Sc^{\,1/3} Re^{0.6} = \frac{k_f d_p}{D_m} \qquad (2.32)$$

$$Re = \frac{\rho v D_H}{\mu} \qquad (2.33)$$

where ρ is the solution density (kg/m^3), μ is the fluid viscosity (kg/m.s), Re is the Reynold's number, Sh is the Sherwood number, Sc is the Schmidt number, d_p is the particle diameter (m), D_m is the aqueous-phase diffusivity (m^2/s), ρ is the fluid density (kg/m^3), v is the mean velocity of the fluid (m/s), D_H is the hydraulic diameter of the pipe (m) and μ is the dynamic viscosity of the fluid (N.S/m^2).

The complicated sets of partial differential equations (2.29 and 2.30) were first discretised by an orthogonal collocation method (OCM) to form a set of first order ordinary differential equations. Then they were solved using the subroutine DVODE. The DVODE program employs Gear's method with variable order and step size. Then the models were fitted to experimental data to optimised the parameters. The determined parameters were verified using the empirical equations given above.

Hekmatzadeh et al. (2012) carried out a fixed-bed column experiment for the removal of nitrate with the anion exchange resin IND NSSR. They found that the axial dispersion coefficient D_L was not influenced by the change in initial concentration from 119.4 to 60.4 mg/L and it decreased in the presence of sulphate and chloride ions.

2.9. Conclusions

Nitrate pollution occurs naturally and due to human activities that affect the ground and surface waters worldwide. The excessive application of fertiliser is a major human activity and in fact a serious problem, in that it severely increases the nitrate concentrations to dangerous levels. Other sources of nitrate pollution are animal manures, sewage leakage, industrial emissions, and municipal waste disposal on lands. Nitrate pollution affects the environment by causing eutrophication in natural water bodies. The health of people and animals is also seriously endangered by high concentrations of nitrate in drinking water. Consequently, the WHO has set the drinking water nitrate safety limit at 50 mg NO_3^-/L or 11.3 mg N/L.

Several nitrate removal technologies have been used to remove nitrate, and of these the adsorption process is considered to be the best in terms of treatment cost, design, operation and waste disposal problems. The effectiveness of the adsorption process depends on the solution pH, temperature, adsorbent dosage, nitrate concentration, co-ions concentration and adsorbent characteristics. Several adsorbents such as ion exchange resins, agricultural materials, natural and industrial materials have been investigated for nitrate removal. Of these, ion exchange resins are generally found to be of promising absorbents with high adsorption capacity, wide pH range effectiveness and reusable characteristics. Adsorbents of agricultural and industrial wastes are not expensive but their adsorption capacities are low. To increase the adsorption capacity of these wastes and other adsorbents, surface modifications techniques such as protonation, amine grafting, metal/metal oxide impregnation, or surfactant modification have been applied to a few adsorbents and tested for their ability to remove nitrate. However, these studies have not been conducted on all potential adsorbents. Considering the marked increase in adsorption capacities achieved by surface modifications of some adsorbents, it is worthwhile investigating surface modification of other forms of wastes which are available in large quantities. Additional studies are needed to investigate whether the adsorption capacities of ion exchange resins can be increased.

Most studies reported in the literature involved static batch experiments and only a few employed dynamic column experiments, which are more relevant to real-operating systems. Studies on column adsorption with mathematical modelling of the data, co-ions effect on adsorption and adsorbent regeneration are limited with reference to nitrate removal. If the adsorbent can be effectively regenerated without losing much of its adsorption capacity the operational cost and the exhausted adsorbent disposal problem can be mitigated. Membrane adsorption hybrid system is another dynamic adsorption system that has been used to remove pollutants through the combined effect of adsorption and microfiltration, and if necessary with repeated partial replacement of adsorbent. The membrane adsorption hybrid system has not been hitherto reported for nitrate removal. In this system, nitrate can be removed by the adsorbent and most other pollutants in the water can be removed by microfiltration so that high quality water can be produced.

Several models are being used to found the adsorbents characteristics /behaviour and the static and dynamic parameters of the experimental systems. For the batch experiments several models such as Langmuir, Freundlich and Sips models. Among them Langmuir model is a popular method and it is being used by lot of researchers to find out the adsorption capacity of the adsorbents and it is used to compare the adsorbents. For the column experiments Thomas model is a popular model and the Thomas model adsorption capacity is used to compare with the manually calculated adsorption capacity. The plug flow model is used to explain the dynamic behaviour of the column adsorption and the model parameters can be used to design the real treatment plant.

The electrochemical process is a cost-effective system and it can be operated in batch and dynamic modes. This process has been used to remove several pollutants such as metals, suspended solids, phosphate, fluoride, dyes, organics, ammonia, nitrite and nitrate. However, the electrochemical system combined with adsorption for nitrate removal has been reported only in one study where the electrode was coated with ion exchange resin (BHP55). The electrochemical system combined with adsorbent particles kept next to the electrode has not been reported for nitrate removal. Such a combined system may be as effective as both the adsorption and electrochemical processes, and could potentially increase the nitrate removal effectiveness compared to the individual systems.

Research on developing economical processes that are very efficient in simultaneously removing nitrate and other pollutants are needed to obtain high quality of water in the future.

CHAPTER 3

Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin

CHAPTER 3

Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies

3.1. Introduction

In Chapter 2, the advantages of using adsorption method for nitrate removal from water were discussed. It was also stated that the adsorption capacities can be increased by surface chemical modification techniques. This chapter presents the results of a study on using a metal modified ion exchange resin for the improvement of the nitrate adsorption capacity of an ion exchange resin.

Strong base anion exchange resins generally have high nitrate adsorption capacity. Indion NSSR (Milmile et al., 2011), Amberlite IRN-78 (De Heredia et al., 2006), Amberlite IRA 400 (Chabani et al., 2006), Imac HP555 (Jackson and Bolto, 1990), and Purolite A100 (Bulgariu et al., 2010) are some ion exchange resins that have been used to remove nitrate and more details on the use of these resins have been given in Chapter 2. However, most studies on ion exchange resins for removing nitrate have been conducted in static batch experiments, while only a few were done in dynamic column experiments with modelling. These latter ones are more relevant to water treatment conditions in the field.

Recently, Nur et al. (2015) compared the nitrate adsorption capacities of the anion exchange resins, Dowex 21K XLT, Purolite A520E, Purolite A500P and Purolite FerrIX A33E in batch experiments. They found that Purolite A520E and Dowex 21K

This chapter was published in Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Naidu, G., Nguyen, T.V., Vigneswaran, S., 2016. Nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies. Separation and Purification Technology, 158, 62-70.

they conducted a detailed nitrate adsorption study using column mode experiments only on Purolite A520E. A similar study is needed on Dowex 21K XLT.

The adsorption capacity of anion exchange resins can be increased by impregnation of metals which increases the surface positive charges (Loganathan et al., 2013a). Increment of positive charges on the surface would increase the adsorption of negatively charged ions such as nitrate by electrostatic attraction. For example, Namasivayam and Sangeetha (2005) impregnated Zn on coconut coir pith and found that the adsorption capacity for nitrate increased from a negligible amount to 2.3 mg N/g. They reported that the adsorption capacity increase was due to increased positive charges, surface area and pore volume of the adsorbent by adding metal ions. In another study, granular activated carbon (GAC) produced from coconut shells was modified with $ZnCl_2$ and tested for nitrate removal (Bhatnagar et al., 2008a). The adsorption capacity significantly increased via this metal impregnation method. Only one study was conducted on metal impregnation on anion exchange resin for removing nitrate (Jiang et al., 2011), but a few such studies have been reported for phosphate removal (Blaney et al., 2007; Sengupta and Pandit, 2011). For the adsorption process to be cost-effective the adsorbent needs to be satisfactorily regenerated for repeated use. Such studies on modified ion exchange resins are also rare.

The objectives of the research were to: (i) study the efficiency of nitrate removal from synthetic water using iron-modified and unmodified Dowex 21K XLT ion exchange resin in batch and fluidised-bed adsorption experiments; (ii) model the equilibrium, kinetics and column data on nitrate removal; (iii) determine the effect of pH and co-existing anions on the adsorption of nitrate; and (iv) investigate desorption of nitrate from the resin and the regeneration of adsorbent for multiple reuse.

3.2. Materials and methods

3.2.1. Ion exchange resin

Dowex 21K XLT, a strong base anion exchange resin used in the study was obtained from Dow Chemical Pte Ltd., USA (Dow, 2015). It consists of a quaternary methylamine functional group with chloride as the counter ion, which gives it the ability to exchange with other anions. The physical state of the Dowex anion exchange resin was yellow spherical beads with particles having 0.3-1.2 mm diameter and density of approximately 1.08 g/mL (Table 3.1).

Table 3.1. Typical chemical and physical properties of Dowex 21K XLT resin (Dow, 2015)

Parameters	Dowex 21K XLT
Type	Strong base anion
Polymer Matrix Structure	Styrene-DVB, gel
Physical Form and Appearance	Spherical yellow beads
Functional Groups	Quaternary ammonium
Ionic Form	Cl^-
Particle Size Range (microns)	300-1200
Particle density	1.08 g/mL
Moisture retention, Cl^- form	50 -60 %
Total Exchange Capacity, Cl- form	1.4 eq/L
pH Range	0-14
Maximum Operating Temperature,	100^0 C

3.2.1.1. Dowex modification

Dowex resin was modified by impregnation of iron (Dowex-Fe). In the impregnation method, 10 g Dowex resin was mixed with 1 L of $FeCl_3.6\ H_2O$ (2.0 g Fe^{+3}/L) for 1 h in a shaker at a speed of 120 rpm (Sengupta and Pandit, 2011). Then pH was increased to 8.0 by slowly adding 1 M NaOH solution for 3 h. The mixing speed was reduced to 30 rpm and the suspension was continuously mixed for 24 h. The resin was then filtered and rinsed with deionised water to remove unreacted Fe and dried in an oven set at 45^o C for 24 h.

3.2.2. Feed solutions

Synthetic water was prepared using Milli-Q water and ANALAR grade KNO_3 to obtain a concentration of 20 mg N/L for use in the batch experiments. The ionic strength was maintained at $1x10^{-3}$ M NaCl and the pH adjusted to 6.5 using a HQ40d portable pH meter by adding dilute HCl and NaOH. These ionic strength and pH were selected for the study because local storm waters were reported to have this ionic strength (electrical conductivity 0.74 dS/m) and average pH of 7.0 which is close to the pH selected (Mohammed et al., 2011). For the ion competition studies the synthetic water was prepared with ANALAR grade KH_2PO_4 and Na_2SO_4. For the fluidised-bed adsorption studies an aqueous solution containing 20 mg N/L was prepared using tap water instead of Milli-Q water. This is because large volumes of Milli-Q water required for the long-term column study were not available. The pH of this solution was 6.5-7.5.

All experiments were conducted in synthetic solutions containing a fixed nitrate concentration and a range of complementary ions concentrations to obtain basic information on the suitability of the adsorbents in the adsorptive removal of nitrate. Phosphate, sulphate and chloride ions were selected for the study as they are common anions present in ground and surface waters (Akan et al., 2012; Shah and Trivedi, 2011; Somasundaram et al., 1993). The concentrations used were in the ranges of ions generally present in these contaminated waters.

3.2.3. Nitrate Analysis

Nitrate concentration was analysed by an ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. The ion chromatograph was cleaned before the analysis using a mobile phase solution (Na_2CO_3, $NaHCO_3$), diluted sulphuric acid and Milli-Q water.

3.2.4. Characteristics of materials

Scanning electron microscope (SEM) images and energy dispersion spectrometry (EDS) results were obtained using the scanning electron microscope (Zeiss Supra 55VP Field Emission) in conjunction with energy dispersion spectrometry operated at 15 kv. This instrument served for the examination of the dried Dowex, Dowex-Fe and nitrate adsorbed materials. The BET surface area and porosity were measured by Micrometrics 3 Flex surface characterisation analyser at 77 K.

Zeta potential measurement was conducted to determine the electrical potential at the boundary of the hydrodynamic shear plane of the charged adsorbents. The zeta potential is related to the surface charge on the adsorbents. The Dowex and Dowex-Fe were ground to a smaller size so they could be suspended, and 0.1 g of these materials were added to 100 ml Milli-Q water and pH adjusted to 4-8 using dilute HCl and NaOH solutions. The flasks were agitated at a speed of 120 rpm and then zeta potential was measured using a Zetasizer nano instrument (Nano ZS Zen 3600, Malvern, UK). A chemical analysis was conducted to determine the Fe content in Dowex-Fe. 0.1 g of Dowex-Fe was ground and then heated with 5 ml HNO_3 and 5 ml HCl at 100^0 C for 5 h.

The samples were then diluted to 40 ml with 30 ml Milli-Q water and Fe concentration was determined by microwave plasma-atomic emission spectrometer (Agilent 4100 MP-AES).

3.2.5. Batch studies

Equilibrium adsorption and kinetic adsorption experiments were conducted using the modified and unmodified anion exchange resin Dowex 21K XLT. All adsorption experiments were conducted at 24 ± 1^0C.

3.2.5.1. Equilibrium adsorption

To 100 ml synthetic water containing 20 mg N/L and ionic strength of 1 x 10^{-3} M NaCl at pH 6.5 in a set of glass flasks, different amounts of adsorbents were added to provide adsorbent dosages of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 g/L. The flasks were agitated in a shaker at 120 rpm for 24 h. The supernatant solution was then filtered using filters with 1.2 μm openings and analysed for nitrate using an ion chromatograph analyser (Model 790 Personal IC). The amount of nitrate adsorption at equilibrium, q_e (mg/g), was calculated using the equation given below (Nur et al., 2014a):

$$q_e = \frac{(C_0 - C_e).V}{M} \qquad (3.1)$$

where, C_0 is initial concentration of nitrate (mg N/L), C_e is equilibrium concentration of nitrate (mg N/L), V is volume of solution (L) and M is mass of adsorbent (g)

Percentage adsorption was calculated using equation 3.2 as follows:

$$\text{Percentage adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (3.2)$$

3.2.5.2. Adsorption kinetics

Adsorption kinetics was conducted with adsorbent concentration of 1 g/L at a nitrate concentration of 20 mg N/L and ionic strength of $1x10^{-3}$ M NaCl in a set of glass flasks at pH 6.5. The flasks were shaken at 120 rpm. Samples were taken at 5, 10, 20, 30, 45, 60, 90, 105, 120, and 150 and 180 min and after filtration the filtrate was analysed for nitrate as before. The amount of nitrate adsorbed (q_t) at time t was calculated using equation (3.3) (Nur et al., 2014a):

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{3.3}$$

where, C_0 is initial concentration of nitrate (mg N/L), C_t is concentration of nitrate at time t (mg N/L), V is volume of the solution (L) and M is mass of dry adsorbent (g).

3.2.5.3. pH effect on adsorption

The effect of pH on adsorption was studied at an adsorbent dosage of 1g/L at a nitrate concentration of 20 mg N/L and ionic strength of $1x10^{-3}$ M NaCl in a set of glass flasks. The pH was adjusted to 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, and 7.5 using dilute HCl and NaOH. The procedure for the adsorption experiment was similar to the equilibrium adsorption experiment described previously.

3.2.5.4. Co-ions effect on nitrate adsorption

Studies on co-ions’ effect on adsorption were carried out using different concentrations of complementary ions, sulphate (10, 20, 30, 50, and 70 mg S/L), phosphate (0.5, 1, 5, 10 and 30 mg P/L) and chloride (20, 30, 50 and 70 mg Cl/L) at a constant nitrate concentration (20 mg N/L). Sulphate, phosphate and chloride were selected as complementary ions because of their common occurrence at high concentrations along with nitrate in both ground water (Shah and Trivedi, 2011;

Somasundaram et al., 1993) and surface water (Akan et al., 2012). The adsorbent dose was kept constant at 1 g/L.

3.2.6. Fluidised-bed studies

Fluidised-bed experiments were conducted using an acrylic glass tube of 2 cm internal diameter and dry resin bed height of 15 cm and passing synthetic water (20 mg N/L) through the column with a filtration velocity of 5 m/h (26.6 mL/min) (Figure 3.1). A peristaltic pump was utilised for pumping the feed water in the up-flow mode through the column. The effluent samples were collected every 1 h interval and nitrate was analysed by ion chromatograph.

The maximum adsorption of nitrate (mg) in the fluidised-bed was calculated from equation 3.4 given below:

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t-total} C_{ad} \, . dt \tag{3.4}$$

where, C_{ad} is the adsorbed nitrate concentration (C_{ad}= C_0-C_t) mg N/L.

The maximum adsorption capacity (mg/g) was calculated from equation 3.5:

$$q_{eq} = \frac{q_{total}}{M} \tag{3.5}$$

where, M is the mass of adsorbent (g) used in the fluidised-bed.

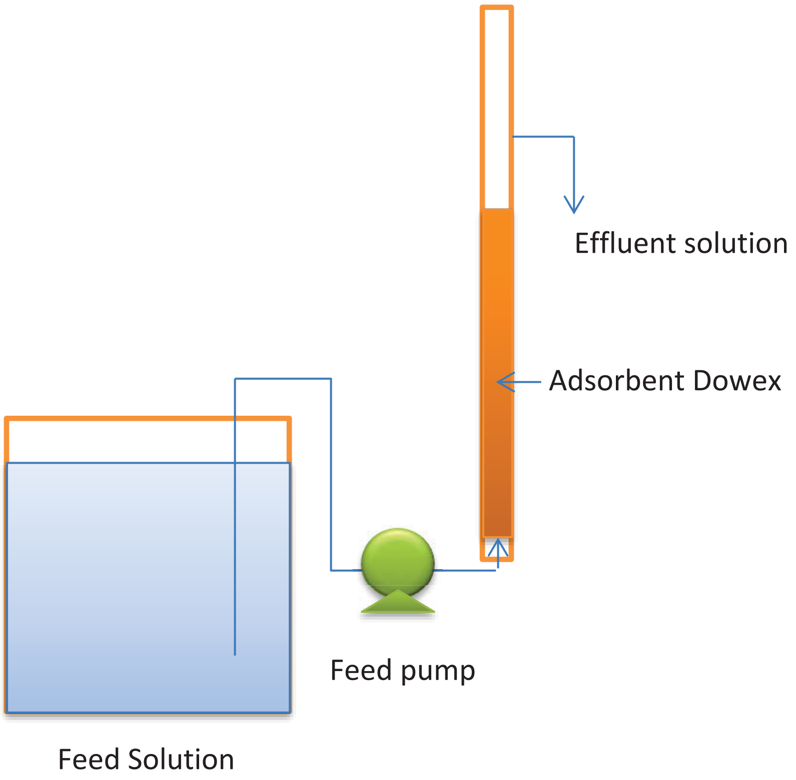

Figure 3.1. A Schematic diagram of column experiment

3.2.7. Adsorption models

The batch and fluidised-bed adsorption data were modelled using the adsorption models presented in Tables 3.2-3.4.

Table 3.2. Equilibrium adsorption models

Model	Equation*	Parameters
Langmuir	$q = \frac{q_m b C_e}{1 + b C_e}$	q_m, b
Freundlich	$q = k_f C_e^{1/n}$	k_f, n
Sips	$q = \frac{q_m b C_e^{1/n}}{1 + b C_e^{1/n}}$	q_m, b, n

*C_e = equilibrium concentration of nitrate (mg N/L), q = amount of nitrate adsorbed per unit mass of adsorbent (mg N/g), q_m = maximum amount of nitrate adsorbed per unit mass of adsorbent (mg N/g), b = Langmuir and Sips affinity constant (L/mg), k_f = Freundlich constant $(mg/g)(L/mg)^{1/n}$, and n = Freundlich and Sips constant.

Table 3.3. Kinetic adsorption models

Model	Equation*	Parameters
Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	k_1, q_e
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	k_2, q_e
Homogeneous surface diffusion model (HSDM)	$\frac{\partial q_{td}}{\partial t} = D_s\left(\frac{\partial^2 q_{td}}{\partial r^2} + \frac{2}{r}\frac{\partial q_{td}}{\partial r}\right)$ Initial and boundary conditions $t = 0;\quad q_{td} = 0$ $r = 0;\quad \frac{\partial q_{td}}{\partial r} = 0$ $r = r_p;\ D_s\rho_p\frac{\partial q_{td}}{\partial r} = k_f(C - C_s)$	D_s, k_f

*q_e = amount of nitrate adsorbed at equilibrium (mg N/g), q_t = amount of nitrate adsorbed at time, t (h) (mg N/g), k_1 = equilibrium rate constant of pseudo-first order sorption (1/h), k_2 = equilibrium rate constant of pseudo-second order (g /mg h), D_s = surface diffusion coefficient (m^2/s), q_{td} = nitrate concentration in the solid phase (mg N/L), C = nitrate concentration in the liquid phase (mg N/L), C_s = liquid phase concentration at adsorbent surface (mg N/L), r = radial distance from the centre of adsorbent particle (m), k_f = external mass transfer coefficient (m/s), and ρ_p = particle density (kg/m^3).

Table 3.4. Dynamic models used for nitrate adsorption

Model	Equation*	Parameters
Thomas model	$\ln\left(\frac{c_0}{c_t}-1\right)=\frac{k_{Th}q_0M}{Q}-k_{Th}c_0t$	q_0, k_{Th}
Plug-flow model	$\frac{\partial c}{\partial t}=-\frac{v}{\varepsilon_r}\frac{\partial c}{\partial z}-\frac{1-\varepsilon_r}{\varepsilon_r}\rho_p\frac{\partial q}{\partial t}$ $\varepsilon_r=1-(1-\varepsilon_{mf})\cdot\left(\frac{L_{mf}}{L_f}\right)$ Initial and boundary conditions $t=0;\quad c=0$ $z=0;\quad c=c_0$	D_s, k_f

*k_{Th} = Thomas rate constant (mL/min mg), q_o = equilibrium nitrate uptake per g of adsorbent (mg N/g), c_0 = inlet nitrate concentration (mg N/L), c_t = outlet nitrate concentration at time t (mg N/L), M = mass of adsorbent (g), Q = filtration velocity (mL/min), t = filtration time (min), D_s = surface diffusion coefficient (m^2/s), c = nitrate concentration in the liquid phase (mg/L), q = nitrate concentration in the solid phase (mg N/L), L_{mf} = height of the initial fluidised-bed (m), L_f = height of the fluidised-bed (m), ε_r = fluidised-bed porosity, ε_{mf} = fixed bed porosity, ρ_p = bulk density (kg/m^3), v = fluid velocity (m/s), and z = bed depth (m).

3.3. Results and discussion

3.3.1. Characteristics of anion exchange resin

3.3.1.1. SEM, EDS and surface area

SEM images of Dowex 21K XLT particles showed a smooth surface (Figure 3.2). In contrast, the images of Dowex-Fe particles showed the deposition of foreign materials on the Dowex surface that could be ascribed to the deposition of the Fe. Typical EDS patterns of Dowex and Dowex-Fe are shown in Figure 3.3. The main difference between the patterns of Dowex and Dowex-Fe is the appearance of a Fe peak in Dowex-Fe, which was not present in Dowex. This clearly demonstrates that Fe was successfully impregnated on the Dowex. The mean elemental compositions of Dowex and Dowex-Fe obtained from the EDS analysis of 5 particles are presented in Table 3.5. The data shows that the mean Fe content was 1.7 ± 0.5 for Dowex-Fe. However, the chemical analysis of Dowex-Fe highlighted that the Fe content was 0.065 ± 0.003%, which is much lower than the Fe content value obtained in EDS. This discrepancy is due to EDS scanning only the surface layer of few micrometres of the Dowex-Fe particle where the Fe is concentrated (Yao et al., 2011) whereas the destructive chemical analysis measured the Fe content in the whole particle.

The Cl content determined by EDS analysis was 11.7 and 12.3% for Dowex and Dowex-Fe, respectively (Table 3.5). The Cl content of Dowex agrees well with the EDS value of 10.1% reported for Cl content of the same resin (Dowex 21K XLT) by Ok and Jeon (2014). Chloride in the resin is present as the main exchangeable anion (Dow, 2015; Ok and Jeon, 2014). The slight increase in the Cl content of Dowex-Fe from that of Dowex is probably due to the presence of few remnants of Cl from the $FeCl_3$ used in the preparation of Dowex-Fe, despite removal of mostly all of the unreacted $FeCl_3$ by washing with distilled water at the end of its preparation.

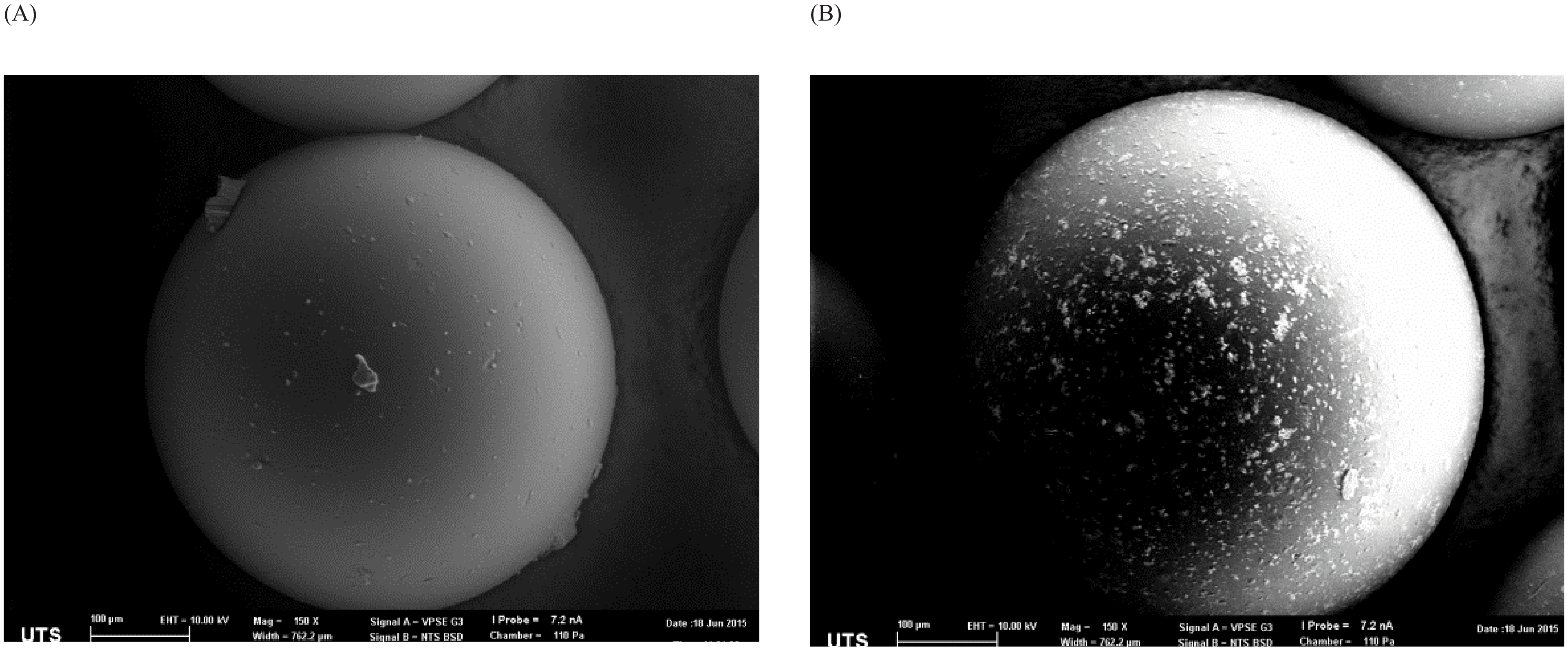

Figure 3.2. SEM images of (A) Dowex and (B) Dowex-Fe (magnification 150 x)

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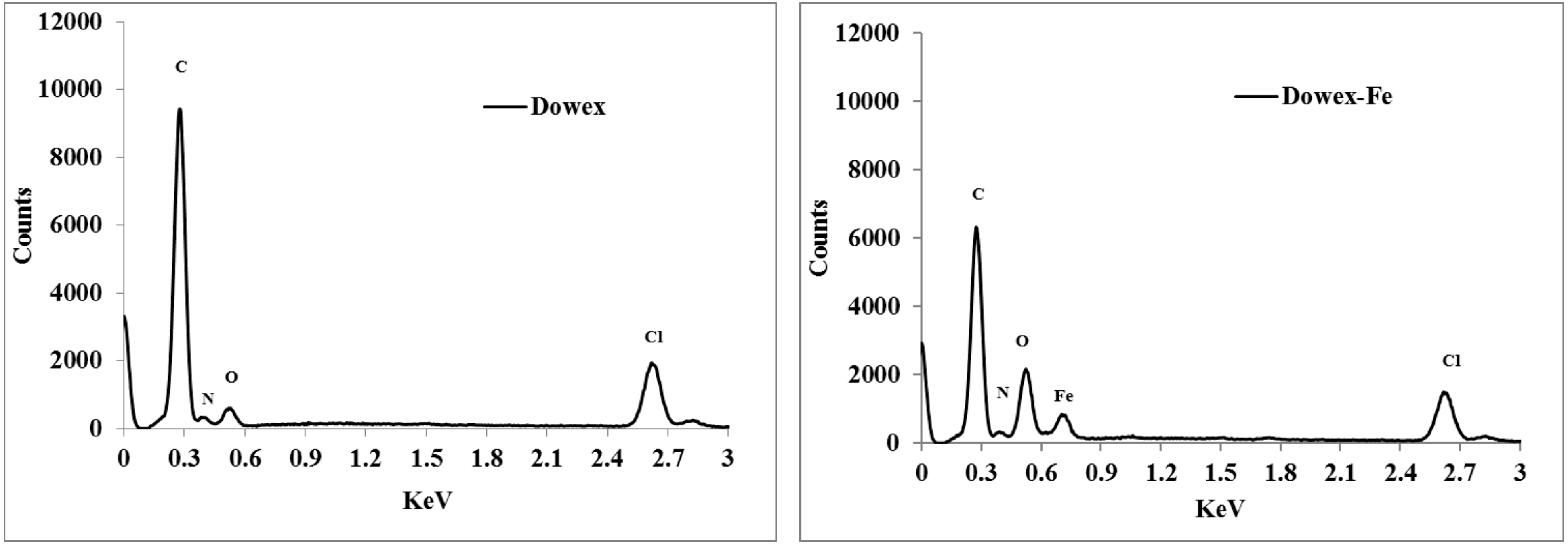
(A)
(B)

Figure 3.3. EDS analysis of (A) Dowex and (B) Dowex-Fe

Table 3.5. Elemental composition of Dowex and Dowex-Fe as determined by EDS

Adsorbent	Carbon (wt %)	Oxygen (wt %)	Chlorine (wt %)	Nitrogen (wt %)	Iron (wt %)
Dowex	71.5 ± 0	6.5 ± 0	11.7 ± 0	10.2 ± 0	0
Dowex-Fe	68.3 ± 1.1	6.8 ± 1.1	12.3 ± 0.4	10.8 ± 0.2	1.7 ± 0.5

3.3.1.2. Zeta potential

Zeta potential data shows that Dowex-Fe had higher positive zeta potential than Dowex at all pHs (Figure 3.4). This means that the Fe impregnation on Dowex increased the surface positive charge at all pHs, which is favourable for the adsorption of the negatively charged nitrate by outer-sphere complexation through electrostatic forces (Loganathan et al., 2014; Oladoja and Helmreich, 2014). Namasivayam and Sangeetha (2005) discovered that Zn impregnation increased the positive zeta potential on coir pith and they explained this as being due to the addition of positive charges in Zn ions. The positive zeta potential values were almost the same for the pH values 4 to 8 and were slightly reduced at pH 8 for both Dowex and Dowex-Fe. The reason for this reduction is that the quaternary methylamine functional groups in Dowex are deprotonated with increasing pH, thus the positive charges decreased at high pH values (Yoon et al., 2009).

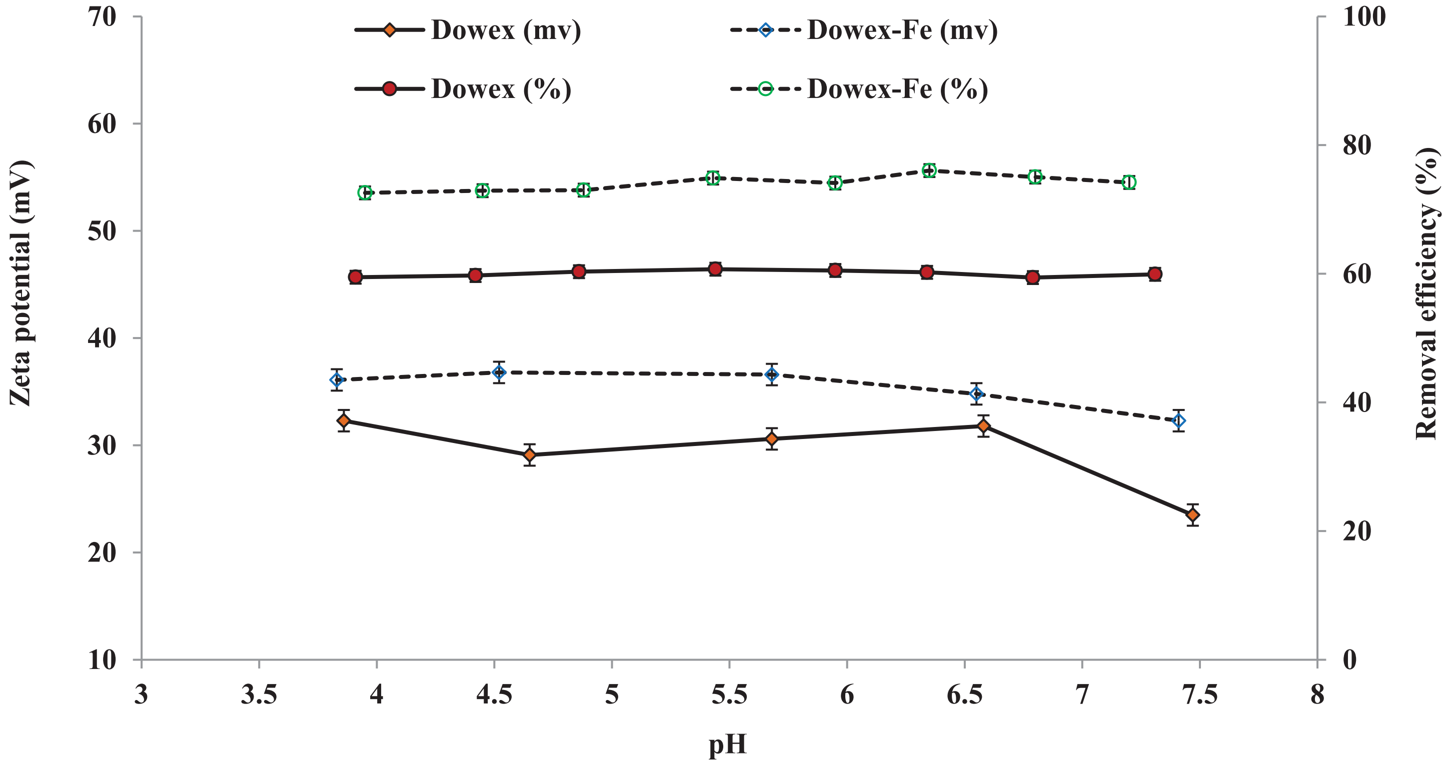

Figure 3.4. Effect of pH on zeta potential and nitrate removal efficiency of Dowex and Dowex-Fe

3.3.2. Batch adsorption studies

3.3.2.1. Effect of pH

Figure 3.4 shows that there is no significant change in the nitrate removal efficiency with varying pH from 3.9 to 7.3 for both adsorbents. This indicates that the adsorption of nitrate on Dowex and Dowex-Fe is independent of pH in this pH range. This is supported by the results of zeta potential, which did not change in this pH range (Figure 3.4), suggesting that the number of surface positive charges remained the same. The nitrate removal efficiency was approximately 60% for Dowex and about 75% for Dowex-Fe. At pH above 7.5, the concentration of OH^- ion increases and therefore there can be competition from OH^- for nitrate adsorption as suggested for F adsorption in alkaline region (Oladoja et al., 2016). It could also be due to the reduction in the number of positive surface charges on the Dowex as indicated by the zeta potential reduction in the alkaline pH condition (Figure 3.4).

3.3.2.2. Nitrate adsorption equilibrium at pH 6.5

Nitrate adsorption increased with a larger dose of adsorbents and Dowex-Fe exhibited higher adsorption capacity than Dowex at all doses (Figure3.5). Increased adsorption with elevated adsorbent dose is due to an increase in the number of adsorption sites. The higher adsorption by Dowex-Fe is due to the higher positive surface charge produced by Fe impregnation on this adsorbent as shown in the zeta potential data (Figure 3.4). EDS peaks for nitrogen increased and those for chloride decreased when nitrate was adsorbed (compare Figure 3.3 and Figure 3.6). The elemental analysis derived from the EDS data gives a more accurate picture of these trends. It showed that N and O contents in both resins increased and Cl content declined, indicating that nitrate has exchanged with chloride ion in the resins (compare Table 3.5 and Table 3.6).

The adsorption data was fitted to the Langmuir, Freundlich and Sips models (Figure 3.7) and the Nelder–Mead simplex method (Ahmad et al., 2012; Nelder and Mead, 1965) was used to determine the optimum isotherm parameters. The R^2 values for the data fit to the models showed that in general, the Langmuir model provided a slightly better fit than the other isotherm models. The Langmuir maximum adsorption capacities (q_{max}) were 27.6 and 75.3 mg N/g for Dowex and Dowex-Fe, respectively (Table 3.7). Dowex-Fe adsorption capacity was more than double that of Dowex, because of the additional positive charges provided by Fe impregnation on Dowex. The Sips model also revealed that the adsorption capacity of Dowex-Fe was higher than that of Dowex, but the magnitude of the difference was 70% of that of Dowex adsorption capacity. The Langmuir adsorption capacity of Dowex-Fe (75.3 mg N/g) is much higher than most of the adsorbents reported in the literature (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a). For example, much lower Langmuir adsorption capacities of 18.5 mg N/g by Samatya et al. (2006) and 33 mg N/g by Nur et al. (2015) were reported for Purolite A520E resin.

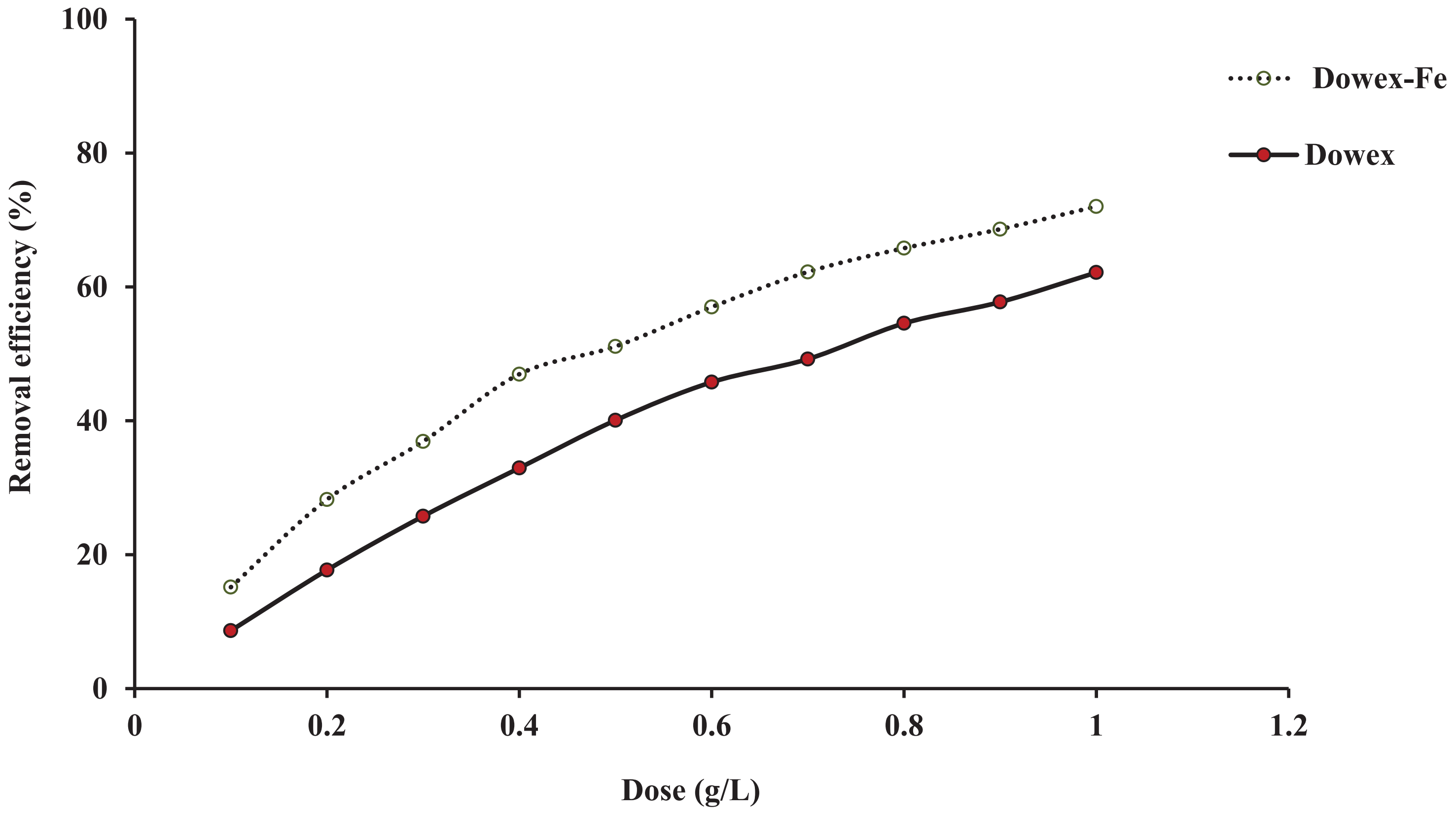

Figure 3.5. Effect of resin dose on the removal efficiency of nitrate (initial nitrate concentration 20 mg N/L)

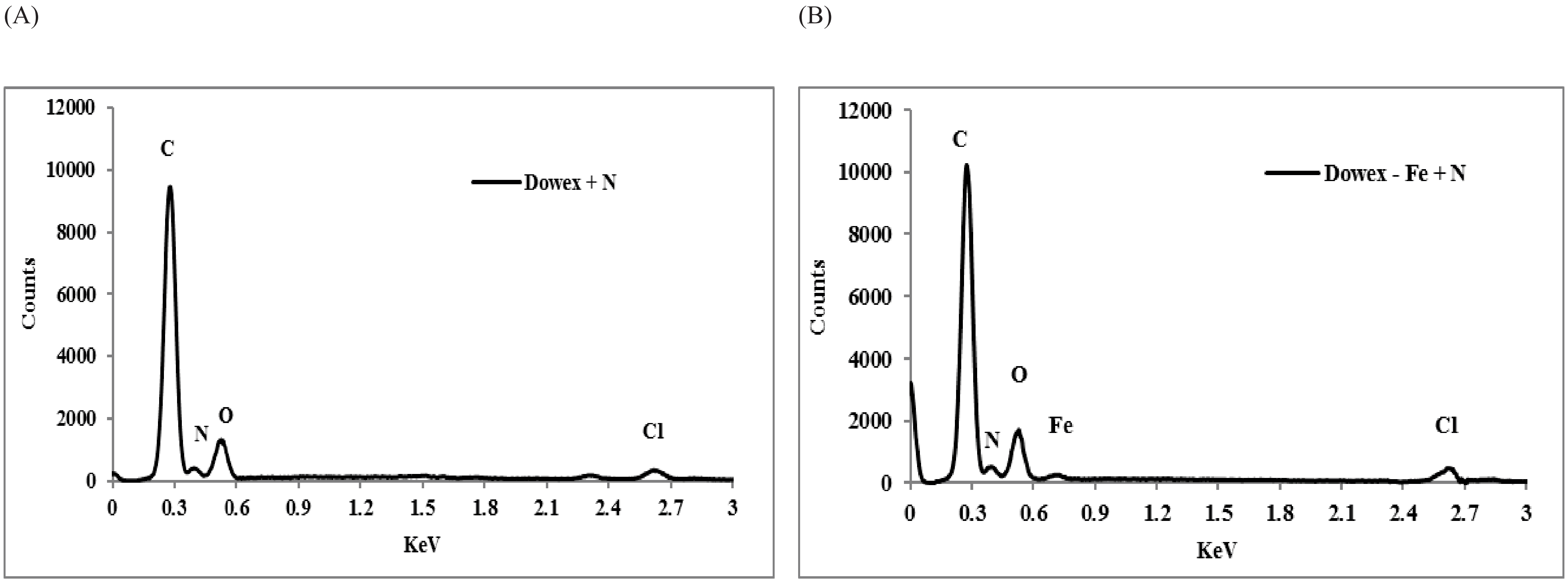

Figure 3.6. EDS analysis of resins after nitrate adsorption (A) Dowex + N and (B) Dowex-Fe + N

Table 3.6. Elemental composition of Dowex and Dowex-Fe after nitrate adsorption as determined by EDS

Adsorbent	Carbon (wt %)	Oxygen (wt %)	Chlorine (wt %)	Nitrogen (wt %)	Iron (wt %)
Dowex + nitrate	58.9 ± 2.4	22.3 ± 1.4	1.2 ± 0.5	14.7 ± 0.4	0
Dowex-Fe+ nitrate	48.2 ± 2.7	28.0 ± 1.2	0.9 ± 0.1	14.7 ± 0.3	0.4 ± 0.1

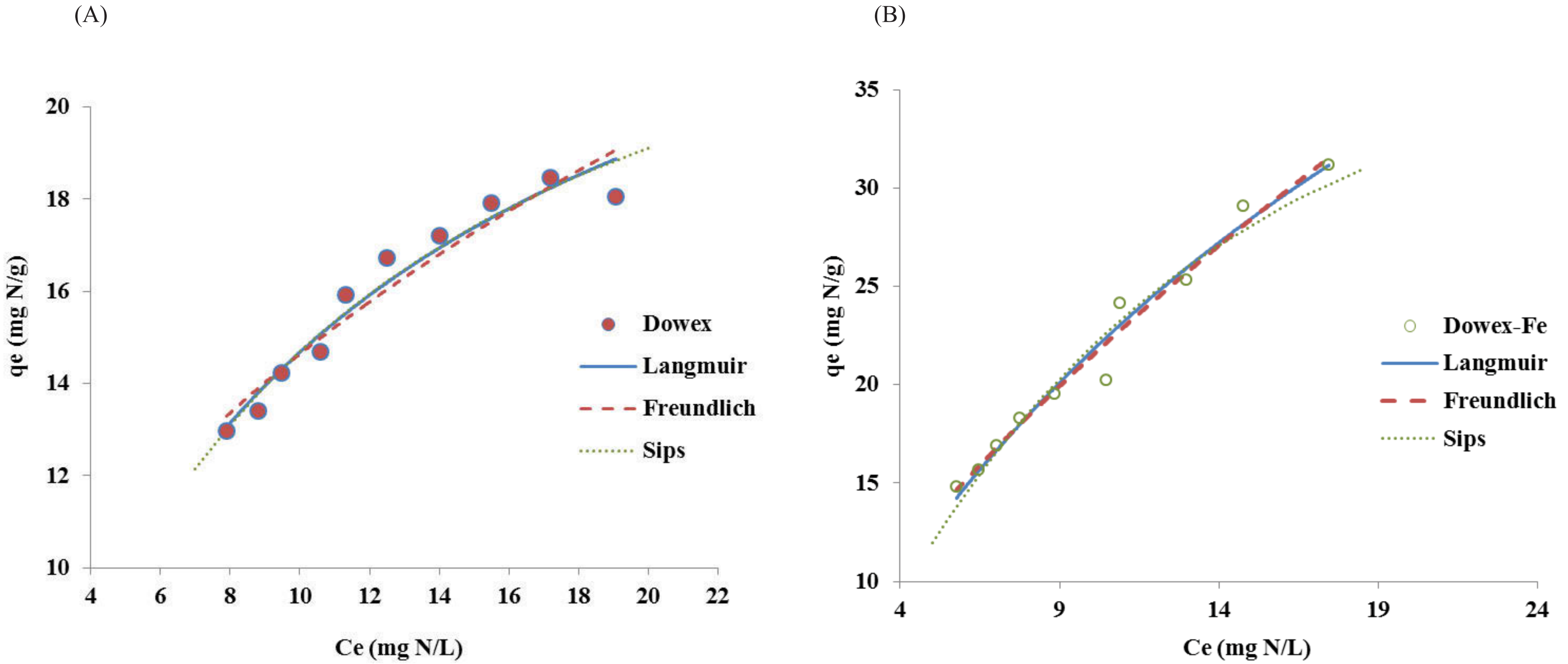

Figure 3.7. Batch equilibrium adsorption modelling on (A) Dowex (B) Dowex-Fe

Table 3.7. Parameter values for batch equilibrium adsorption models

Models	Parameters	Dowex	Dowex-Fe
Langmuir	q_m (mg N/g)	27.6	75.3
	b (L/mg)	0.11	0.04
	R^2	0.9653	0.9749
Freundlich	k_f (mg/g)(L/mg)$^{1/n}$	5.69	4.34
	n	2.44	1.44
	R^2	0.9292	0.9761
Sips	q_m (mg N/g)	25.8	44.2
	b (L/mg)	0.1	0.04
	n	0.9	0.71
	R^2	0.9574	0.9622

3.3.2.3. Effects of complementary ions

The nitrate removal efficiencies of Dowex and Dowex-Fe were tested in the presence of competing anions such as phosphate, chloride and sulphate at various concentrations in the synthetic water (Table 3.8). Figure 3.8 shows that nitrate removal efficiency did not change in the presence of phosphate and chloride anions at all concentrations whereas sulphate anion reduced nitrate adsorption drastically even at a concentration equal to that of nitrate (20 mg N/L); this reduction increased with increased sulphate concentration for both adsorbents. This is because sulphate has two negative charges and nitrate has one negative charge, and consequently sulphate has a higher affinity to the positively charged adsorbents. Phosphate has more than 80% single negative charge/ion and less than 20% two negative charges/ion at the pH 6.5 tested in the study (Pan et al., 2009) and therefore slightly reduced the nitrate adsorption at low concentrations. Differences in the competitiveness of co-existing anions based on their magnitude of charges has also been explained by Oladoja and Ahmad (2013) for the adsorption of Cr(VI) on binary metal oxides. Another reason for the ineffectiveness of phosphate in reducing nitrate adsorption is that the phosphate concentration is lower than nitrate concentration at all levels except level 5. Even though the phosphate concentration was higher than that of nitrate in level 5, the moles of phosphate/L (0.97 mole P/L) were lower than the moles of nitrate /L (1.42 mole N/L) and therefore phosphate did not significantly compete with nitrate. Chloride has the same number of charge as nitrate and the moles/L was higher (~ 2 moles/L) than nitrate only at the highest chloride concentration of 70 mg/g. Therefore it did not significantly reduce the nitrate adsorption capacity. Competition among the anions usually depends on the ratio of the concentration of nitrate to other anions and therefore the nitrate removal efficiencies may vary according to wastewater characteristics

Table 3.8. Concentrations of complementary ions (concentration of nitrate ion is 20 mg N/L)

Complementary ions	Level 1	Level 2	Level 3	Level 4	Level 5
Phosphate (mg P/L)	0.5	1	5	10	30
Chloride (mg Cl/L)	20	30	50	70	-
Sulphate (mg S/L)	10	20	30	50	70

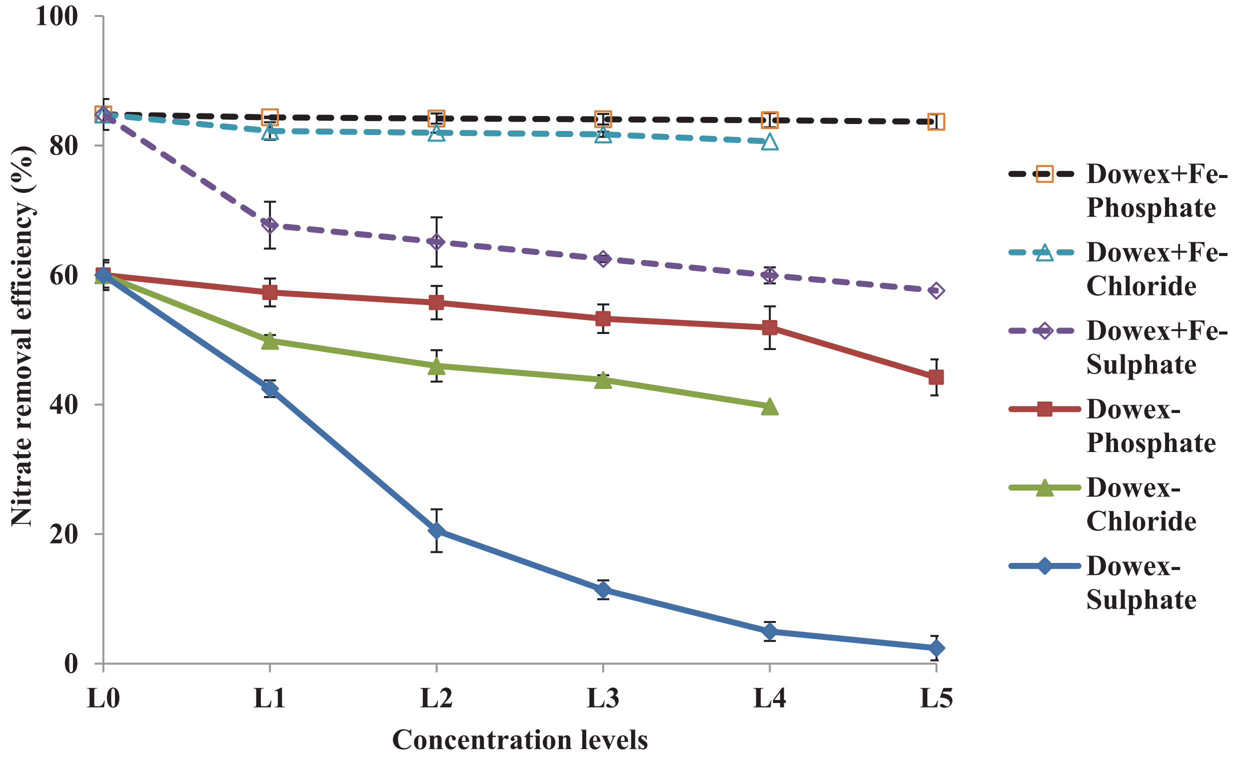

Figure 3.8. Effect of complementary ions on the removal of nitrate by Dowex and Dowex-Fe

3.3.2.4. Adsorption kinetics

The rate of adsorption can be predicted by the adsorption kinetics. In fact the rate of adsorption is determined by the mass transfer and diffusion of the adsorbate particles from liquid phase to adsorbent surface. The pseudo-first order, pseudo-second order and HSDM models were used to investigate the adsorption kinetics of nitrate on Dowex and Dowex-Fe (Figure 3.9). The pseudo-first order and pseudo-second order fitted well to the adsorption data for both Dowex and Dowex-Fe. However, the experimental q_e values agreed with the model values better for the pseudo-first order than the pseudo-second order for Dowex and the latter model agreed better than the first model for Dowex-Fe (Table 3.9).

The HSDM also fitted well to the kinetics data for both adsorbents as made evident by the high R^2 values (Figure 3.9, Table 3.9). The HSDM parameters, D_s and k_f determined from the model are presented in Table 3.9. The orthogonal collocation method (OCM), the variable coefficient ordinary differential equation solver (VODE) and the Nelder–Mead simplex method were used to calculate D_s and k_f (Brown et al., 1989; Matulionytė et al., 2007; Villadsen and Stewart, 1967). Furthermore, the Langmuir isotherm model was employed to represent the equilibrium relationship at the adsorbent–adsorbate interface. The D_s depends on the concentration of nitrate and the k_f relies on the agitation speed of the batch system (Ahmad et al., 2012). In the batch kinetics adsorption experiments, the same concentration of nitrate and the same conditions were used for Dowex and Dowex-Fe. Therefore the obtained D_s and k_f values are almost the same range as those generated in these experiments. Dowex surface modification with Fe had no effect on the kinetics of adsorption.

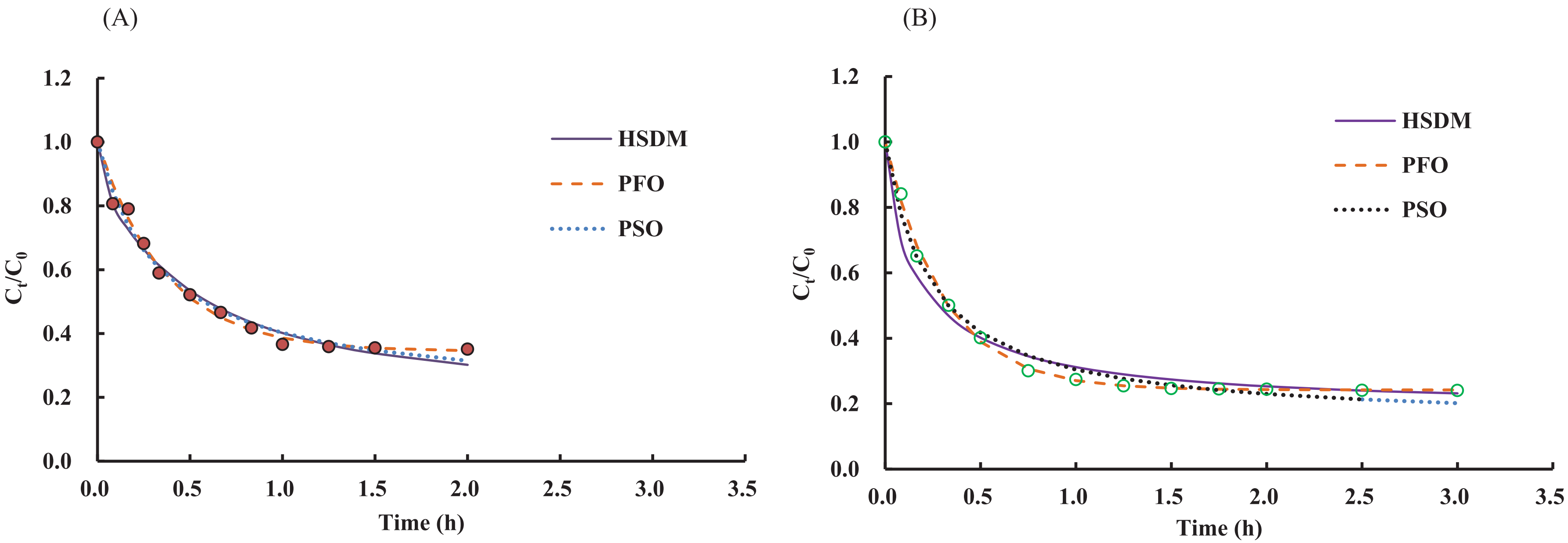

Figure 3.9. Pseudo-first order (PFO), Pseudo-second order (PSO) and HSDM adsorption kinetics models fits to the data on nitrate adsorption on (A) Dowex and (B) Dowex-Fe at pH 6.5 (initial nitrate concentration 20 mg N/L, adsorbent dose 1 g/L). Circles represent the experimental data and lines represent models fittings to the data.

Table 3.9. Batch adsorption kinetic parameters of pseudo-first order (PFO), pseudo-second order (PSO) and HSDM models for the adsorption on nitrate on Dowex and Dowex-Fe

Models	Parameters	Dowex	Dowex-Fe
	q_{exp} (mg N/g)	12.97	15.69
PFO	q_e (mg N/g)	13.03	12.15
	k_1 (h^{-1})	2.99	4.53
	R^2	0.9717	0.9899
PSO	q_e (mg N/g)	15.50	17.18
	k_2 (g/mg h)	0.20	0.46
	R^2	0.9884	0.9954
HSDM	k_f x 10^{-4} (m/s)	3.11	5.30
	D_s x10^{-12} (m^2/s)	1.61	2.00
	R^2	0.9812	0.9601

3.3.3. Fluidised-bed adsorption studies

3.3.3.1. Nitrate with and without complementary ions

The breakthrough curves for nitrate adsorption on Dowex and Dowex-Fe at solution velocity of 5 m/h for the influent concentration of 20 mg N/L, 20 mg N/L + 5 mg P/L, and 20 mg N/L + 50 mg S/L are presented in Figure 3.10. The figure shows that the adsorbent approached the fluidised-bed saturation level faster and the breakthrough curves were steeper in the Dowex fluidised-bed than in the Dowex-Fe fluidised-bed for all influent solutions. The reason for this is that the Dowex-Fe fluidised-bed had higher adsorption capacity than Dowex as shown in the batch study (Table 3.7).

The fluidised-bed adsorption capacity for nitrate in the absence of co-ions up to the saturation point of 44 h (1400 bed volumes) for Dowex was 18.6 mg N/g, which is lower than the batch Langmuir adsorption capacity of 27.6 mg N/g. Similarly the Dowex-Fe adsorption capacity up to the saturation point of 80 h (2500 bed volume) was 31.4 mg N/g and the Langmuir adsorption capacity was 75.3 mg N/g. The fluidised-bed adsorption capacities were lower than the batch Langmuir adsorption capacities because in the batch experiments, equilibrium was reached and maximum adsorption occurred on the adsorbent unlike in the fluidised-bed experiment, where the residence time of adsorbate is shorter at the high flow rate of 5 m/h (Ghorai and Pant, 2004). The longer time (higher bed volumes) taken for fluidised-bed saturation of Dowex-Fe indicates that larger volumes of water containing nitrate can be treated by the modified ion exchange resin than the unmodified resin. Consequently it is a more efficient adsorbent for removing nitrate.

Figure 3.10 compares the nitrate adsorption by Dowex and Dowex-Fe for the influent aqueous solutions containing nitrate, nitrate + phosphate and nitrate + sulphate. The breakthrough curve was steeper and approached the saturation point faster for N+S feed than the N+P feed and N feed for both the Dowex and Dowex-Fe fluidised-beds. The N+P curves were also steeper than the N only curves. These results are consistent with those of the batch experimental results showing that sulphate competes more than phosphate with nitrate for adsorption. The decrease in nitrate adsorption capacities of Dowex and Dowex-Fe in the presence of sulphate was much higher than in the presence of phosphate (Table 3.10).

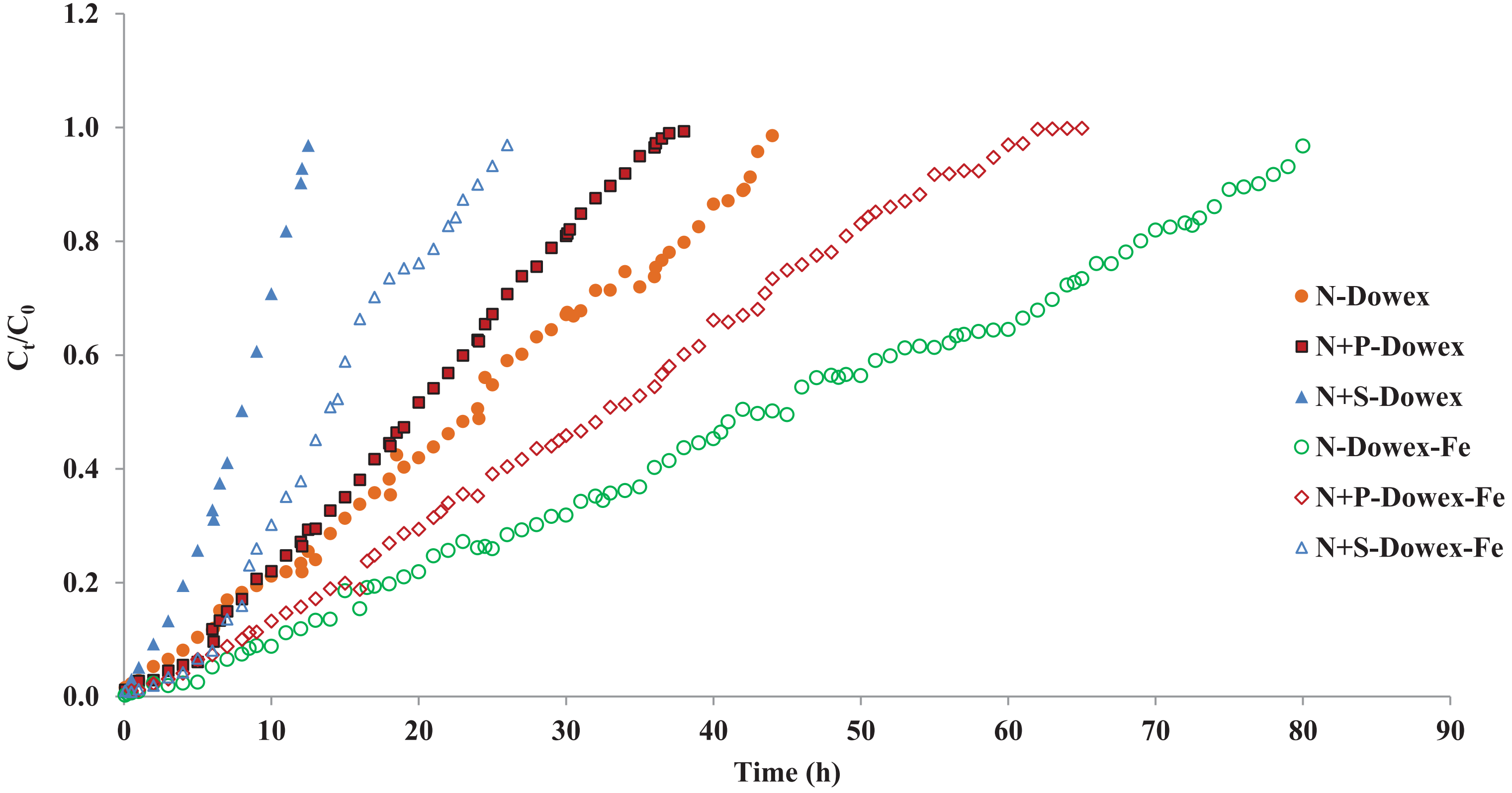

Figure 3.10. Breakthrough curves for nitrate adsorption on Dowex and Dowex-Fe for synthetic water containing nitrate only and nitrate plus other ions (initial concentration of ions were 20 mg N/L; 5 mg P/L; 50 mg S/L)

Table 3.10. Nitrate adsorption and desorption in Dowex and Dowex-Fe fluidised-bed in the presence of sulphate and phosphate in influent solution for three adsorption /desorption cycles

Adsorbents	Feed concentration	Adsorption-desorption cycle	Adsorption bed volume	Adsorption capacity (mg N/g)	Amount of N adsorbed (mg)	Amount of N desorbed (mg)	% N desorbed	Desorption bed volumes*
Dowex	20 mg N/L	1	1400	18.6	653	652	99.8	16.5
		2	1400	17.0	621	591	95.2	16.5
		3	1400	16.6	603	584	96.8	16.5
	20 mg N/L+	1	1200	15.1	533	516	96.8	16.5
	5 mg P/L	2	1200	13.1	458	444	96.9	16.5
		3	1200	12.8	440	421	95.6	16.5
	20 mg N/L+	1	400	5.3	185	176	95.1	16.5
	50 mg S/L	2	400	5.1	178	170	95.5	16.5

Table 3.10 (Continued)

		3	400	5.1	177	172	97.2	16.5
Dowex-Fe	20 mg N/L	1	2500	31.4	1270	1255	98.8	49.7
		2	2500	30.9	1239	1233	99.5	49.7
		3	2500	29.0	1164	1139	97.8	49.7
	20 mg N/L+ 5 mg P/L	1	2150	24.7	990	982	99.2	49.7
		2	2150	24.2	968	953	98.4	49.7
		3	2150	24.1	965	953	98.8	49.7
	20 mg N/L+ 50 mg S/L	1	850	11.3	451	443	98.2	49.7
		2	850	10.8	433	429	99.1	49.7
		3	850	10.6	426	417	97.9	49.7

* Desorption bed volumes = Volume of KCl solution used to desorb the nitrate/Ion exchange resin bed volume (1 bed volume = 47.1 cm^3)

3.3.3.2. Desorption of nitrate and resin regeneration

The nitrate desorption from Dowex was tested using 0.01 M, 0.1 M, and 1 M KCl in batch experiments. Of these solutions it was found that 1 M KCl solution desorbed nearly all the adsorbed nitrate within the shortest time (Figure 3.11). Thus 1 M KCl solution was used to desorb the nitrate in the fluidised-bed experiments. The nitrate in the resin was desorbed by chloride in solution by an anion exchange process. Chloride is known to be a non-specific adsorbing anion (Loganathan et al., 2014). The fact that it can easily desorb nitrate indicates that nitrate was non-specifically adsorbed to Dowex by outer sphere complexation (Oladoja et al., 2014).

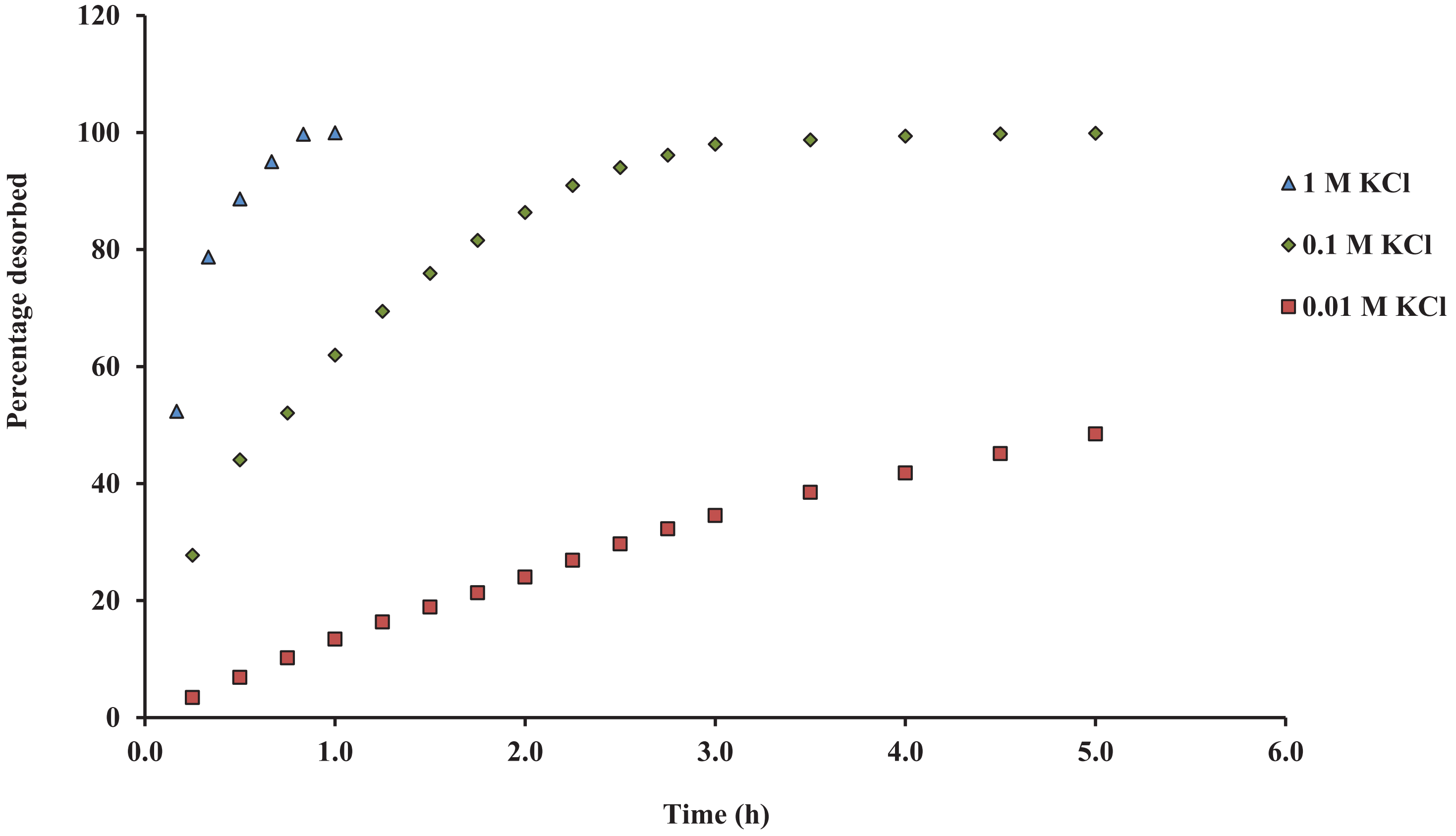

Figure 3.11. Desorption of nitrate using different concentrations of KCl solutions

Regeneration of Dowex and Dowex-Fe fluidised-beds after their use in nitrate adsorption was done by desorbing the adsorbed nitrate using 1 M KCl. The regenerated resins were utilised for two more adsorption-desorption cycles. Table 3.10 shows that the adsorbed nitrate was almost completely desorbed by 1 M KCl in the three adsorption/desorption cycles. The adsorption capacity decreased only marginally after each of the regenerations. The decrease in adsorption capacity from the first to the third cycle was only 2.4-7.7%. The small decrease in adsorption capacity indicates that the resin can probably be effectively used for few more cycles. The present study was conducted using a high nitrate concentration of 20 mg N/L. In reality the nitrate concentrations are lower and therefore the fluidised-bed can be used for many more cycles. Their repeated use reduces the cost of the treatment process.

The adsorption capacity at the end of each adsorbent regeneration reduced only slightly because the decrease in the total Fe content of the Dowex-Fe as determined by chemical analysis was very little (decrease was from 0.065 ± 0.003 to 0.062 ± 0.003%, a 4.6% decrease). EDS analysis before and after regeneration also showed that the Fe content in the surface layers of the resin reduced by as little as 4.9%. This indicates that the Fe incorporated onto the resin remained largely intact during the regeneration process to maintain the higher adsorption capacity of Dowex-Fe.

In the competitive adsorption study with sulphate and phosphate more than 95% of adsorbed nitrate was desorbed in all the adsorption/desorption cycles and the capacity to adsorb nitrate fell only very little after each regeneration as in the case of influent solution containing nitrate only (Table 3.10). It took 49.7 bed volumes to completely desorb nitrate from Dowex-Fe beds compared to 16.5 bed volumes for Dowex beds. At 16.5 bed volumes, only 62% of nitrate was desorbed from Dowex-Fe beds.

3.3.3.3. Modelling fluidised-bed adsorption of nitrate

The fluidised-bed nitrate adsorption data was fitted to the Thomas model and the resulting model parameters are shown in Table 3.11**.** The Thomas model fitted the data fairly well as seen from the high R^2 values. The Thomas model fluidised-bed adsorption capacity (q_o) predictions were higher for Dowex-Fe than for Dowex as also found in batch studies. These values were close to the respective values determined by manual calculations from the breakthrough curves.

A plug-flow model coupled with HSDM and Langmuir isotherm equation was also used to simulate the adsorption behaviour of nitrate in the fluidised-bed (Shanmuganathan et al., 2014). The mathematical model equations of adsorption were solved using the OCM and the subroutine VODE program as in the batch kinetic study. Model parameters, D_s and k_f, were determined using the Nelder–Mead simplex method. The optimised D_s values (Dowex: 1.8 x 10^{-12} – 2.4 x 10^{-12}, Dowex-Fe: 2.0 x 10^{-12}) (Table 3.11) are in the similar range as in the batch kinetics results (Dowex: 1.6 x 10^{-12}, Dowex-Fe: 2.0 x 10^{-12}) (Table 3.9), because nitrate concentration ranges were similar in the two studies. However, the k_f value determined from the batch kinetics was not the same as the fluidised-bed k_f value, because this k_f value is a function of agitation speed which differed in the two kinetics studies. As shown in Figure 3.12, the plug-flow model could satisfactorily simulate the experimental data. This indicates that the fluidised-bed adsorption system followed the plug flow conditions, for example, no axial dispersion of adsorbate and the adsorbent in the bed was uniformly distributed. The results show that the parameter values for the three cycles were nearly equal for Dowex and Dowex-Fe, because in these experiments all the conditions such as filtration velocity, and nitrate influent concentrations were the same for both Dowex and Dowex-Fe.

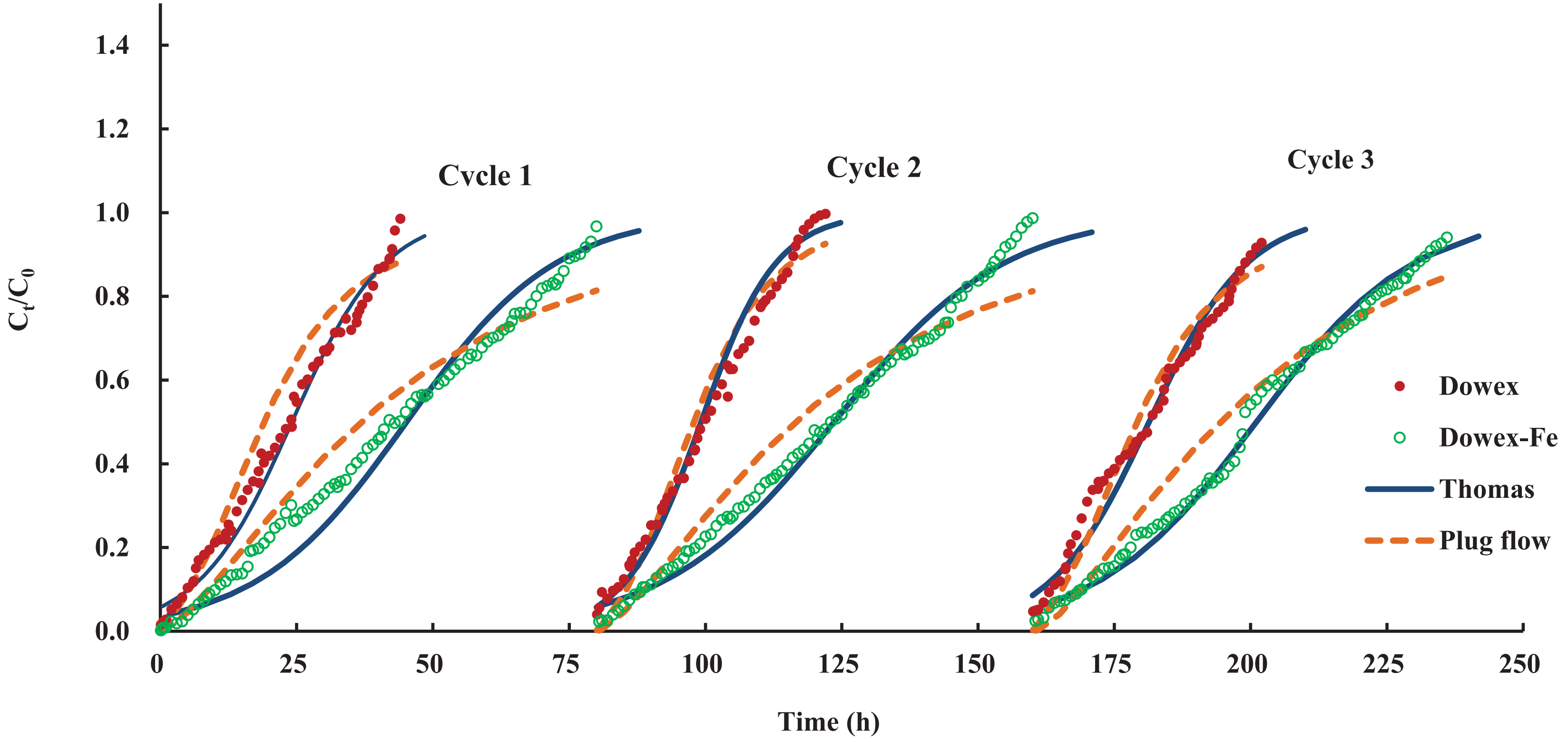

Figure 3.12. Breakthrough curves for nitrate before and after desorption of nitrate on Dowex and Dowex-Fe for synthetic water containing nitrate only for three cycles of adsorption/ desorption (initial concentration of synthetic water 20 mg N/L). Plug-flow and Thomas models fit to data are shown in dash and solid curves, respectively..

Table 3.11. Thomas and plug-flow models parameters for nitrate adsorption on Dowex and Dowex-Fe

Models	Parameters	Dowex			Dowex-Fe		
		1st cycle	2nd cycle	3rd cycle	1st cycle	2nd cycle	3rd cycle
Thomas model	k_{TH} (ml/min mg)	0.097	0.104	0.09	0.06	0.053	0.058
	q_0 (mg N/g)	21.5	18	19.1	35.2	34	32
	R^2	0.9529	0.9864	0.9633	0.9021	0.9658	0.9822
Plug- flow model	D_s (m^2/s) x 10^{-12}	1.81	2.37	1.8	1.97	1.97	1.97
	K_f (m/s) x 10^{-4}	1.22	1.22	1.22	3.97	3.97	3.97
	R^2	0.9599	0.9717	0.9717	0.9608	0.9574	0.9753

3.3.3.4. Sensitivity analysis

The sensitivity analysis was done for the three parameters D_s, $K_{f,}$ and D_{ax} to determine the influence on the adsorption behaviour. For this analysis the break through curve of the nitrate alone with the feed concentration of 20 mg N/L with the bed height of 15 cm was used as a reference and the parameters were increased by 1.5 times and decreased by 0.5 times from the reference curve. The Figure 3.13 shows the adsorption behaviour, sensitive on the intra-particle diffusivity, D_s and film mass transfer coefficient, k_f rather than axial dispersion coefficient $D_{ax.}$ So for the parameters which were sensitive with the changes should consider for the design purpose.

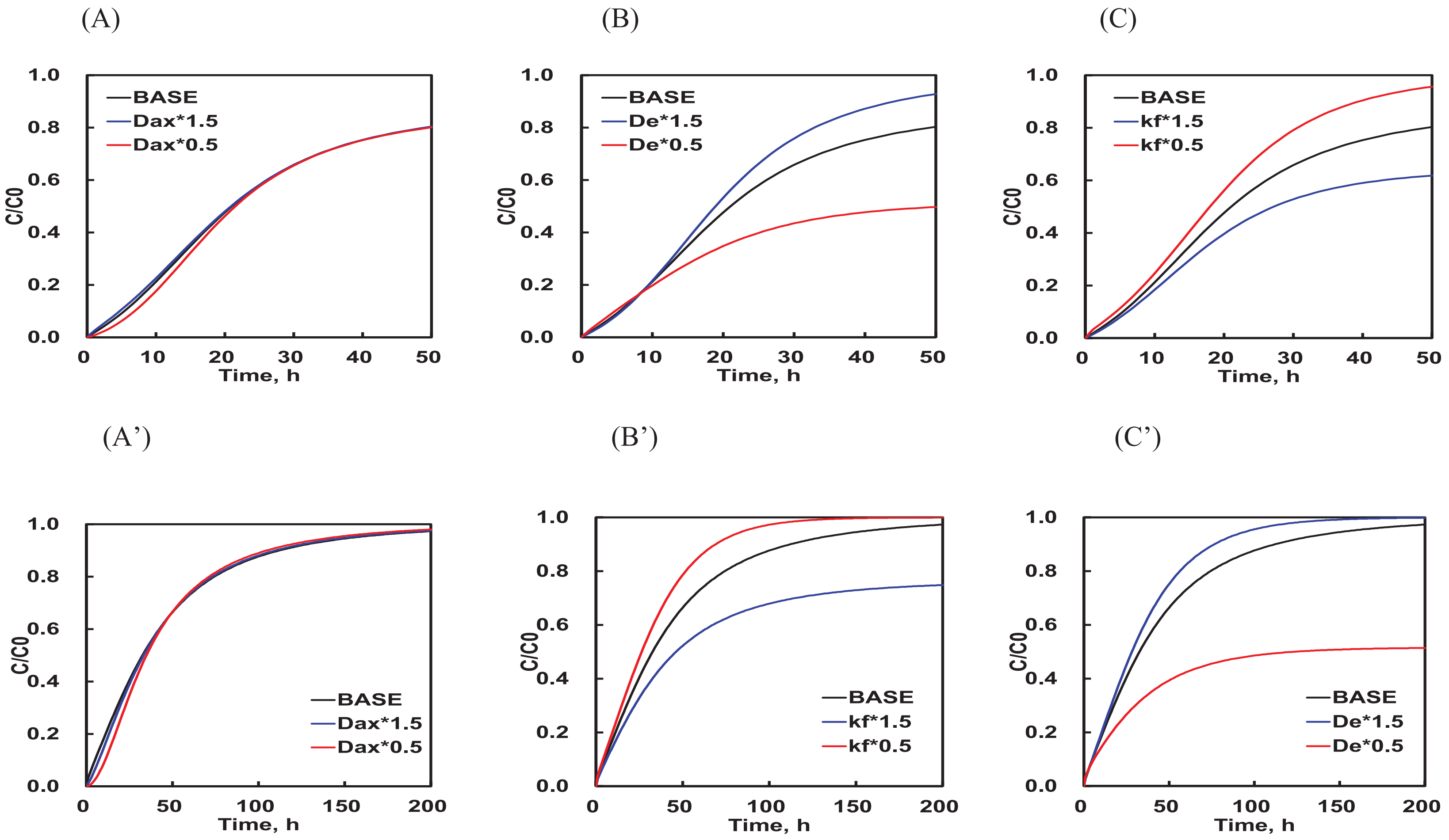

Figure 3.13. Effect of numerical model parameters on the adsorption breakthrough curve dowex and dowex+Fe: (A), (A') intra-particle diffusivity, (B),(B') axial dispersion coefficient , and (C),(C') film mass transfer coefficient.

3.4. Conclusions

Surface modification of Dowex 21K XLT anion exchange resin by incorporation of Fe (Dowex-Fe) increased the resin's nitrate adsorption capacity more than twice the original value. This increased adsorption capacity was explained using zeta potential measurements as due to increased surface positive charges induced by Fe. The Langmuir adsorption capacity of Dowex-Fe at an ionic strength of $1x10^{-3}$ M NaCl and pH of 6.5 was 75.3 mg N/g which is much higher than many of the values reported in studies involving other adsorbents. Both the batch and fluidised-bed adsorption experiments confirmed that the nitrate removal efficiency of Dowex and Dowex-Fe was markedly reduced by sulphate but only marginally reduced by chloride and phosphate. The two resins were successfully regenerated by desorbing more than 95% of nitrate adsorbed by leaching the resin beds with 1 M KCl. The adsorption capacities of the two resins decreased only very little after two successive regenerations. The high adsorption capacity and easy regeneration of Dowex-Fe for its repeated use makes it an attractive adsorbent for removing nitrate from water.

Batch equilibrium adsorption data of Dowex and Dowex-Fe was successfully modelled using the Langmuir, Freundlich and Sips models. The batch kinetic data fitted well to pseudo-first, pseudo-second, and homogeneous surface diffusion models. The fluidised-bed data was successfully modelled using the Thomas and plug-flow models.

CHAPTER 4

Enhanced removal of nitrate from water using amine-grafted agricultural wastes

UNIVERSITY OF TECHNOLOGY SYDNEY

CHAPTER 4

Enhanced removal of nitrate from water using amine-grafted agricultural wastes

4.1. Introduction

In Chapter 3, a commercially available anion exchange resin Dowex 21K XLT and iron-modified form of this resin were tested for nitrate removal in batch and column studies. Though, the anion exchange resins are promisable adsorbents with higher adsorption capacity, usable at wide range of pH has and has reusable characteristics, their costs are high and creates a disposal problem of the used adsorbent. Therefore, low-cost adsorbents such as agricultural wastes, natural adsorbents and industrial wastes have been given more attention to overcome the above problems during the last two decades.

Agricultural wastes have been investigated as adsorbents for the removal of contaminants from waste water (Loganathan et al., 2013a). Agricultural wastes are widely available at low cost with no disposal problems and therefore their use incurs low operational expense. In previous studies, a number of agricultural wastes such as rice hull, sugarcane bagasse, coconut shells, wheat straw and almond shell have been tested for the removal of nitrate from water. Another advantage of using agricultural wastes as adsorbent is that when they are fully saturated with nitrate and cannot be used further for the removal of nitrate the nitrate-rich wastes can be disposed to agricultural lands to supply nitrate as fertiliser.

One of the disadvantages of using agricultural wastes in removing nitrate is that they have low adsorption capacities. However, if they are chemically or physically

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This chapter was published in Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Ngo, H., Vigneswaran, S., 2016. Enhanced removal of nitrate from water using amine-grafted agricultural wastes. Science of the Total Environment. 565, 503-510.

modified they can prove to be good adsorbents (Loganathan et al., 2013a). Various methods of modification such as protonation (Chatterjee et al., 2009), metal impregnation (Namasivayam and Sangeetha, 2005) and amine-grafting (Orlando et al., 2002a; Orlando et al., 2002b) have been used to increase the nitrate adsorption capacity of adsorbents. Of these, the amine grafting method is a highly efficient method for agricultural wastes where the amine groups possessing positive charges can increase the adsorption of negatively charged nitrate (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a). For example, , Orlando et al. (2002a) reported that grafting amine groups onto lignocellulosic agricultural wastes such as moringa oleifera husk, rice husk, sugarcane bagasse, and pine bark resulted in high Langmuir nitrate adsorption capacities of 14.2-16.7 mg N/g. They stated that these increased adsorption capacities as a result of amine- grafting was approximately equal to that of the commercial anion exchanger, Amberlite IRA-900. Most studies on the use of agricultural wastes for nitrate removal were tested in static batch adsorption experiments (Bhatnagar and Sillanpää, 2011; Loganathan et al., 2013a), yet only a few have been tested using dynamic fixed-bed adsorption experiment (Xing et al., 2011; Xu et al., 2010b). Findings from fixed-bed experiments are more relevant to real operating systems in treatment plants.

The main objectives of the research were to: (i) study the efficiency of nitrate removal from synthetic water using amine-grafted (AG) corn cob and coconut copra in batch and fixed-bed adsorption experiments; (ii) model the batch equilibrium, batch kinetics and fixed-bed data on nitrate removal; (iii) study the effect of co-existing anions at different concentrations on the adsorption of nitrate; and (iv) investigate desorption of nitrate from the adsorbents and the regeneration of adsorbents for multiple reuse. The new aspect of the study is to test the nitrate adsorption behaviour of amine-grafted agricultural wastes in column mode dynamic system consisting of many repeated adsorption/desorption cycles which have more practical application. Further the mathematical modelling of the dynamic system used in this study has not been dealt previously for agricultural wastes. Though amine-grafting to increase the nitrate adsorption capacity is not new, previous studies on this subject were conducted mainly in static batch mode and only two studies on fixed-bed system (Xing et al., 2011; Xu et al., 2012). However, these two column studies neither tried to model the adsorption behaviour nor considered complementary ions effects on nitrate as in our study. Corn cob was selected as an agricultural waste as corn is one of the largest grain crops cultivated in many parts of the world with an annual worldwide production of about 520 x 10^9 kg (Ioannidou et al., 2009) and corn cob waste is available in large quantities. Coconut is one of the main palm trees cultivated throughout the tropical world to produce copra which is used to make vegetable oil (Bhatnagar et al., 2010). Large quantities of copra waste are available from the total annual coconut production of about 50 million tonnes in various countries.

4.2. Materials and methods

4.2.1. Materials

Fresh corns were obtained from Paddy’s Market in Sydney, New South Wales, Australia, and waste corn cobs were separated from the corn kernels. The corn cobs were cut into small pieces, washed with distilled water and heated for 24 h at 100^0C inside an oven. Then they were ground and sieved to a size of 300- 600 µm.

Fresh coconuts were also obtained from the same market and each coconut was cut into two pieces. The coconut kernels were scraped manually from these pieces and milk extracted by hand-squeezing as much as possible. The residue was kept in an oven at 100^0C for 48 h. The dried material known as copra was ground and sieved to 300-600 µm.

4.2.2. Material modification

Samples of the corn cob and coconut copra (300 - 600 µm) were surface modified by amine grafting using Orlando et al.'s method (Orlando et al., 2002a). In this method, 20 g corn cob or coconut copra were reacted with 200 ml of epichlorohydrin in 240 ml N, N-dimethyl formamide (DMF) at 100^0C for 1 h. Pyridine (80 mL) was added to the solution and stirred for 1 h at 100^0C. Amine groups were then introduced by adding 200 ml of 50% dimethylamine solution. The mixture was stirred for 3 h at 100^0C and washed with 2 L 0.1 M NaOH, 0.1 M HCl and 2 L diluted ethanol (ethanol: water volume ratio = 1:1). Finally, it was washed with a large volume of 0.1 M NaCl and heated at 100^0C for 24 h.

The preparation of feed solutions and nitrate analysis are same as described in Chapter 3.

4.2.3. Adsorbent characterization

Samples of dried corn cob, coconut copra, AG corn cob and AG coconut copra were analysed using Zeiss supra 55VP field emission model scanning electron microscope in conjunction with energy dispersion spectrometry operated at 15 kv to determine the elemental composition. The materials' BET surface area and pore size distribution were determined using a Micrometrics 3 Flex surface characterisation analyser at 77K. The total nitrogen and carbon were measured using a Leco TruSpec CN instrument. X-ray diffraction was conducted using a XRD Shimadzu S (6000) diffractometer. FTIR pattern was recorded using a Nicolet 6700 FT-IR spectrometer equipped with a room temperature DLaTGS detector and a Nicolet FT-IR Smart system with smart accessories using a Diamond crystal HATR.

Zeta potential measurement was done to characterise the surface electrical potential of the adsorbents. Unmodified and AG corn cob and coconut copra were suspended in Milli-Q water at a dosage of 1 mg/L and pH adjusted to various values in the 3-8 range using diluted HCl and NaOH solutions. The flasks were shaken at 120 rpm in a flat shaker for 3 h and then the zeta potential was measured on the suspensions using a Zetasizer nano instrument (Nano ZS Zen 3600, Malvern, UK). The measurements were conducted on three replicates and the means and standard errors were calculated.

4.2.4. Batch adsorption experiments

The batch equilibrium and adsorption kinetics experimental methods were same as explained in Chapter 3. All experiments were conducted in duplicate and the means and standard errors of the data of duplicate samples were calculated.

4.2.5. Effect of pH on nitrate adsorption

The experiment on the effect of pH on nitrate adsorption was carried out using the same procedure as described for equilibrium adsorption. The initial nitrate concentration was the same as before but only one adsorbent dose of 0.5 g/L and initial pHs of 3, 4, 5, 6, 7, 8 and 9 were used. The pH was adjusted by adding diluted HCl or NaOH. The final pHs were measured and these values were used to determine the relationship of pH and amount adsorbed.

4.2.6. Complementary ions effect

Studies on the complementary ions effect were done using different concentrations of sulphate (20, 30, 50, and 70 mg S/L), phosphate (0.5, 1, 5, 10 and 30 mg P/L) and chloride (20, 30, 50 and 70 mg Cl/L) with a fixed dose of adsorbent (1 g/L) and a constant concentration of nitrate (20 mg N/L) at pH 6.5. These three ions were selected for the study as they are common anions present in ground and surface waters (Akan et al., 2012; Shah and Trivedi, 2011; Shanmuganathan et al., 2014). The concentrations used were in the ranges of ions generally present in contaminated ground and wastewaters.

4.2.7. Fixed-bed adsorption studies

Fixed-bed column adsorption experiments were performed using 2 cm internal diameter acrylic glass columns packed with 20 g of modified and unmodified corn cob and coconut copra to a height of 15 cm. Influent solution containing nitrate at a concentration of 20 mg N/L was passed through the columns at a filtration velocity of 5 m/h (26.6 mL/min). A peristaltic pump was used for pumping the feed water in the up-flow mode through the column. The effluent solutions were collected on an hourly basis and nitrate was examined as before.

The maximum amount of nitrate adsorption (mg) onto the fixed-bed is defined by the equation given below (Nur et al., 2015),

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t-total} C_{ad} \, . dt \qquad (4.1)$$

where, C_{ad} is the adsorbed nitrate concentration ($C_{ad} = C_0 - C_t$) mg N/L and Q is the flow velocity (L/min). q_{total} is equal to the area under the plot of C_{ad} vs time and was calculated manually from the breakthrough curves using Microsoft Excel spreadsheet. The maximum adsorption capacity was calculated by dividing the maximum adsorption of nitrate by the amount of adsorbent used in the column.

4.2.8. Adsorption models

The batch and fixed-bed adsorption data were analysed using the adsorption models presented in Chapter 3 Table 3.1- 3.3 (Langmuir, Freundlich, Sips, Pseudo-first order, Pseudo-second order and Thomas model). The models not used in Chapter 3 (Elovich and axially dispersed plug-flow model), are presented below in Table 4.1.

Table 4.1. Adsorption models

Experiment	Models	Equation	Parameters
Batch kinetics	Elovich	$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$	α ,β
Column	Axially dispersed plug-flow model	$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - \frac{1-\varepsilon_b}{\varepsilon_b} \rho_p \frac{\partial q}{\partial t}$ Initial and boundary conditions $0 < z < L;\ \ t = 0;\ \ c = 0$ $z = 0;\ t > 0\ \ D_L \left.\frac{\partial c}{\partial z}\right\|_{z=0} = -v\left(\left.c\right\|_{z=0^-} - \left.c\right\|_{z=0^+}\right)$ $z = L;\ t > 0\ \ \left.\frac{\partial c}{\partial z}\right\|_{z=L} = 0$	D_L

* α = initial adsorption rate (mg/g min), β = related to extent of surface coverage and activation energy for chemisorption (g/mg), D_L = axial dispersion coefficient (m^2/s), c = nitrate concentration in the liquid phase (mg N/L), q = nitrate concentration in the solid phase (mg N/L), ϵ_B= bed porosity , ρ_p = bulk density (kg/m^3), v = fluid velocity (m/s) and z = bed depth (m)

4.3. Results and discussion

4.3.1. Characteristics of adsorbents

4.3.1.1. X-ray diffraction

X-ray diffraction data of unmodified and amine grafted corn cob (Figure 4.1) and coconut copra (Figure 4.2) showed that all materials were poorly crystalline (amorphous) which is characteristics of most agricultural wastes (Mafra et al., 2013).

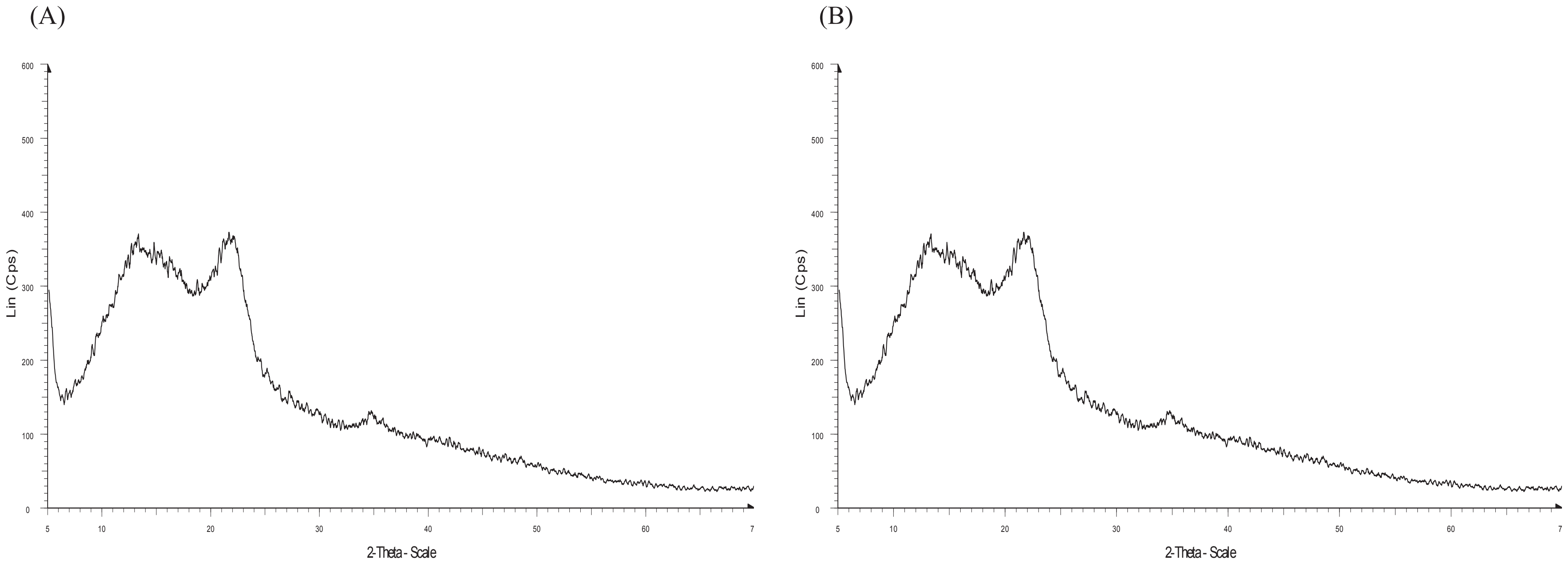


Figure 4.1. X-ray diffraction pattern of (A) unmodified corncob and (B) AG corn cob

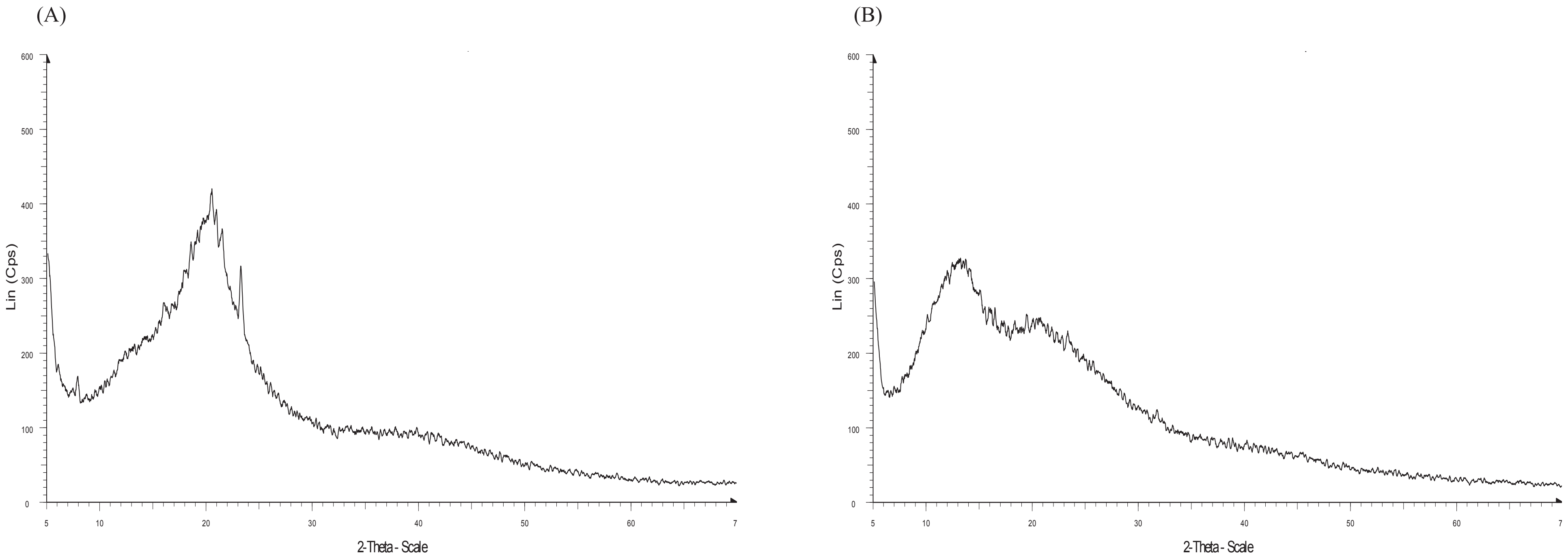


Figure 4.2. X-ray diffraction pattern of (A) unmodified coconut copra and (B) AG coconut copra

4.3.1.2. Chemical composition and surface area

The EDS data showed that the N content increased in the coconut copra and corn cobs after the amine modification (Table 4.2). The Cl percentage also increased because the AG materials were finally washed with large amounts of NaCl to remove the excess acid and alkali used in the preparation of these materials. The Cl^- ions in the NaCl would have adsorbed onto the positive charges on the amine groups by electrostatic attraction.

The total N contents of the materials estimated by chemical combustion method were much lower than those estimated by EDS. This is probably because EDS measures only the surface layer of a few micro meters of the adsorbents (Yao et al., 2011), whereas the combustion method measured the whole particle elemental composition. However, the increase in N content following amine grafting in the materials is approximately the same in the two methods. Xu et al. (2010a) reported virtually the same amount of N increased (32 mg/g) after amine grafting of wheat straw using the method used in the present study.

The BET surface areas were 10.3 m^2/g and 9.8 m^2/g for the corn cob and AG corn cob, respectively, and 8.1 m^2/g and 7.1 m^2/g for the coconut copra and AG coconut copra, respectively.

Table 4.2. Elemental composition of adsorbents as determined by EDS and chemical combustion methods and nitrate adsorption on the adsorbents

Adsorbent	EDS		Leco Chemical combustion	Batch adsorption
	Nitrogen (mg /g)	Chlorine (mg /g)	Nitrogen (mg /g)	Nitrogen (mg /g)
Corn cob	94.0	0	10.3	-
AG corn cob before adsorption	141.0	93	52.6	-
AG corn cob after adsorption	163.5	39	83.7	-
N adsorbed	22.5	-	31.1	34
Coconut copra	61.0	0	11.5	-
AG coconut copra before adsorption	113 .0	70	57.8	-
AG coconut copra after adsorption	168 .0	24	89.8	-
N adsorbed	55.0	-	32.0	39

4.3.1.3. Zeta potential

The unmodified corn cob and unmodified coconut copra both had a zero point of charge (ZPC) of approximately pH 3.0 whereas the AG corn cob and AG coconut copra had ZPC greater than pH 8.5 (Figure 4.3). This shows that amine grafting of the adsorbents has changed the surface charges on the adsorbent from negative to positive in the entire pH range of 3 to 8.5, which is favourable for nitrate adsorption by electrostatic forces. This is in agreement with the results of Deng et al. (2013) who found that the amine modification of rice husk increased the ZPC from pH 2.7 to 8.5, suggesting that the net surface charge was positive up to pH 8.5. Xing et al. (2011) also reported that amine grafting changed the surface charge from negative to positive in wheat straw in the pH range of 2 to 9.

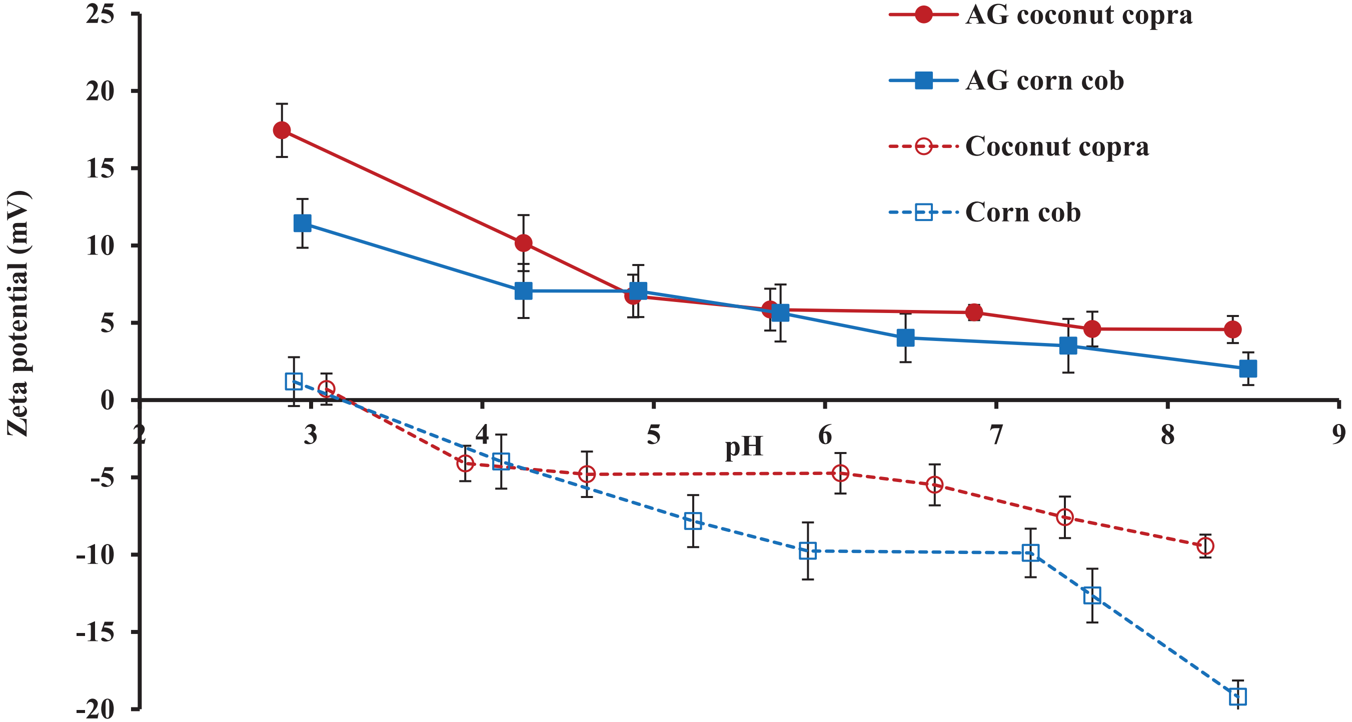
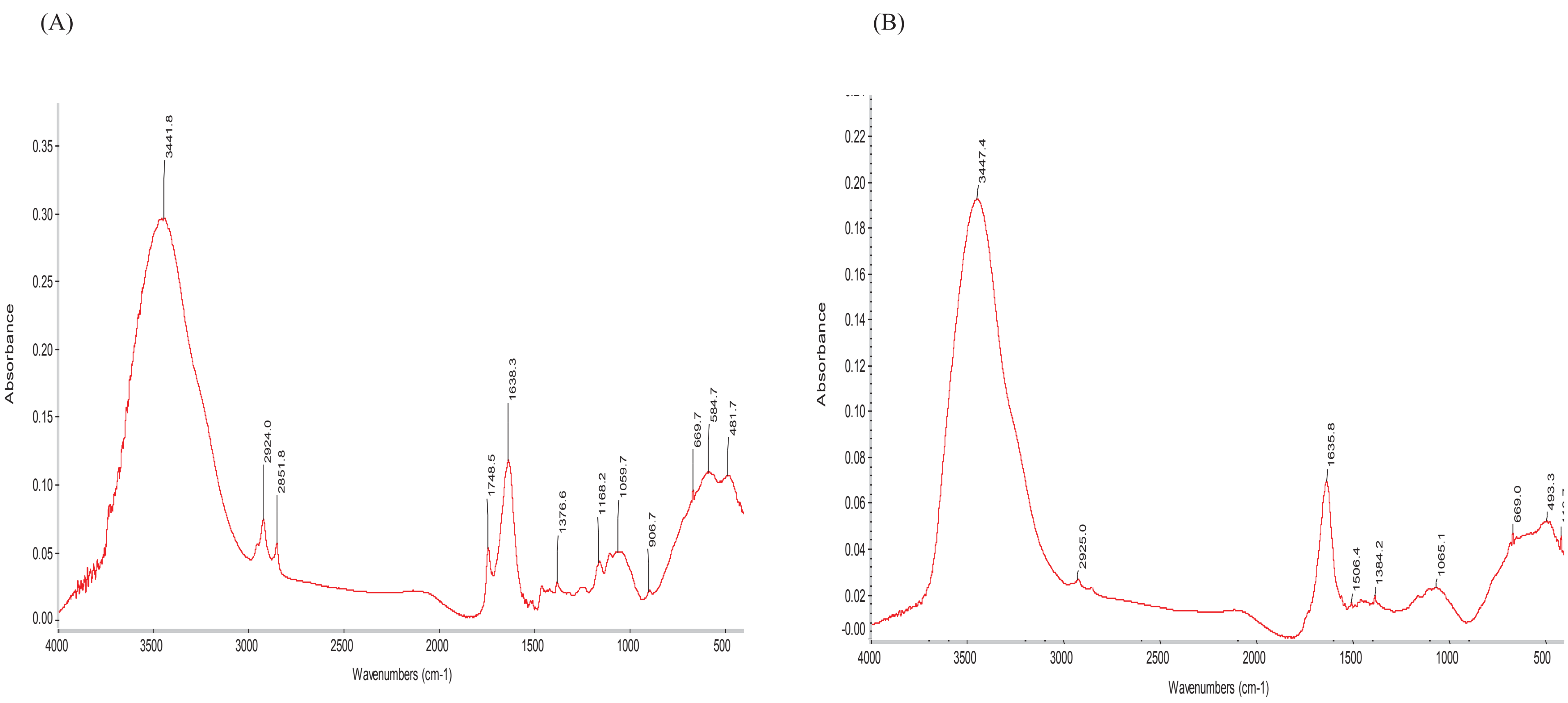


Figure 4.3. Effect of pH on the zeta potential at the adsorbent/solution interface for corn cob, AG corn cob, coconut copra, and AG coconut copra. Vertical bars on the graphs represent standard errors of means of the data points.

4.3.1.4. FT-IR spectra

The FT-IR spectra of amine grafted and unmodified corn cob and coconut copra are shown in Figure 4.4 and Figure 4.5, respectively. The huge peak at 3441 cm^{-1} for unmodified corn cob and 3450.7 cm^{-1} for unmodified coconut copra are responsible for -OH (Anirudhan et al., 2012; Tofighy and Mohammadi, 2012) or NH_2 stretching vibrations (Anirudhan et al., 2012; Garg et al., 2007). Because of the overlap of the vibration peaks of these chemical groups, it was not possible to ascertain whether the adsorption modification made by the amine group grafting of the adsorbents produced any significant increase in its peak. The peaks observed at the wave range 2850-2950 cm^{-1} can be assigned to the stretching vibration of the C-H group (Anirudhan et al., 2012; Saad et al., 2008). This C-H group vibration peak intensity reduced or disappeared in the both amine grafted adsorbents. This fading of peaks may be due to the acidification step in the modification process (Saad et al., 2007). Additional bands appearance in modified corncob at 1506.4 cm^{-1} and modified coconut copra at 1508.9 cm^{-1} are attributed to the amine group of aniline containing substances (Foschiera et al., 2001). Vibrations at 1638.3 cm^{-1} in unmodified corn and at 1636.6 cm^{-1} in unmodified coconut are also an N-H bend and its intensity was increased in modified coconut copra. The new aniline type peaks and increase in intensity of N-H bend peak in modified adsorbents are indication of successful amine grafting of adsorbents. The disappeared or reduced bands at 1748.5 cm^{-1} in corn cob and at 1743.5 cm^{-1} corresponds to C=O bond of acidic carbonyl group (Tofighy and Mohammadi, 2012).



(A)

(B)

Figure 4.4. FT-IR spectra of (A) unmodified corn cob and (B) AG corn cob

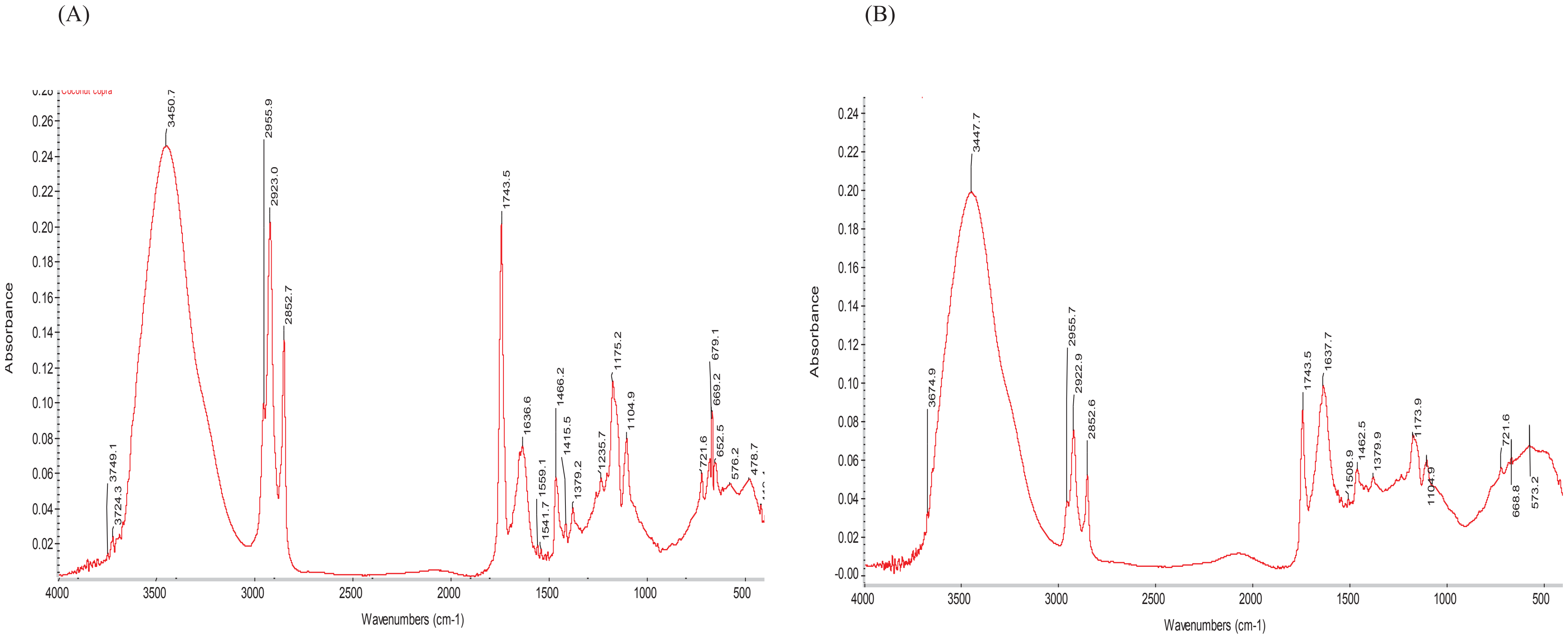


Figure 4.5. FT-IR spectra of (A) unmodified coconut copra and (B) AG coconut copra

4.3.2. Batch adsorption studies

4.3.2.1. Effect of pH

The effect of pH on nitrate adsorption showed that for the AG materials there was no significant change in the percent adsorption in the pH range from 3 to 9. The percentage adsorbed increased from 42% to 49% as the pH increased for the AG coconut copra and 37% to 45% for the AG corn cob. For the unmodified corn cob and the unmodified coconut copra, percentage adsorbed increased from 3% to 8% and 3% to 9%, respectively. The much higher adsorption capacity of the AG materials is due to the positive surface charges produced by the amine groups (Figure 4.6). The unmodified materials showed a very low percentage of adsorption because of net negative surface charges on the adsorbent surface.

4.3.2.2. Adsorption isotherms

The nitrate removal efficiencies of the AG adsorbents were much higher than those of the unmodified adsorbents (Figure 4.6). Langmuir, Freundlich and Sips models were used to model the experiment data. The data fitted satisfactorily to all the three models (Table 4.3). The Langmuir maximum adsorption capacities for the AG coconut copra and AG corn cob were 59.0 mg N/g and 49.9 mg N/g, respectively. The maximum adsorption capacities obtained for AG coconut copra and AG corn cob are higher than the corresponding values reported by others for amine grafted wheat straw, moringa hull, lauan sawdust, coconut husk, rice husk, pine bark and sugarcane bagasse (11-17 mg N/g; (Orlando et al., 2002b; Xu et al., 2010b). They are also higher than those reported for commercially available anion exchange resins such as Purolite A520 E (33 mg N/g) (Orlando et al., 2002b; Xu et al., 2010b), and NDP-2 (39.3 mg N/g), Purolite A 300 (33.3 mg N/g) and D201 (39.2 mg N/g) (Song et al., 2012). The corresponding values obtained from the Sips model were 67.4 mg N/g and 59.2 mg N/g, respectively. Nitrate adsorption on the unmodified adsorbents failed to fit the models.

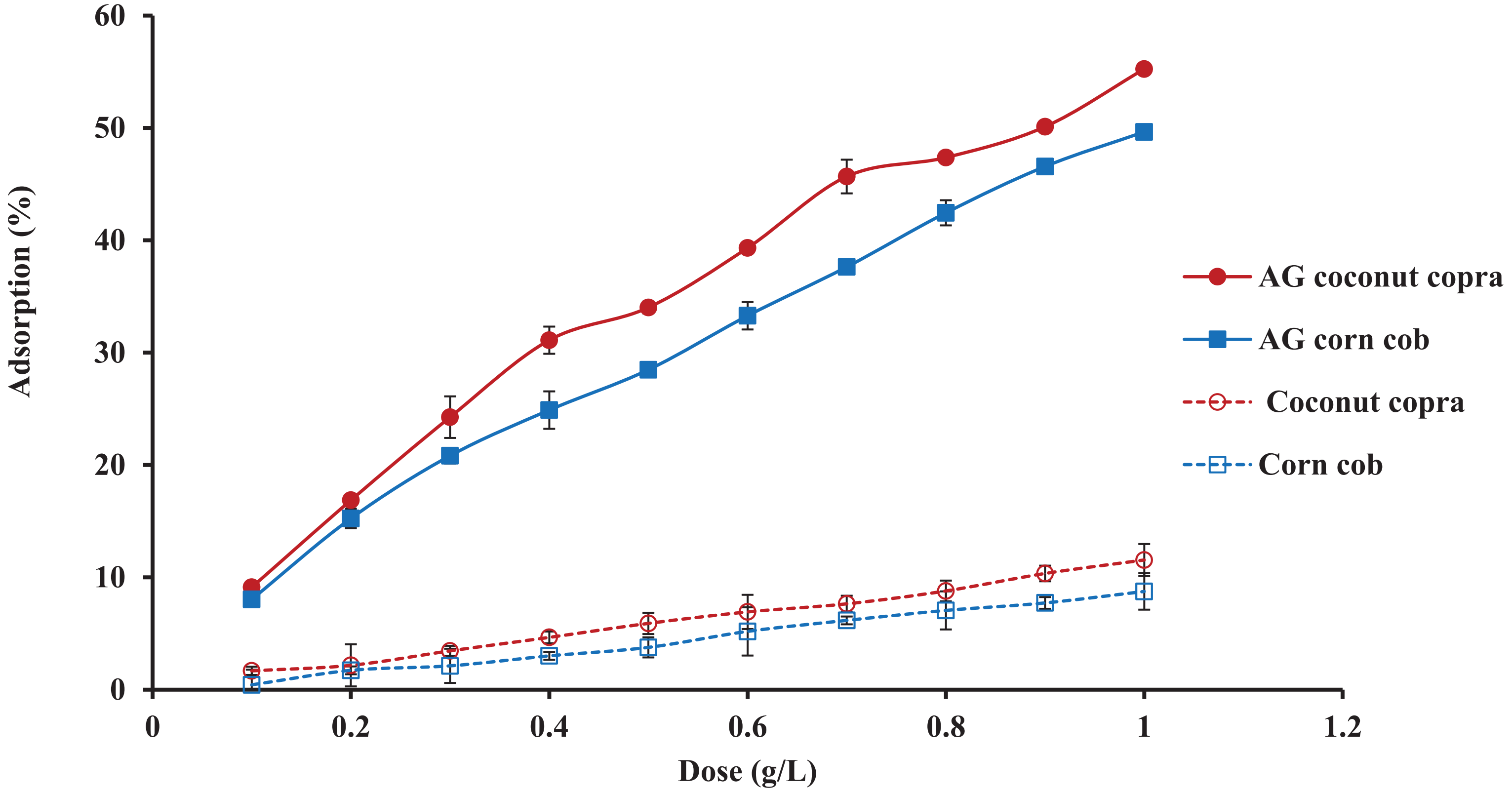


Figure 4.6. Effect of adsorbent dose on the removal of nitrate at pH 6.5 (initial nitrate concentration 20 mg N/L). Vertical bars on the graphs represent standard errors of means of the data points.

Table 4.3. Model parameters for the adsorption of nitrate

Model	Parameters	AG corncob	AG coconut copra
Langmuir	q_m (mg N/g)	49.9	59.2
	b (L/mg)	0.02	0.02
	R^2	0.8769	0.9606
Freundlich	k_f (mg/g)(L/mg)$^{1/n}$	1.24	2.07
	n	1.15	1.33
	R^2	0.9041	0.9615
Sips	q_m (mg N/g)	59.2	67.4
	b (L/mg)	0.01	0.02
	n	1.09	0.96
	R^2	0.8938	0.9610

4.3.2.3. Competition effects of anions

Figure 4.7 illustrates that nitrate removal efficiency drastically fell in the presence of sulphate ion and moderately decreased in the presence of phosphate and chloride ions. The adsorption occurred through the electrostatic attraction between positive surface charges on the adsorbent and negative charges on the anions by outer sphere surface complexation (non-specific adsorption) (Loganathan et al., 2014; Oladoja and Helmreich, 2014). Sulphate has two valance charges, and therefore it has a tendency to adsorb stronger than chloride which has one charge and phosphate which has predominantly one-charged species ($H_2PO_4^-$) and some two-charged species (HPO_4^{2-}) at pH 6.5 of the study. At pH 6.5 more than 80% phosphate is in the form of $H_2PO_4^-$ and the rest is in the form of HPO_4^{2-} (Pan et al., 2009). The differences in the magnitude of charges in the anions have also been used by Oladoja and Ahmad (2013) to explain the differences in the competitiveness of the anions for the adsorption of Cr(VI) on binary metal oxides. Because the chloride ion has one negative charge like nitrate its competition with nitrate was significant only at high concentrations especially in corn cob. The reason for the reduced competition of the chloride at concentrations similar to nitrate is that its hydration energy is higher than that of nitrate, and lower hydration energy favours adsorption (Song et al., 2012). Phosphate's competition with nitrate was the lowest because of its low concentrations in terms of moles/L. For example, only at L5 (30 mg P/L) is its competitiveness equal to that of chloride at L1 (20 mg Cl/L), where the concentrations (moles/L) of the two ions are nearly equal. The extent of complementary ions competition with nitrate adsorption may vary according to wastewater conditions and the concentration of complementary ions.

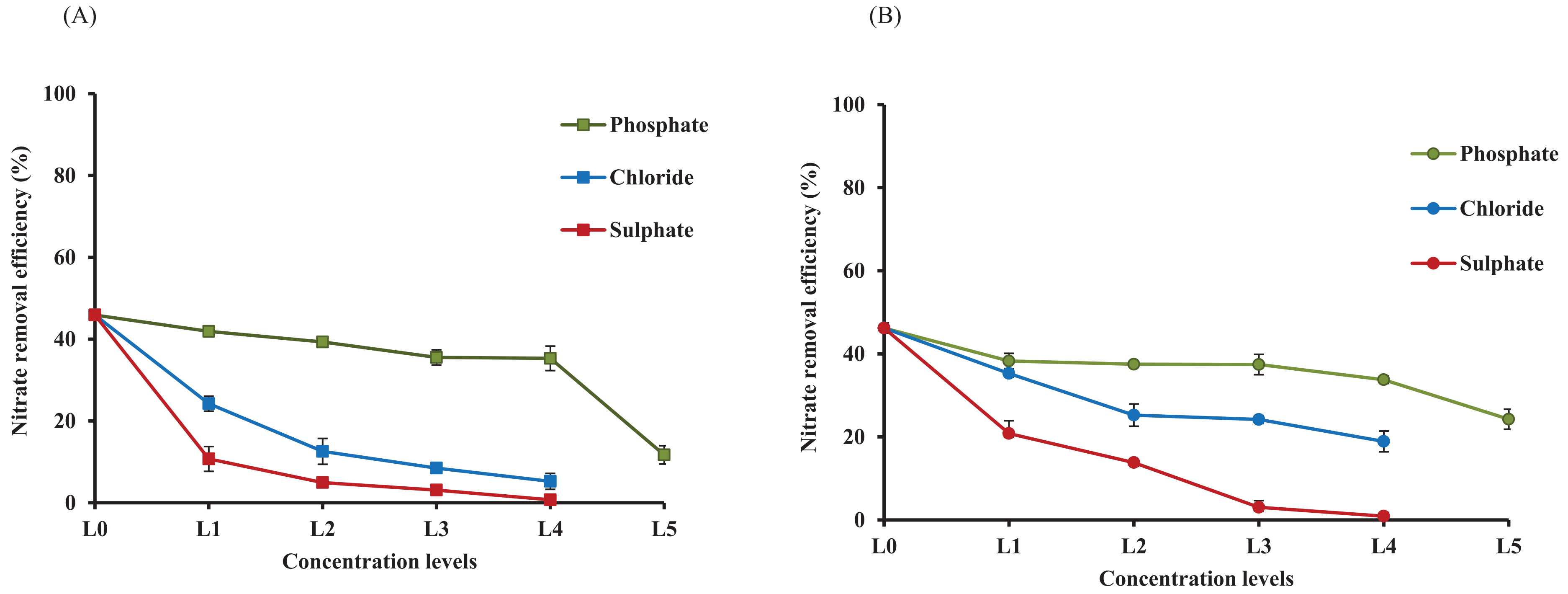


Figure 4.7. Effect of complementary ions on the removal of nitrate by (A) AG corn cob, and (B) AG coconut copra (initial nitrate concentration 20 mg N/L). L1, L2, L3, and L4 for sulphate chloride and sulphate are 20, 30, 50, and 70 mg Cl or S/L. For phosphate L1, L2, L3, L4, and L5 represent 0.5, 1, 5, 10, and 30 mg P/L. Vertical bars on the graphs represent standard errors of means of the data points.

4.3.3. Adsorption kinetics

The study on the adsorption kinetics was conducted to predict the rate of nitrate removal by the adsorbents. The data was fitted to pseudo-first order, pseudo-second order and Elovich models and the values for the model parameters are given in Table 4.4. Of the three models, the Elovich model fitted the data well for both the AG adsorbents (R^2 = 0.96-0.97), whereas the PFO and PSO models' fits to data were poor (R^2 = 0.46-0.81). The reason for the good fit of data to Elovich model is that this model is applicable to kinetics of adsorption of solutes on heterogeneous surfaces with variation of adsorption energies (Özacar and Şengil, 2005; Riahi et al., 2013). The surfaces of the agricultural wastes being heterogeneous (Riahi et al., 2013), this model was found to describe the adsorption kinetics very well.

Table 4.4. Batch adsorption kinetic parameters for the pseudo-first order (PFO) and pseudo-second order (PSO) models fit to the adsorption of nitrate on AG corn cob and AG coconut copra

Models	Parameters	AG corn cob	AG coconut copra
	q_{exp}	11.1	11.5
PFO	q_e (mg N/g)	10.3	10.4
	k_1 (/h)	19	14.8
	R^2	0.5208	0.4557
PSO	q_e (mg N/g)	10.7	11.1
	k_2 (g/mg h)	3.7	2.11
	R^2	0.8132	0.7654
Elovich	β (g/ mg)	1.33	0.91
	α (mg/ g min)	10886	250
	R^2	0.9707	0.9604

4.3.4. Fixed-bed adsorption experiment

4.3.4.1. Nitrate adsorption with and without complementary ions

Synthetic solutions were used for this study as in the case of the batch studies. However, the concentrations of nitrate and the complementary ions, phosphate and sulphate used were similar to those generally found in contaminated ground and wastewaters as stated earlier in this paper. The breakthrough curves for the nitrate adsorption on AG and unmodified corncob and coconut copra at the influent concentration of 20 mg N/L are given in Figure 4.8. The breakthrough curves for the unmodified adsorbents reached the adsorption saturation level faster (2 h and 3 h for the corn cob and coconut copra, respectively) than the curves for the AG adsorbents (12 h and 14 h for AG corn cob and AG coconut copra, respectively). This is due to the higher number of adsorption sites in the AG materials compared to the unmodified materials as explained under batch studies results.

The adsorption capacities were calculated from the breakthrough curves manually (Eq 4.1) and are shown in Table 4.5. Consistent with the batch adsorption results, the fixed-bed adsorption capacities for the AG adsorbents were very much higher than the unmodified adsorbents. While the AG corn cob adsorption capacity up to the saturation time of 12 h (400 bed volumes; bed volume = flow velocity (m/h) * time (h) / bed height (m)) was 15.3 mg N/g, the unmodified corn cob up to the saturation time of 2 h (66 bed volume) was 0.6 mg N/g. The AG coconut copra adsorption capacity was a little higher than that of the AG corn cob and was 18.6 mg N/g up to 14 h (460 bed volume) and 0.9 mg N/g for up to 3 h (100 bed volume) for the unmodified coconut copra. The fixed-bed adsorption capacities were lower than the batch Langmuir adsorption capacities, because in the batch experiments, adsorption reached equilibrium and Langmuir model predicted the maximum adsorption capacity at high nitrate concentration unlike in the fixed-bed experiment, where adsorption capacity was measured at a lower concentration of 20 mg N/L. Another reason for the lower nitrate adsorption capacity in the column experiment is the use of tap water in this experiment where the presence of chloride (30 mg /L) may have competed with nitrate for adsorption. In the batch experiment Milli-Q water with negligible concentrations of anions was used.

In the presence of complementary ions the complete breakthrough occurred at 1 h, 5 h and 8 h for the N+S, N+P and N feed, respectively, for the AG corn cob and 3 h, 6 h and 9 h for the AG coconut copra (Figure 4.9). The results showed that, when the complementary ions are present in the water less time was needed to reach saturation in the fixed-bed due to reduction in the nitrate's adsorption capacity. The sulphate ion competed most with nitrate adsorption resulting in a significant reduction in nitrate adsorption capacity as observed in batch studies. This is because it has more negative charges.

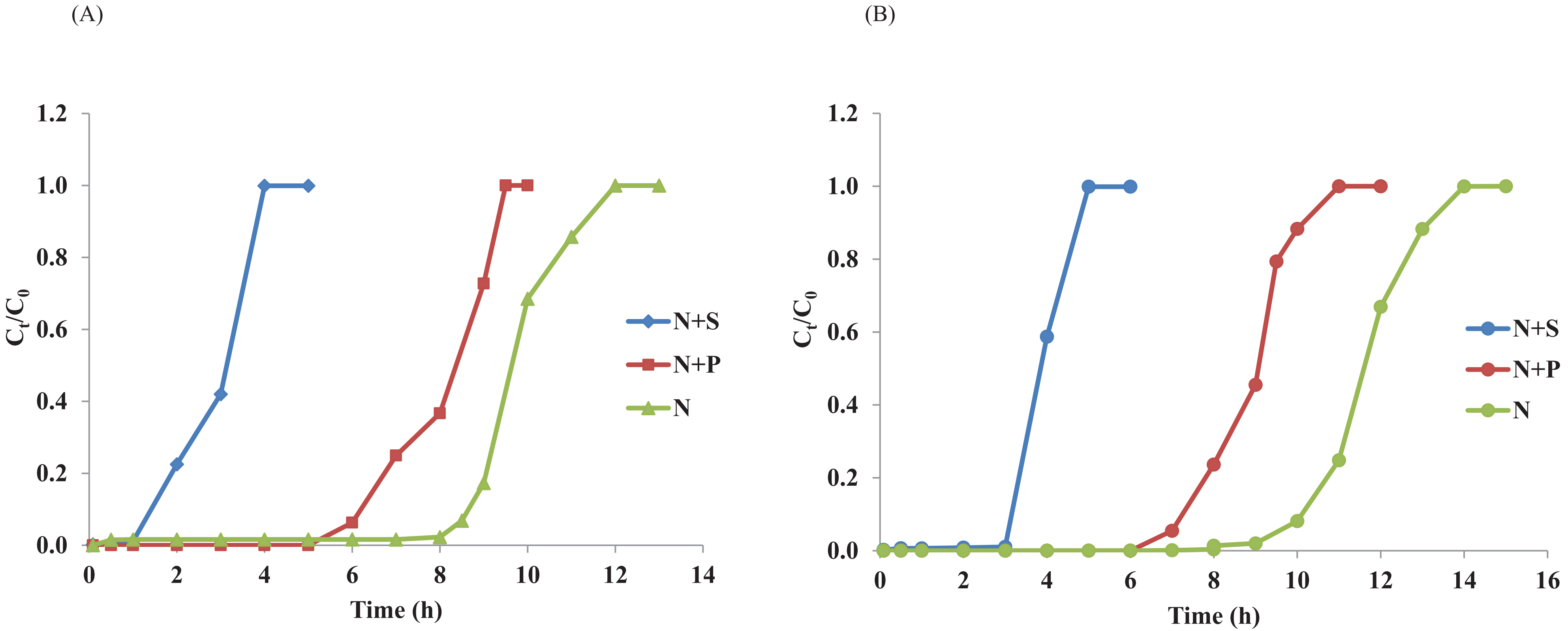


Figure 4.8. Breakthrough curves for nitrate adsorption on AG (A) corn cob and (B) coconut copra (influent solution contains 20 mg N/L, 20 mg N/L + 5 mg P/L, and 20 mg N/L + 50mg S/L).

4.3.4.2. Nitrate desorption and adsorbent regeneration

The regeneration of the adsorbents was carried out by leaching the adsorbed nitrate from the fixed-bed by 1 M KCl solution at a flow rate of 26.6 mL/min to desorb the nitrate from the adsorbents and determine whether the adsorbents can be reused. Results showed that the high concentration of chloride ions displaced the nitrate from the adsorption sites. Four adsorption-desorption cycles were conducted for the influent solution containing nitrate alone (Figure 4.9). 97-100% of the adsorbed nitrate was desorbed during the adsorption-desorption cycles for the AG corn cob and AG coconut copra adsorbents (Table 4.5). The number of bed volumes of 1 M KCl required for desorption of nitrate was 35-40 compared to the number of bed volumes required for adsorption of 300-460 (Table 4.5). This means the desorbed solution was about 10 times concentrated than the influent nitrate concentration. When the volume of the desorbing KCl solution was reduced to half (16 bed volumes), the amount of nitrate desorbed was still high at 76-86% (Table 4.5). Thus the cost of the desorbing reagent can be cut down by half with only 20-30% reduction in desorption. Chloride concentration in the desorbed solution is also cut down by half which may cause less or no damage to crops if the desorbed solution is used as nitrate fertiliser. The nitrate adsorption capacity dropped by approximately 30% in the second cycle and then marginally decreased thereafter for each cycle for both the adsorbents. Thus, the AG corn cob and coconut copra can be reused several times by maintaining good adsorption capacity for nitrate adsorption, reducing operational costs. Alternatively, the used bio adsorbents can be used as fertiliser. The nitrate in the desorbed solution can be used in fertigation to supply nitrogen to plants. The K in the desorbed solution will also benefit plants.

Table 4.5. Nitrate adsorption capacity of AG and unmodified corn cob and coconut copra and percentage of nitrate desorbed for different adsorption/desorption cycles

Adsorbents	Feed Concentration	Number of adsorption-desorption cycles	Adsorption bed volumes*	Adsorption capacity (mg N/g)	Amount of N adsorbed (mg)	Amount of N desorbed (mg)	% Desorbed	Desorption bed volumes*	Desorption % at half the bed volumes*
Corn cob	20 mg N/L	1	66	0.6	11	10	83.9	16	72
AG corn cob	20 mg N/L	1	400	15.3	307	305	99.9	40	78
		2	300	11.3	227	224	99.2	35	84
		3	300	10.7	215	215	99.9	35	86
		4	300	10.7	213	212	99.6	35	86
	20 mg N/L + 5 mg P/L	1	315	12.7	255	242	95.1	33	81

Table 4.5 (Continued)

	20 mg N/L + 50 mg S/L	1	132	3.9	79	70	88.9	25	83
Coconut copra	20 mg N/L	1	100	0.9	17	15	84.6	16	74
AG coconut copra	20 mg N/L	1	460	18.6	372	366	98.3	40	76
		2	360	12.9	259	251	96.9	40	80
		3	360	12.5	251	250	99.8	40	84
		4	360	11.6	232	231	99.3	40	84
	20 mg N/L + 5 mg P/L	1	365	14.1	282	274	97.2	33	79
	20 mg N/L + 50 mg S/L	1	165	5.7	114	107	93.8	25	82

* Bed volume = Flow velocity (m/h) * time (h) / bed height (m)

4.3.4.3. Fixed-bed column modelling

To properly design the adsorption process, one needs to clearly understand the relationship between the adsorption equilibrium, intra particle diffusion and hydrodynamic condition of the fixed-bed column. In this work, the axially dispersed plug-flow model with several correlation parameters were used to predict the fixed-bed column behaviour. In addition, the Freundlich isotherm parameters (Table 4.3) were used to explain the adsorption equilibrium at solid/liquid interfaces.

The main parameters controlling the fixed-bed adsorption characteristics are axial dispersion and the external film mass transfer coefficients. Regarding axial dispersion, the adsorption front axially increases due to flow in the inter particle voids. It is derived from the contribution of the molecular diffusion and dispersion caused by the fluid flow. The adsorbate diffuses from the bulk liquid phase to the stagnant boundary layer of the adsorbent external surface which is referred to as the film mass transfer. The axially dispersion coefficient (D_L) parameter values determined using equation 2.31 were 3.5×10^{-6} and 3.4×10^{-6} m/s for the AG corn cob and AG coconut copra, respectively, for the first adsorption/desorption cycle. The film mass transfer coefficient (k_f) values were obtained using equation 2.32. These values were 4.3×10^{-3} and 2.2×10^{-3} m/s for the AG corn cob and AG coconut copra, respectively, for the first adsorption-desorption cycle. The surface diffusion coefficient (D_S) was determined by matching the simulation values with the experimental adsorption values obtained from the breakthrough curve. The D_s values for the corn cob and AG corn cob were 1.96×10^{-9} and 1.64×10^{-10} m^2/s, respectively, and 1.58×10^{-9} and 1.28×10^{-10} m^2/s for the coconut copra and AG coconut copra, respectively, for the first adsorption/ desorption cycle.

To predict the adsorption breakthrough curves for the 2nd to the 4th adsorption/desorption cycles, the assumption was further taken that the parameter values are the same for all the cycles, even though adsorption capacity of the AG materials for the 2nd to 4th cycles decreased around 20-30% of the 1st cycle. The model parameters D_s, k_f and D_L depend on the influent concentration and/or filtration velocity which are the same for all the cycles. Therefore the assumption that the parameter values are same for all the cycles is reasonable.

As shown in Figure 4.9, the axially dispersed plug-flow model reasonably fitted the adsorption breakthrough curve patterns, even though some deviations were observed for the 2nd to 4th cycles, probably because the adsorption capacity decreased from the values of the first cycle and the ratio of the adsorption capacity decrease was utilised in the model prediction. In comparison to this finding, our recent study on nitrate adsorption by Fe-coated Dowex ion exchange resin showed that the adsorption capacity remained nearly the same during three adsorption/desorption cycles and plug-flow model satisfactorily fitted to the data of all the three cycles (Chapter 3).

The empirical Thomas model was also used to predict the fixed-bed experimental results. The model equation and the parameter values are given in Table 3.3 and Table 4.6, respectively. This model fit to the data was better than that of axially dispersed plug-flow model, especially for the second cycle onwards. The Thomas model adsorption capacities (q_0) agreed well with the adsorption capacities, calculated manually from the breakthrough curve (Table 4.6).

Table 4.6. Thomas model parameters for the adsorption of nitrate ion in fixed-bed containing corn cob, coconut copra, AG corn cob and AG coconut copra for different adsorption-desorption cycles.

Models	Parameters	Corn cob	AG corn cob				Coconut copra	AG coconut copra			
		1st cycle	1st cycle	2nd cycle	3rd cycle	4th cycle	1st Cycle	1st cycle	2nd cycle	3rd cycle	4th cycle
Thomas model	k_{TH} (ml/min mg)	2.58	1.59	2.84	2.46	5.15	1.45	1.19	1.53	1.54	1.28
	q_0 (mg N/g)	0.83	15.4	10.34	10.88	10.41	0.95	18.12	12.76	13.71	13.2
	R^2	0.974	0.9825	0.9624	0.9623	0.9669	0.9921	0.9786	0.9832	0.9584	0.9717

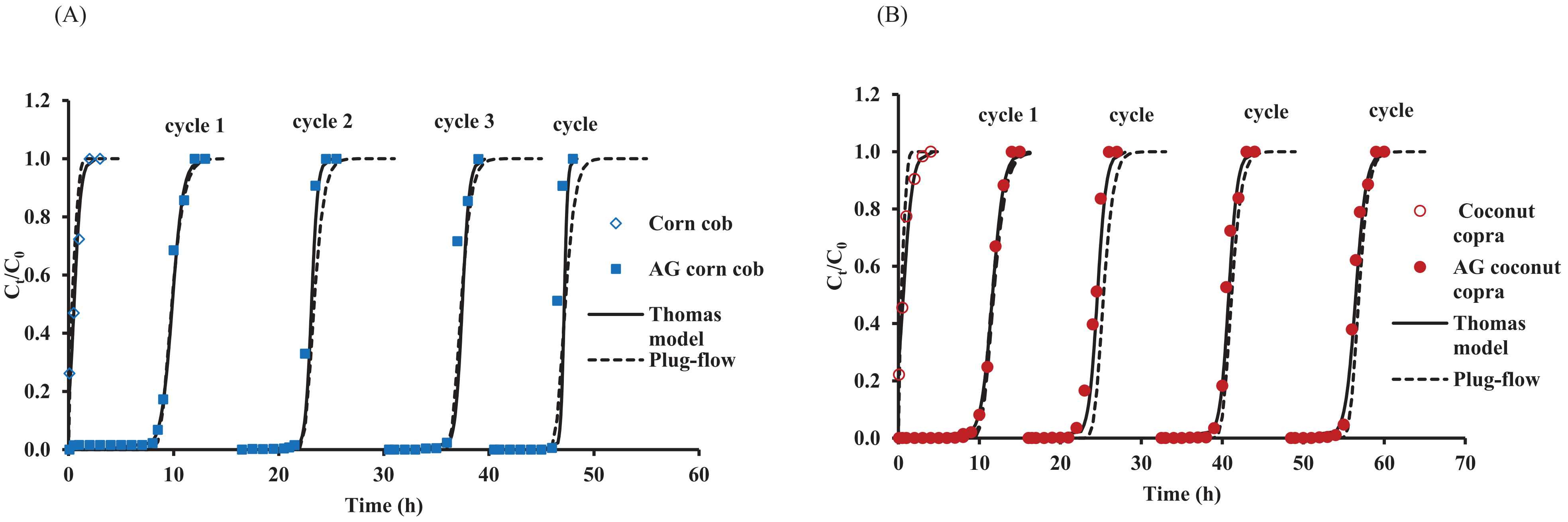


Figure 4.9. Breakthrough curves for nitrate adsorption on AG (for 4 adsorption/ desorption cycles) and unmodified (A) corn cob and (B) coconut copra (nitrate only in influent solution.

4.4. Conclusions

Amine-grafted (AG) biosorbents such as corn cob and coconut copra are very effective in removing nitrate from water. They have adsorption capacities many times higher than those of the respective unmodified materials. The Langmuir maximum adsorption capacities (mg N/g) of AG corn cob (50) and coconut copra (59) are also higher than many of the other amine-grafted biosorbents (15-17) and commercially available ion exchange resins (28-39) reported in literature. They are attractive low-cost biosorbents that can be used in many countries, especially in rural areas where large quantities of these wastes are produced. The used adsorbents can be directly applied to lands as nitrate fertilisers and the desorbed nitrate solution containing K can be used in fertigation to supply nutrients (N and K) to plants. Mathematical models developed for fixed-bed column mode adsorption behaviour can be successfully used in designing full-scale treatment plant. It is recommended that this study with synthetic solutions be extended to real ground and surface waters contaminated with nitrate.

CHAPTER 5

Submerged membrane adsorption hybrid system using four adsorbents in removing nitrate from water

CHAPTER 5

Submerged membrane adsorption hybrid system using four adsorbents to remove nitrate from water

5.1. Introduction

In Chapter 3 and Chapter 4 the nitrate adsorption characteristics of the anion exchange resin Dowex, Fe modified Dowex and agriculture materials corn cob and coconut copra with and without amine grafting on the materials were discussed. The adsorption studies presented in those chapters were conducted in static batch and dynamic column mode experiments. This Chapter is presenting the results obtained in another dynamic adsorption system called submerged membrane adsorption hybrid system (SMAHS) used for nitrate removal. In this chapter, all those four adsorbents were used and their performances were compared under different flow rate of water.

Adsorption integrated with membrane filtration is a currently developing water treatment process. Membrane filtration with micro-filter and ultra-filter systems require considerably less energy and it also has the advantages such as producing high quantities of good quality water with controllable membrane fouling, and incurring low capital and operational costs. Although the micro filter membrane fails to remove nitrate, it can remove colloids, macro molecules, micro particles, microorganisms. It also separates the adsorbent particles from the water stream (Guo et al., 2005).

The benefits of this submerged membrane adsorption hybrid system is that the adsorbent particle size can be small so that high adsorption capacities are achieved. This is in contrast to the commonly used column mode of adsorption where very small sized adsorbents reduce the flow rate and require more energy to pump the feed water.

This chapter is submitted to Kalaruban, M., Loganathan, W., Kandasamy, J., Vigneswaran, S., 2016. Submerged membrane adsorption hybrid system using four adsorbents in removing nitrate from water. Environmental Science and Pollution Research.

Furthermore, the fine particles can clog the filter beds in columns causing increased pressure heads. This clogging problem is significantly reduced in SMAHS, because the particles are kept in suspension by pumping air into the system. The adsorbent particles in this system provide mechanical scouring on the membrane surface and remove deposits from the membrane. Consequently there is less membrane fouling and the operational time increases (Johir et al., 2011; Johir et al., 2013).

Most of the previous SMAHS studies have mainly focused on the removal of metals (Bryjak et al., 2008), phosphate (Johir et al., 2016), colour and reactive dyes (Lee et al., 2006), and organic micropollutants (Shanmuganathan et al., 2015b). To our knowledge, no studies have yet reported on nitrate removal using SMAHS. The length of treatment time varied in these SMAHS studies with some experiments conducted on a short-term (6 h) (Shanmuganathan et al., 2015b) and long-term period (14 days) basis with partial replacement of adsorbents (Shanmuganathan et al., 2015a). The partial replacement of adsorbent helps to prevent cake formation on the membrane surface, resulting in reduced transmembrane pressure (Smith and Vigneswaran, 2009) as well as providing fresh adsorption sites for the removal of additional nitrate.

The SMAHS performance depends on the adsorbent’s capacity to remove pollutants, adsorbent dose, reactor configuration, operation condition such as water flux and feed water characteristics (Vigneswaran et al., 2003). High flux of water reduces operation costs due to large amounts of water being treated in a short period of time. However, because the hydraulic retention time is short the removal efficiency of pollutants can decrease with increasing flux. Also, the high flux can cause the rate of fouling on the membrane to increase. However, applying aeration to the adsorbent suspension keeps the adsorbent particles dispersed in the reactor and helps to reduce the solid deposition on the membrane surface by the air scouring effect.

The adsorbents used in this study were ion exchange resin Dowex 21K XLT, iron-modified Dowex (Dowex-Fe), and modified bio-adsorbents, specifically amine-grafted (AG) corn cob and AG coconut copra. These adsorbents have proved to be suitable for nitrate removal in our previous research using batch and column modes experiments (Chapter 3 and 4).

The objectives of the research were to: (i) compare the nitrate adsorption performance of the ion exchange resin, Dowex, iron-coated Dowex (Dowex- Fe), amine grafted (AG) corn cob and AG coconut copra in a SMAHS with frequent adsorbent replacement under four filtration flux; and (ii) determine the volume of water that can be treated to produce high quality water (nitrate concentration below the recommended WHO limit). This research is new because hitherto no SMAHS experiment under continuous operation with small amounts of adsorbent replacement has been reported for removing nitrate from water.

5.2. Experimental

5.2.1. Materials

5.2.1.1. Adsorbents

The anion exchange resin Dowex 21K XLT, iron-modified Dowex 21K XLT (Dowex-Fe), AG corn cob and AG coconut copra served as adsorbents. Characteristics of these adsorbents were described in previous chapters. They are summarized in Table 5.1. The preparation of feed solution is same as described in Chapter 3.

Table 5.1. Characteristics of the adsorbents (Chapter 3 and 4).

Adsorbent	Particle size (μm)	Zero point of charge pH	Langmuir adsorption capacity (mg N/g)	Column adsorption capacity* (mg N/g)
Dowex-Fe	300-1200	-	75.3	31.4
Dowex	300-1200	-	27.6	18.6
AG coconut copra	300-600	> 8.5	50.2	18.6
AG corn cob	300-600	> 8.5	49.9	15.3

*Nitrate initial concentration 20 mg N/L; Flow velocity 5 m/h, Initial dry bed height 15 cm. Adsorption capacity calculated at column saturation (complete breakthrough of nitrate).

5.2.1.2. Membrane characteristics

A hollow fibre membrane with the specifications of 0.1 μm nominal pore size and 0.1 m^2 surface area was used. It consists of hydrophilic modified poly acrylic nitrile (PAN) type membrane with 1.1 mm inner and 2.1 mm outer diameter. This product is manufactured by Mann+Hummel Ultra –Flo Pty Ltd, Singapore.

5.2.2. Methodology

5.2.2.1. Submerged membrane adsorption hybrid system (SMAHS)

The experiments were carried out in a dynamic system with a continuous mode operation which can be applied in a real practical process. The membrane was submerged into the reactor and the adsorbents were added to the water. The adsorbent performance was evaluated in terms of volume of treated water and the amount of nitrate adsorption. Figure 5.1 is a schematic diagram of the SMAHS. The water volume was maintained at 4 L in the reactor. A peristaltic pump was used to feed the influent to the reactor and periodically remove effluent from the tank at a controlled flux. The effect of filtration flux was studied by varying the flux at 2.5, 5, 10 and 15 L/m^2h. 10 g adsorbent was initially added to the reactor and 2 g of adsorbent was replaced each time when the effluent reached the WHO nitrate concentration limit of 11.3 mg N/L. This was done by removing a measured volume of suspension, filtering the adsorbent contained in it and adding fresh adsorbent equal to the weight of adsorbent removed from the filtered water. The transmembrane pressure (TMP) was continuously measured using a pressure transducer (PTX 1400 Druck Industrial Pressure Sensor, Druck Limited, UK). Air was pumped at a rate of 3.5 L/min to keep the adsorbent particles in suspension. The membrane was cleaned using 0.4% NaOCl before commencing each experiment. Nitrate analysis is described in Chapter 3.

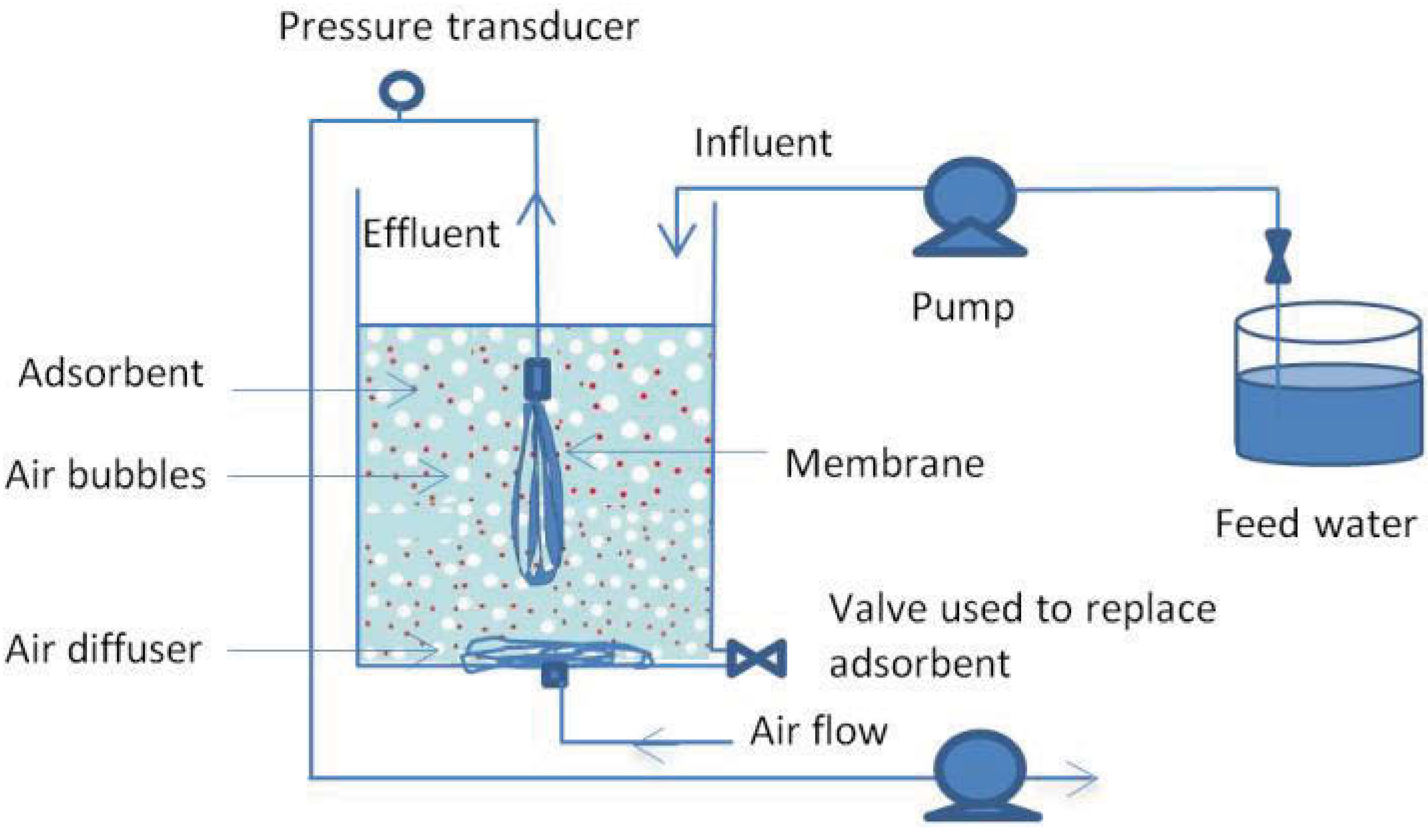


Figure 5.1. A schematic diagram of the submerged membrane adsorption hybrid system used

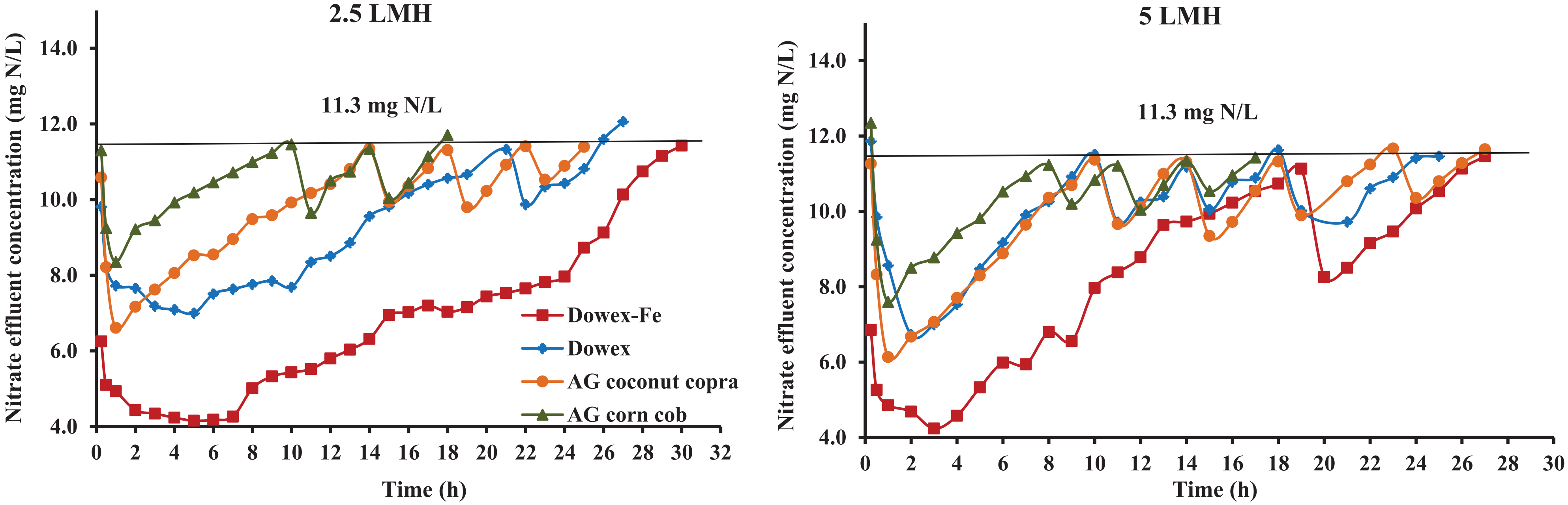
5.3. Results and discussion

5.3.1. Nitrate adsorption

Nitrate adsorption capacities of the four adsorbents for all the flux conditions in the SMAHS (Table 5.2) were much lower than the Langmuir adsorption maxima for the respective adsorbents obtained in a previous batch study (Table 5.1). The adsorption capacities obtained in a previous column study were also lower than those in the batch study (Table 5.1). The reason for the lower adsorption capacities in SMAHS and column studies is the higher mass transfer limitations in these studies. The higher mass transfer limitations are due to the lower concentration gradient between the nitrate in solution and the solid surface as well as the shorter contact time between the nitrate and the adsorbent. The intense agitation in the batch study resulted in longer and closer contacts. Furthermore, the Langmuir adsorption capacity represents the maximum adsorption capacity which was calculated at a much higher nitrate concentration than the concentrations used in the SMAHS and column studies. However, the mass transfer limitation in the column study can be reduced by either increasing the feed nitrate concentration or reducing the flow rate of the solution as reported for phosphate adsorption on Zr-loaded okra (Nguyen et al., 2015) and nitrate adsorption onto an ion exchange resin (Nur et al., 2015).

The nitrate removal efficiency in the SMAHS was in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob for all the flux conditions (Table 5.2; Figure 5.2). This order is slightly different from the Langmuir maximum adsorption capacities determined in batch experiments where the order was Dowex-Fe > AG coconut copra > AG corn cob > Dowex (Table 5.1). However, the adsorption capacities determined in column experiments had the same order as in the SMAHS experiments (last column of Table 5.1). The reason for Dowex having higher adsorption capacity than the bio-adsorbents in SMAHS and column experiments is that chloride in tap water used in these experiments might have competed with nitrate for adsorption in the case of bio-adsorbents. In the batch experiment, Milli-Q water was used and consequently no chloride was present to compete with nitrate. The tap water contained 30 mg /L concentration of chloride ions. The co-ions effect studies revealed that the efficiency of removing nitrate declined considerably in the presence of chloride for bio-adsorbents but only slightly for Dowex (Figure 5.3). Although the phosphate concentration in tap water was also high (1 mg P/L) it did not reduce the efficiency in removing nitrate much for all the adsorbents (Figure 5.3). Chapter 3 and 4 also reported that phosphate had low affinity for these adsorbents. Sulphate which competed with nitrate in those studies had low concentration in tap water (0.04 mg S/L) and therefore it might not have affected nitrate adsorption in the present study.

The amount of nitrate adsorption increased with flux for all the adsorbents (Figure 5.4). Mass balance of nitrate during the experimental period showed that increase of flux increased the amount of nitrate removed mainly because at increased flux, the amount of nitrate that entered the reactor per unit time increased (Table 5.2). Because both the nitrate input and removal increased at approximately similar rates, the percentage removal remained nearly the same. The rate of nitrate removal also increased with flux (Table 5.2). This is due to higher mass transfer of nitrate at higher flux as a result of more nitrate ions contacting the adsorption sites per unit time, though the retention time decreased with increased flux. Retention times of nitrate were 16, 8, 4, and 2.7 h at 2.5, 5, 10, and 15 L/m^{2}h. The fact that nitrate adsorption increased with flux shows that retention time is less important compared to the total amount of nitrate flowing through the reactor, and therefore the latter is the overall factor controlling the adsorption.


2.5 LMH
Nitrate effluent concentration (mg N/L)
14.0
12.0
10.0
8.0
6.0
4.0
11.3 mg N/L
Dowex-Fe
Dowex
AG coconut copra
AG corn cob
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
Time (h)
5 LMH
Nitrate effluent concentration (mg N/L)
14.0
12.0
10.0
8.0
6.0
4.0
11.3 mg N/L
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
Time (h)

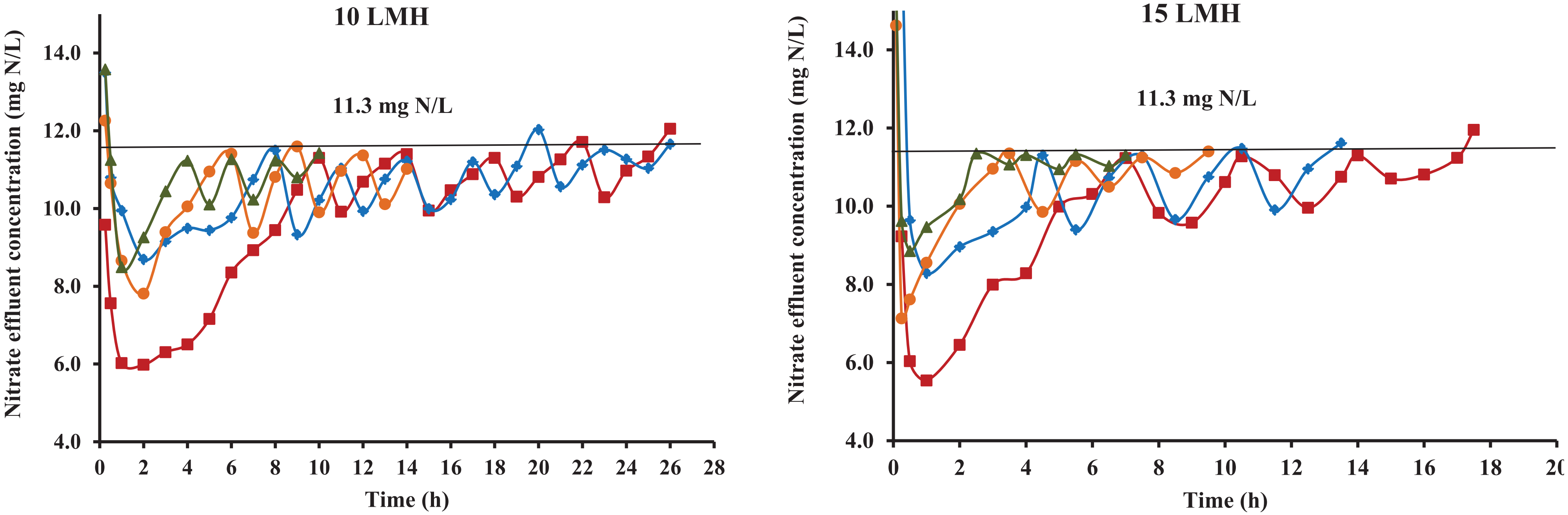


Figure 5.2. Comparison of adsorbents' performance in maintaining nitrate concentration in water for four flux filtration (adsorbent amount of 0.5 g/L of tank volume was replaced when N concentration exceeded the WHO limit of 11.3 mg N/L).

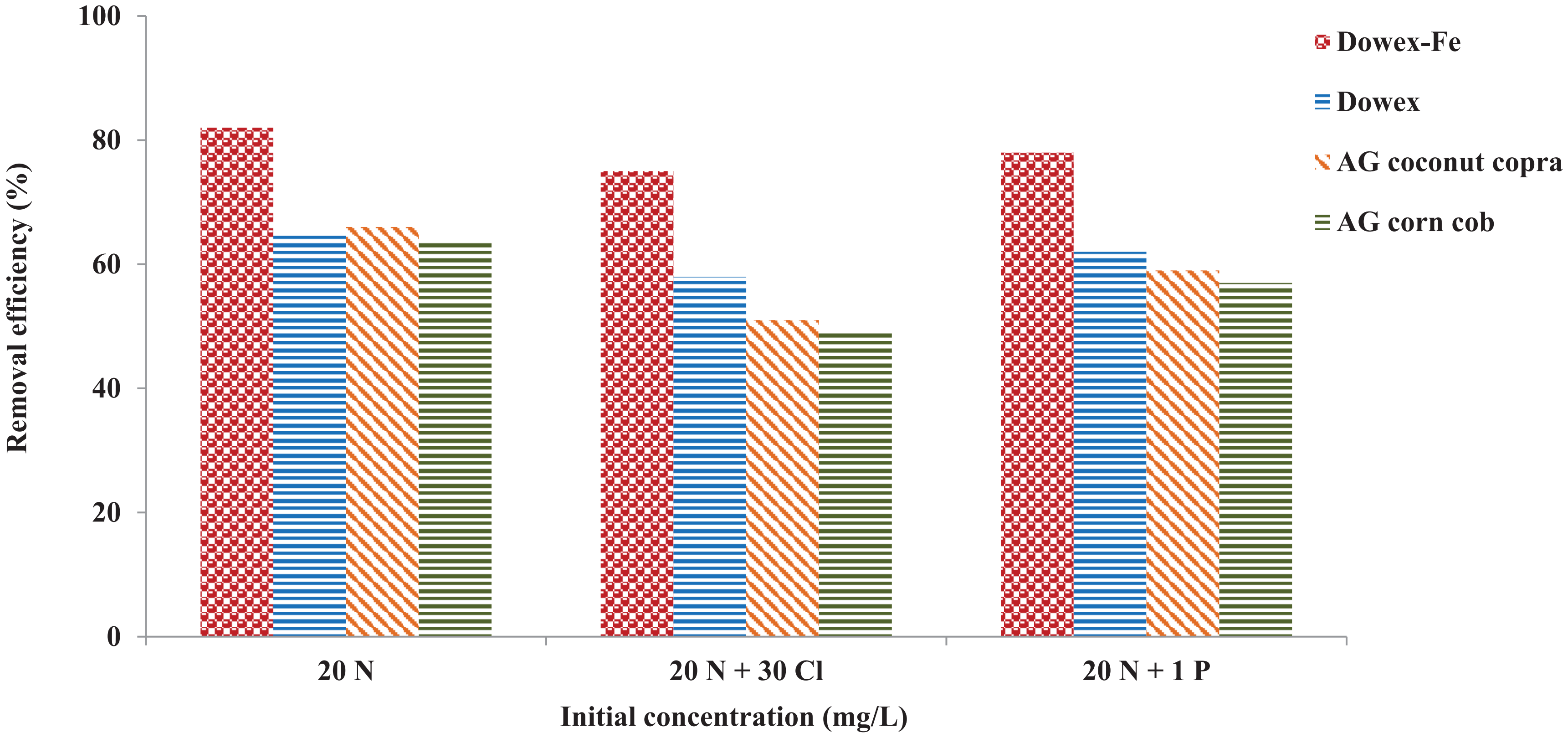


Figure 5.3. Effect of chloride and phosphate ions on nitrate removal efficiency

5.3.2. Volume of treated water

The volume of water treated to reduce the nitrate concentration below the WHO standard limit per mass of adsorbent was calculated using Microsoft Excel spreadsheet and presented in Table 5.2 (9th column of Table 5.2). The volume of water treated per mass of adsorbent increased with flux for all the adsorbents (Figure 5.4). This is because at increased flux the volume of water that entered the reactor per unit time increased. The increased amounts of nitrate that entered the reactor were increasingly removed by the adsorbents and in this way the WHO nitrate limit of 11.3 mg N/L was maintained. The volume of water treated per mass of adsorbent at any flux was in the order, Dowex-Fe > Dowex > AG coconut copra > AG corn cob. This order was the same as that for nitrate adsorption (Table 5.2 and Figure5.4).

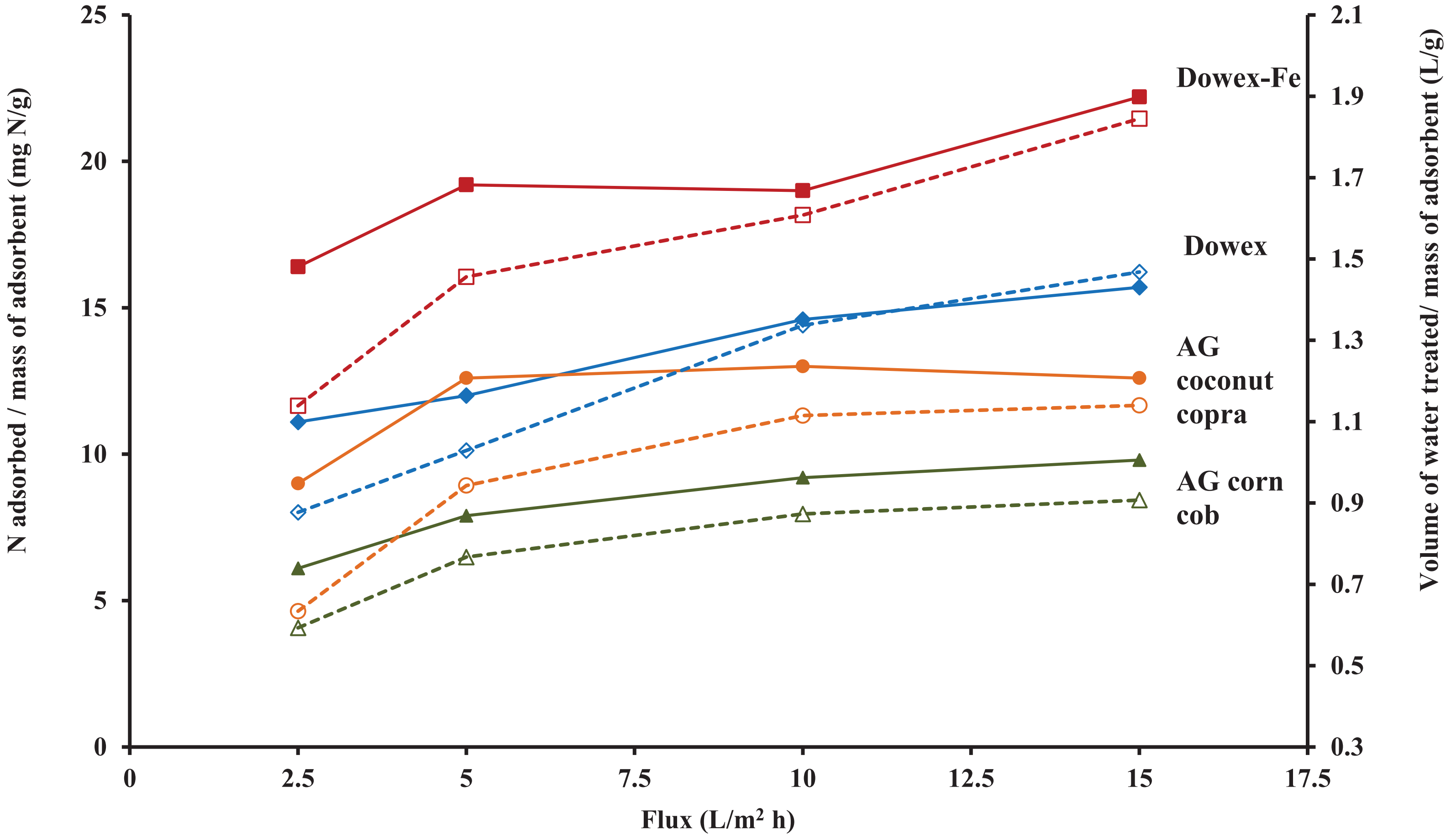


Figure 5.4. Effect of flux on nitrate adsorption (closed symbols) and volume of water treated (open symbols)

Table 5.2. Nitrate removal performance and volume of water treated for the four adsorbents at four different flux.

Flux (L/m^{2}h)	Adsorbent	Total time (h)	Total Volume (L)	Nitrate inlet (mg)	Nitrate outlet (mg)	Total amount of adsorbent used (g)	Nitrate adsorbed/mass of adsorbent (mg N/g)	Volume of water treated / g of adsorbent (L/g)	Total amount adsorbed (mg)	Rate of removal (mg N/h)	Rate of removal/g of adsorbent (mg N/h g)	% removal
15	Dowex-Fe	17.5	29.5	590	235	16	22.2	1.85	355	20	1.27	60
	Dowex	13.5	23.5	470	219	16	15.7	1.47	251	19	1.16	53
	AG coconut copra	9.5	18.2	364	154	16	13.1	1.14	210	22	1.38	58
	AG corn cob	7.0	14.5	290	133	16	9.8	0.91	157	22	1.40	54
10	Dowex-Fe	26	28.9	607	265	18	19.0	1.61	342	13	0.73	56
	Dowex	26	29.0	609	288	22	14.6	1.34	321	12	0.56	53
	AG coconut copra	14	17.9	376	168	16	13.0	1.12	208	15	0.93	55
	AG corn cob	10	23.5	494	346	16	9.2	0.87	147	15	0.92	30
5	Dowex-Fe	27	17.4	365	135	12	19.2	1.46	230	9	0.71	63
	Dowex	25	16.5	347	155	16	12.0	1.03	192	8	0.48	55
	AG coconut copra	27	16.9	355	128	18	12.6	0.94	227	8	0.47	64
	AG corn cob	17	12.2	256	130	16	7.9	0.77	126	7	0.46	49
2.5	Dowex-Fe	30	11.4	239	75	10	16.4	1.14	164	5	0.55	69
	Dowex	27	10.5	221	87	12	11.1	0.88	133	5	0.41	60
	AG coconut copra	25	10.1	212	68	16	9.0	0.63	144	6	0.36	68
	AG corn cob	18	8.3	174	89	14	6.1	0.59	85	5	0.34	49

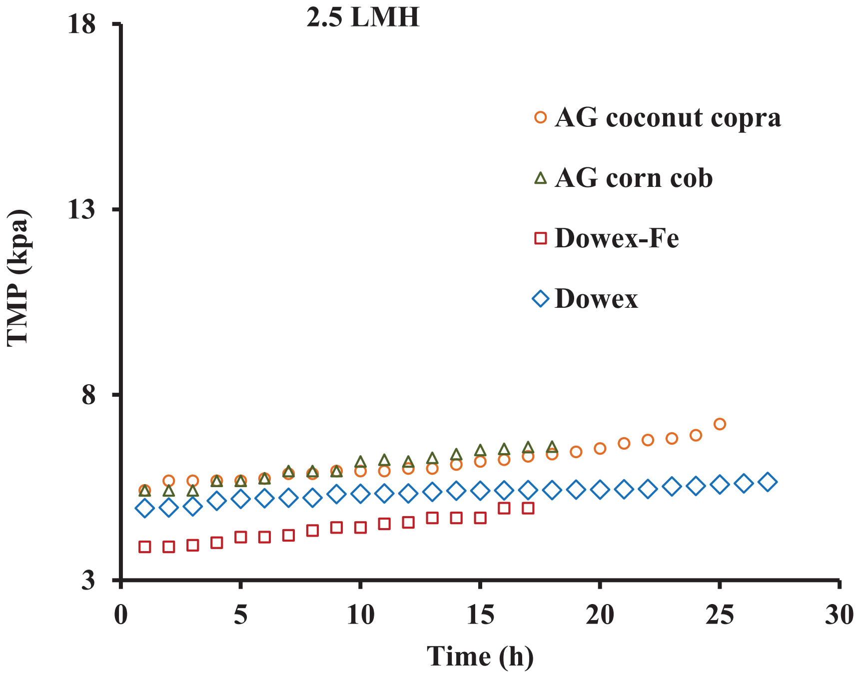
* Reactor volume 4L ** Each replacement was 0.5 g/L when N concentration exceeded the WHO standard limit of 11.3 mg N/L

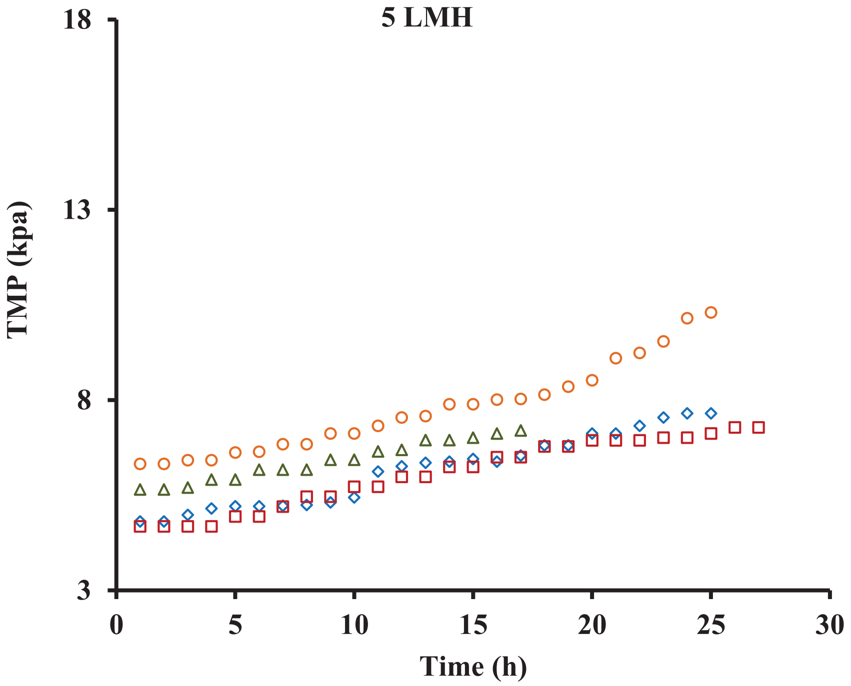
5.3.3. Adsorbent replacement

During the experiment, when the effluent reached the WHO standard concentration of 11.3 mg N/L, 20% (2 g) adsorbent was replaced (i.e. 0.5 g/L of adsorbent in the 4L tank volume). Various amounts of adsorbent replacements were earlier tried and 0.5 g/L was found to be the best, considering the efficiency of nitrate removal, cost effectiveness and practicability of replacement frequency. Immediately after the replacement the effluent nitrate concentration fell to a low level due to adsorption on the newly added adsorbent and then increased with time as before (Figure 5.2). The replacement interval of an adsorbent depended on the adsorption capacity of the adsorbent; it was more frequent for the adsorbent with poorer adsorption capacity. It was also shorter for the higher flux conditions because the adsorbents treated a larger volume of water in a shorter period of time by adsorbing a larger amount of nitrate. In accordance with these observations the replacement interval declined when the adsorption capacity of the adsorbents also decreased (Dowex-Fe > Dowex > AG coconut copra > AG corn cob). Thus, the number of replacement cycles for the adsorbents followed the reverse order. According to these observations, the decrement of effluent concentration soon after adsorbent replacement was higher in lower flux conditions and for the adsorbent having higher adsorption capacity.

5.3.4. Transmembrane pressure (TMP)

The transmembrane pressure (TMP) rose with the increasing flux for all adsorbents (Figure 5.5). When the flux increased the membrane treated more water and the rate of fouling increased. The TMP of membrane with bio-adsorbents in suspension was higher than ion exchange resins because of higher specific volumes of bio-adsorbents. The specific volumes were 1.1m^3/kg and 0.9 m^3/kg for bio-adsorbents and ion exchange resins, respectively. Consequently the bio-adsorbents might have blocked the membrane surface more than the ion exchange resins and thereby increased the TMP. Also, the very fine particles produced during the grinding of the bio-adsorbents would have deposited in between adjacent membranes to cause this blockage. This deposition was noticed during the experiments.


2.5 LMH
18
13
8
3
TMP (kpa)
0
5
10
15
20
25
30
Time (h)
○ AG coconut copra
△ AG corn cob
□ Dowex-Fe
◇ Dowex


5 LMH
18
13
8
3
TMP (kpa)
0
5
10
15
20
25
30
Time (h)

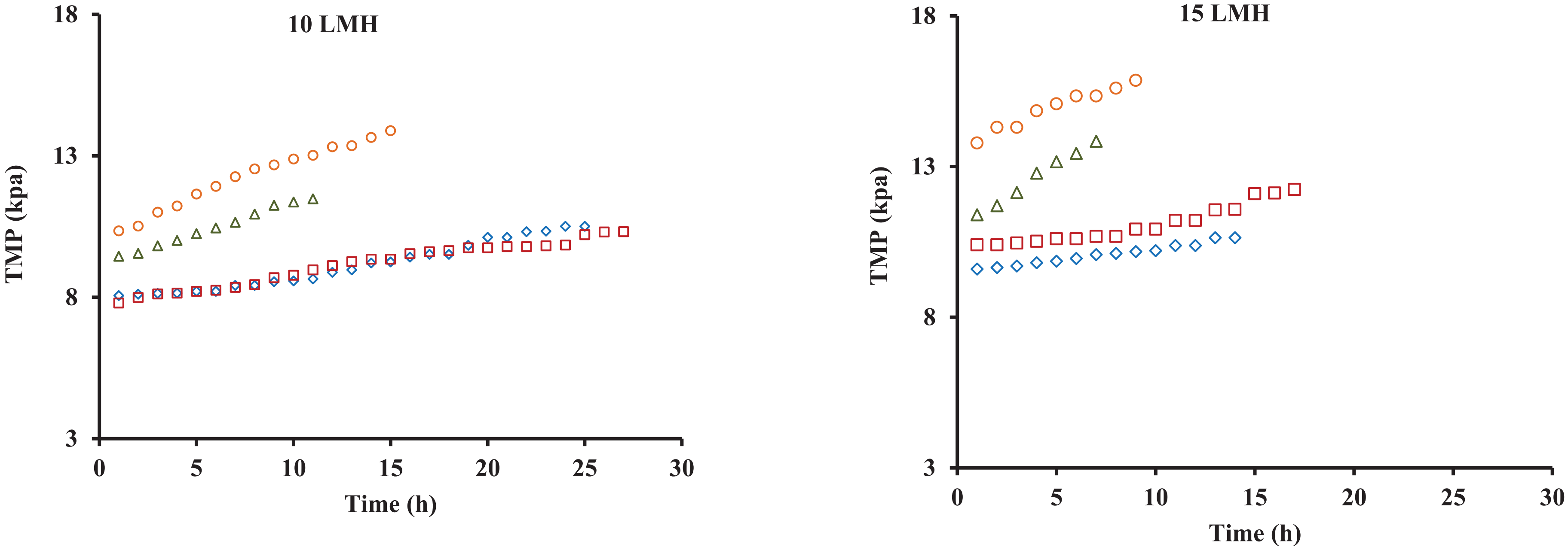


Figure 5.5. Transmembrane pressure (TMP) build-up with time for different flux and adsorbents

5.3.5. Comparison of SMAHS and column-mode nitrate removals

Table 5.3 compares the nitrate adsorption performance and volume of water treated to meet the WHO drinking water limit of 11.3 mg N/L in SMAHS and data obtained in a previous study (Chapter 3 and 4) using column experiments for an influent nitrate concentration of 20 mg N/L and flow rate of 1.5-1.6 L/h. As the data for the column experiment was available only for the flow rate of 1.6 L/h (27 mL/min) the comparison was made only for this flow rate. The data showed there was no significant difference in volume of water treated or the amount of nitrate adsorption between the two experiments for all adsorbents (Table 5.3). This could be due to two opposing factors influencing the processes. Mass transfer of nitrate is expected to be greater in SMAHS due to better contact of solution nitrate with the adsorbent because of agitation of the suspension by aeration. However, because the concentration gradient was lower at most of the time (4-11 mg N/L solution concentration, Figure 5.2) compared to column filtration (more fresh solution of 20 mg N/L), mass transfer would be lower in SMAHS.

The advantage of the SMAHS is that the medium is in suspension unlike in column mode of treatment. Also, very fine sized adsorbents with higher surface area can be used in this system. This is not possible in a column experiment due to the column clogging problem. In this study, adsorbents with 300-600 µm diameter were used to compare the results with those from column experiments. However, use of adsorbents of finer size (< 300 µm) will lead to higher nitrate removal due to higher surface area. Another advantage of SMAHS is that simultaneous removal of colloids, microorganisms and suspended solids can be achieved.

The material cost for the removal of 1000 mg of nitrate as N was 2.52, 3.81, 0.72 and 0.96 USD for Dowex-Fe, Dowex, AG coconut copra and AG corn cob, respectively. These costs were calculated using the market prices of the ion exchange resin and chemicals used to modify the adsorbents and assuming that coconut copra and corn cob have no cost. The only bio-adsorbent-related cost is that of amine-grafting reagents which are used to modify these adsorbents. If finer-sized adsorbents are used, the material cost would have further been reduced because a finer size can produce higher adsorption capacity. The bio-adsorbents used are agricultural wastes, which can be applied after their use to agricultural lands to provide nitrate for increasing crop production. This beneficial outcome can solve problems associated with the cost of chemicals used to modify the bio-adsorbents.

Table 5.3. Comparison of volume of water treated (nitrate concentration < 11.3 mg N/L) and nitrate adsorption between SMAHS and column-based system for similar flow rates (SMAHS 25 mL/min, column 27 mL/min) and influent nitrate concentration (20 mg N/L).

Adsorbent	SMAHS		Column*	
	Nitrate adsorbed/ mass of adsorbent (mg N/g)	Volume of water treated per mass of adsorbent (L/g)	Nitrate adsorbed/ mass of adsorbent (mg N/g)	Volume of water treated per mass of adsorbent (L/g)
Dowex-Fe	22.2	1.85	26.7	1.96
Dowex	15.7	1.47	15.4	1.14
AG coconut copra	13.1	1.14	18.0	0.92
AG corn cob	9.8	0.91	15.0	0.76

* Chapter 3 and 4

5.4. Conclusions

The SMAHS with 20% adsorbent replacement at appropriate times during the treatment process proved to be highly effective in the continuous removal of nitrate from water, and nitrate concentration was maintained below the WHO limit of 11.3 mg N/L. In terms of volume of water treated and the amount of nitrate removed per unit mass of adsorbent, Dowex-Fe recorded the best performance out of the four adsorbents which included two chemically modified bio-adsorbents. These results agree with those reported in previous column studies (Chapter 3 and 4). However, when considering the cost of adsorbents, bio-adsorbents may constitute a better choice, especially when implementing the technology in developing countries. Another advantage of bio-adsorbents is that the exhausted adsorbents can be directly applied to agricultural lands as nitrate fertilisers. SMAHS has the advantage of continuous treatment operation. It also leads to simultaneous removal of colloids, suspended solids and microorganisms that are present in the water.

CHAPTER 6

Nitrate removal performance of four adsorbents in a novel integrated electrochemical- adsorption system

UNIVERSITY OF TECHNOLOGY SYDNEY

CHAPTER 6

Enhanced removal of nitrate in an integrated electrochemical-adsorption system

6.1. Introduction

In previous chapters, four adsorbents were tested for nitrate removal in batch, column and submerged membrane adsorption hybrid systems. In those chapters, removing nitrate was tested mainly using the adsorption process. In this chapter the results of a study on nitrate removal using adsorption and electrochemical (EC) processes as an integrated technology are presented.

EC is a widely used process for water and wastewater treatment. It is an environmentally friendly treatment technology for removing nitrate and a wide range of pollutants with less sludge production and less use of chemicals (Chen, 2004; Rajeshwar & Ibanez, 1997). In this treatment method, nitrate ions are converted to N_2 gas as the major product and released into the environment (Pressley et al., 1972). Other pollutants such as ammonia (Kapałka et al., 2010), oil (Rubach & Saur, 1997), dye (Gürses et al., 2002), heavy metals (Poon, 1997), viruses (Zhu et al., 2005), E-Coli (Matsunaga et al., 1992), turbidity (Abuzaid et al., 1998), phosphate (Bektaş et al., 2004), and fluoride (Hu et al., 2005) can also be removed from water through this method. Another advantage of this method is that the bubbles produced at the electrodes carry pollutants to the water's surface and they can be easily removed by skimming or flotation. This technology is fairly inexpensive to operate and it can be further reduced if renewable energy sources are employed. Though this method has several advantages, it also has some disadvantages such as metal oxide formation on the cathode and the need to regularly replace sacrificial electrodes.

The EC process has been used at several locations for ground water nitrate treatment (Joffe & Knieper, 2000). Nitrate electro-reduction has been studied over the last few decades using electrode metals such as Ni, Fe, Al, Zn, Au, Pt, Pd, Ag, Cu, Ru, and Rh (Bouzek et al., 2001; Da Cunha et al., 2000; Dima et al., 2003; Li et al., 1988a; Li et al., 1988b; Reyter et al., 2008). Of these metals, Cu emerged as the best cathode for reducing nitrate (Bouzek et al., 2001; Reyter et al., 2008). Stainless steel plate was used in previous studies for the removal of nitrite (Abuzaid et al., 1998), nitrate (Lacasa et al., 2012) and ammonia (Vanlangendonck et al., 2005). In those studies on nitrite removal, stainless steel served as the cathode and anode electrodes while for ammonium and nitrate removal it was used as the cathode and other metals were used as anode.

Although the nitrate is decomposed to harmless nitrogen gas as the main product, low concentration of some by-products such as ammonia and nitrite may also be produced in the solution (Kim et al., 2006). Consequently, the ammonia is oxidised to nitrogen gas at anode (Li et al., 2009). If the Cl^- ions are present in the water, they are oxidised at the anode as hypochlorite which reacts with the ammonia/ ammonium ions, subsequently producing nitrogen gas (Pressley et al., 1972). In the study by Li et al. (2009), nitrite or ammonia was not detected in the final solution due to the presence of Cl^- ions.

The possible reactions at the cathode are (Paidar et al., 1999) as follows:

$H_2O + 2e^- \rightarrow H_2 + 2\,OH^-$ $E^0 = -0.83$ V   (6.1)

$NO_3^- + 3\,H_2O + 5e^- \rightarrow \frac{1}{2}N_2 + 6\,OH^-$, $E^0 = 0.26$ V   (6.2)

$NO_3^- + 6\,H_2O + 8e^- \rightarrow NH_3 + 9\,OH^-$, $E^0 =-0.12$ V   (6.3)

$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2\,OH^-$, $E^0 = 0.01$ V   (6.4)

$NO_2^- + 2\,H_2O + 3e^- \rightarrow \frac{1}{2}N_2 + 4\,OH^-$, $E^0 = -0.406$ V   (6.5)

$NO_2^- + 5\,H_2O + 8e^- \rightarrow NH_3 + 7\,OH^-$, $E^0 = -0.165$ V   (6.6)

$NO_2^- + 4\ H_2O + 4e^- \rightarrow NH_2OH + 5\ OH^-$, $E^0 = -0.45$ V (6.7)

The possible reactions at anode area are:

$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e^-$ (6.8)

$NH_3 + 6\ OH^- \rightarrow N_2 + 6\ H_2O + 6e^-$ (6.9)

$M(s) \rightarrow M^{n+}_{(aq)} + n\ e$ (If sacrificial electrodes are used)

The following are possible reactions when Cl^- ions are present in the water:

$2\ Cl^- \rightarrow Cl_2 + 2\ e^-$ (6.10)

$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+$ (6.11)

$2\ NH_4^+ + 3\ HClO \rightarrow N_2 + 3\ H_2O + 5\ H^+ + 3Cl^-$ (6.12)

Several research studies were reported for nitrate removal using EC technology (Emamjomeh & Sivakumar, 2005; Paidar et al., 1999; Uğurlu, 2004). However, only one study investigated the removal of nitrate using ion exchange resin-coated electrodes in the EC system. Kim and Choi (2012) conducted an experiment using a nitrate selective BHP55 anion exchange resin-coated carbon electrode and tested it for nitrate and chloride removal. The nitrate and chloride removal were 19 and 15 mmol/m^2 from solutions containing 2 and 5 mM, respectively. When a nitrate non-selective anion exchanger coating was utilised, the amount of nitrate removed fell 2.3 fold. However, no study was reported on the relative contribution of adsorption and EC on nitrate removal using an integrated EC -adsorption system.

In the integrated system the adsorbent was added to the EC system. A stainless steel sieve box was used as the anode and the adsorbent was packed inside it. Here the nitrate is removed by adsorption and EC reaction simultaneously. Theoretically, the nitrate concentration will be high near the sieve box because of the positive electrical potential of the anode; therefore, removal will be quicker than normal adsorption.

Generally, the adsorbents contain the Cl^- ion as a counter ion and during nitrate adsorption the Cl^- ion is released to the solution. The Cl^- ion is converted to OCl^- and this OCl^- ion reacts with the ammonia/ammonium ions by-product. In this process ammonia/ammonium ions are oxidised to N_2 gas and released into the environment. Another advantage of the sieve box is that the adsorbent inside the sieve box can be regenerated by removing the box from the system and immersing it in a KCl solution. The regeneration of the adsorbent is difficult if the electrode is coated with the adsorbent as done previously (Kim & Choi, 2012). The main objectives of the research were to: (i) study the efficiency in removing nitrate using the integrated EC-adsorption system and compare the removal with the same technologies when they are used separately; (ii) investigate the effect of operating conditions such as pH, voltage, current, and distance between electrodes; and (iii) compare the nitrate removal amounts using different adsorbents, namely Dowex, Dowex-Fe, AG coconut copra and AG corn cob in the integrated system.

6.2. Experimental details

6.2.1. Materials and methods

Four different adsorbents such as Dowex, Dowex-Fe, AG corn cob, and AG coconut copra were used in this integrated system. In the EC system, Cu plate and stainless steel sieve box were used as cathode and anode electrodes, respectively. The dimensions of the Cu plate were 11 cm x 6 cm x 0.5 cm and the dimensions of the submerged part in the solution were 9 cm x 6 cm x 0.5 cm. A stainless steel (304) sieve with aperture size of 0.25 mm was employed to make the electrode box and dimensions of the submerged part inside the solution 9 cm x 6 cm x 2 cm. The preparation of feed solutions (Nitrate- 20 mg N/L, Phosphate - 5 mg P/L, sulphate - 50 mg S/L) and their analysis were the same as those described in Chapter 3.

In each experiment, 2 g of adsorbent was packed inside the stainless steel sieve box (anode electrode) and immersed in a 2 L solution in parallel with the Cu plate (Figure 6.1). The EC and adsorption experiments were conducted individually at the same conditions to compare the advantage of the integrated system. A magnetic stirrer rotating at a speed of 120 rpm was used at the bottom of the container. A Powertech MP 3086 model AC to DC converter provided direct current and the voltage/current was adjusted and noted for analysis. The performance was studied in terms of nitrate removal at different conditions, i.e.: distances between the electrodes (0.5, 1, 2 and 3 cm), voltages (15, 20, 25, and 30 V), current (0.2, 0.5, 0.7, and 1 A) and pH (3, 5, 7, 9, and 11). Finally, the nitrate removal was tested using several adsorbents, Dowex-Fe, AG corn cob, AG coconut copra. The solution with a pH of 7 was used in all the experiments and temperature was maintained at 25-27^0 C.

6.2.2. Ions analysis

Nitrate, phosphate and sulphate concentrations were analysed by an ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. The ion chromatograph was cleaned before the analysis using a mobile phase solution (Na_2CO_3, $NaHCO_3$), diluted sulphuric acid and Milli-Q water. Ammonium ion concentration was measured using a HACH DR 3900 test kit. The solutions' pH was measured using an HQ40d portable pH meter. The dissolved Fe ions concentration was measured using a Microwave Plasma-Atomic Emmison Spectrometer (Agilent 4100 MP-AES).

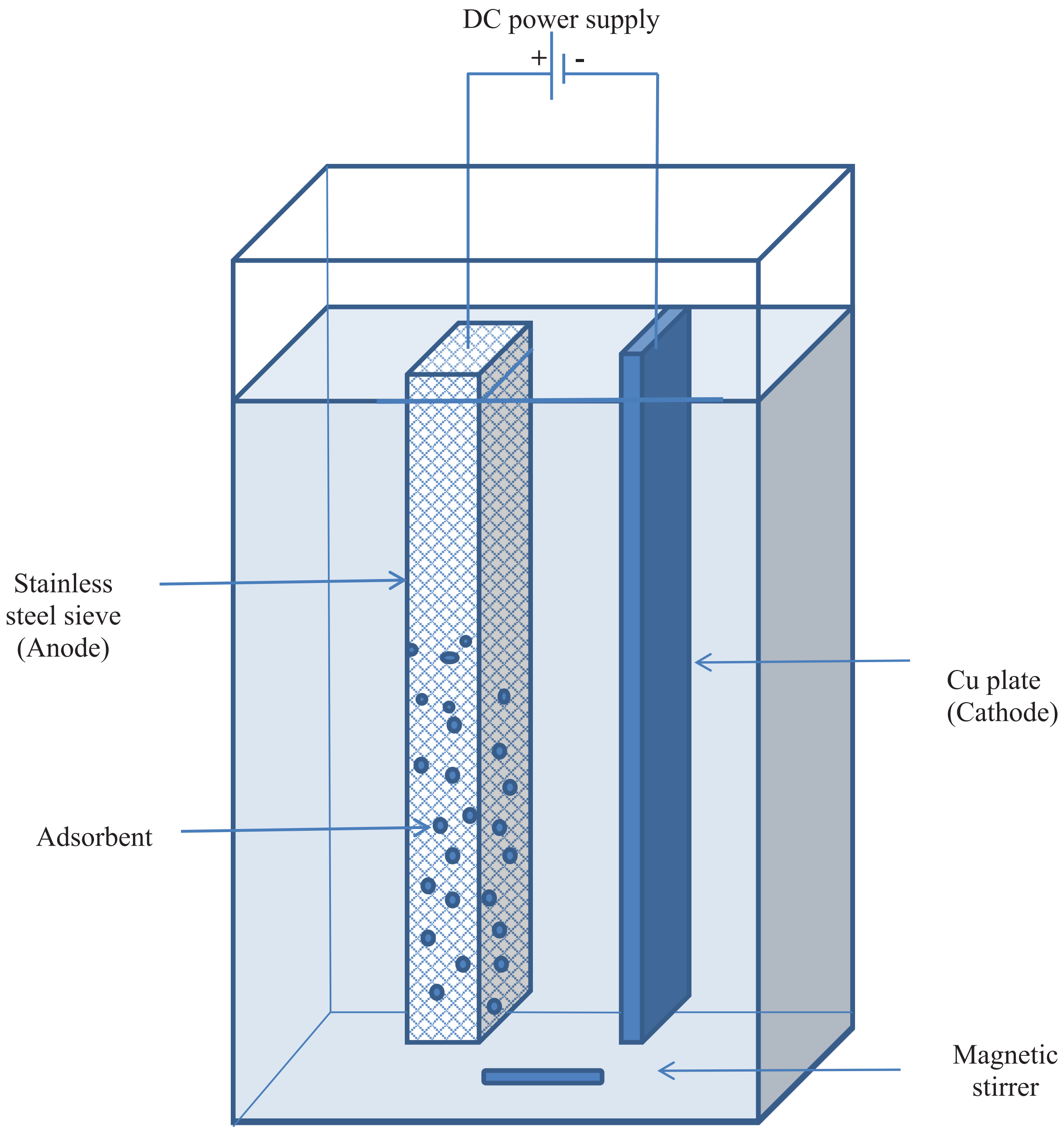


Figure 6.1. Integrated EC-adsorption system

6.3. Results and discussions

A stainless steel sieve with a pore size of 0.25 mm was used to make an electrode box to prevent any adsorbents of 0.3- 1.2 mm size passing through the sieve. The anion exchange resin Dowex was added inside the sieve box at a dosage of 1 g/L in all the experiments. The nitrate removal efficiency was investigated using several factors considered to influence the EC-adsorption integrated system performance. The factors were distance between electrodes, pH, complementary ions, and current which were varied and tested for nitrate removal. The nitrate removal efficiencies were investigated for EC and adsorption systems individually and together.

6.3.1. Effect of distance between electrodes

The effect of distance between electrodes on the removal of nitrate was investigated using 0.5, 1, 2 and 3 cm distances between the electrodes; results are presented in Tables 6.1 and 6.2 and Figures. 6.2 and 6.3. Because the voltage was maintained constant at 30 V, the current decreased from 1.3 A to 0.2 A with increasing distance between the electrodes. The nitrate removal increased when the distance for both EC and integrated system decreased. The explanation for this is that when the gap between electrodes narrows, the resistance between the electrodes reduced and the current increased (Malakootian et al., 2010). Thus, the rates of oxidation-reduction reactions in solution increased and larger amounts of the nitrates were reduced to other forms of nitrogen species near the cathode (Eq 6.2- Eq 6.7). In the integrated system, in addition to the reduction of nitrate at the cathode, nitrates moved to the anode at a faster rate and were adsorbed by the adsorbents.

The integrated system's removal efficiency was almost equal to the sum of the individual adsorption and EC system's removal efficiency. The highest removal efficiency of 68% was achieved at 0.5 cm electrodes distance and this was only marginally higher than that at 1 cm electrode distance (67%). However, the power consumption (voltage x current x time) for 0.5 cm electrodes distance (1.3 A x 30 V x 3 h) was higher (0.12 kWh) than that for 1 cm electrodes distance (1 A x 30 V x 3 h = 0.09 kWh). Therefore the remaining experiments were conducted utilising 1 cm electrode distance.

The ammonium concentration in the final solution increased with distance between the electrodes for the EC (0.12- 0.64 mg/L) and integrated (0.01- 0.25 mg/L) systems. The increase in ammonium concentration was due to only a limited amount of hypochlorite being available in the solution to oxidise ammonium (Eq 6.12). Hypochlorite limitation was due to the low current values at large distances between electrodes and these were not enough to oxidise the Cl^- ion to hypochlorite (Eq 6.10, 6.11). Chloride ions in the solutions originated from tap water used in the experiment. This explanation is consistent with that of Vanlangendonck et al. (2005) where decreased current was found to decrease the ammonium oxidation rate.

It is interesting to note that the ammonium ion in solution was lower in the integrated system than in the EC system. This is probably due to the Cl^- released from the adsorbents during nitrate adsorption (Chapters 3, 4) in addition to the Cl^- present in tap water. The higher concentration of Cl^- in the system would have produced a larger concentration of hypochlorite, which oxidised greater amounts of ammonium ions and resulted in a smaller ammonium concentration.

Table 6.1. The amount of nitrate removal (mg N) with the change of distance between electrodes after 3 h at 30 V, pH 7

Removal method	0.5 cm (1.3 A)	1 cm (1 A)	2 cm (0.7 A)	3 cm (0.2 A)
EC only	3.41	3.17	2.87	2.18
Adsorption only	9.06	9.06	9.06	9.06
EC-adsorption	13.41	12.86	11.88	11.43

Table 6.2. Percentage removal (%) of nitrate with the change of distance between electrodes after 3 h at 30 V, pH 7

Removal method	0.5 cm (1.3 A)	1 cm (1 A)	2 cm (0.7 A)	3 cm (0.2 A)
EC only	17.1	16.6	14.7	11.2
Adsorption only	49.1	49.1	49.1	49.1
EC-adsorption	67.9	67.0	62.9	60.5

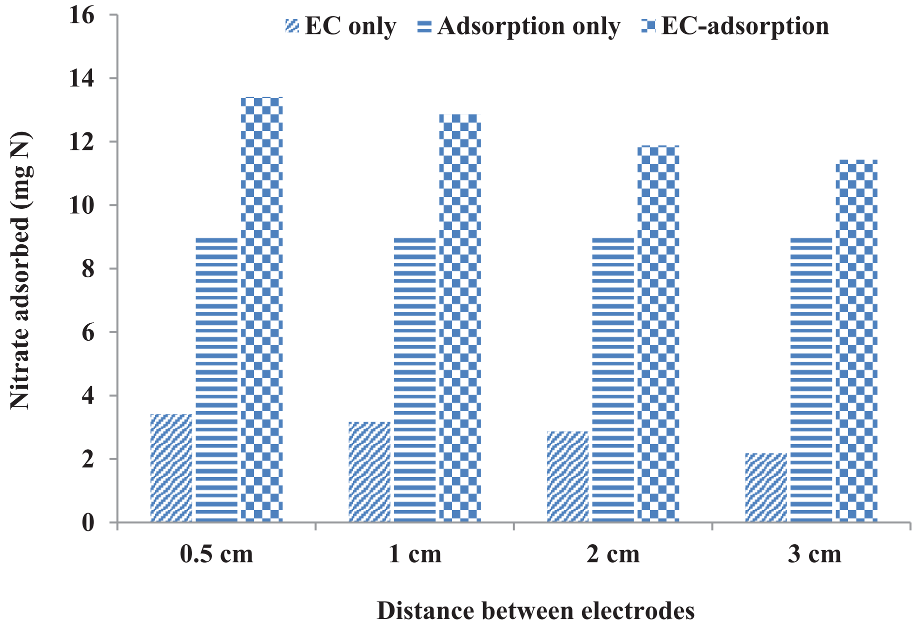


Figure 6.2. Amount of nitrate removed with change of distance between electrodes

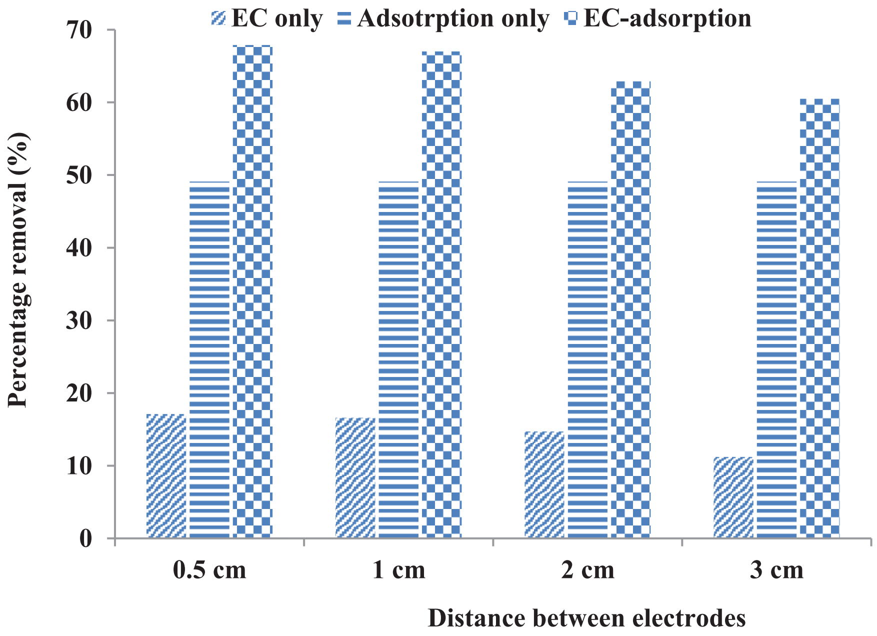


Figure 6.3. Percentage removal of nitrate with change of distance between electrodes

6.3.2. Effect of current

The effect of current on nitrate removal was investigated using the current values of 0.2, 0.5, 0.7 and 1 A with 1 cm distance between the electrodes; results are presented in Tables 6.3 and 6.4 and Figures. 6.4 and 6.5. The voltages increased automatically while increasing the current and they were recorded as 9, 18, 24 and 30 V for the current values of 0.2, 0.5, 0.7 and 1 A, respectively. The nitrate removal efficiency increased with current for the EC and integrated systems. The high current always speeds up the oxidation-reduction reaction rate at the electrode (Vanlangendonck et al., 2005). Therefore at higher current, higher amount of nitrate was converted to N_2 or NH_3 gas/NH_4^+ (Eq 6.2- 6.6) resulting in reduced nitrate concentration in the solution (Emamjomeh & Sivakumar, 2005).

In the nitrate removal process, the economic evaluation of the process should also be considered. The total power consumption (current x voltage x time) increased with the increase in current and they were 0.005, 0.027, 0.050, and 0.090 kWh for the current of 0.2, 0.5, 0.7 and 1 A for 3 h operation. For the EC system, the nitrate removal efficiency was almost double at the highest current (16.6% for 1 A) than at the lowest current (8.7% for 0.2 A) used. The costs of removing 1000 mg N for the highest and lowest currents were \$8.52 and \$0.95, respectively (cost = current x voltage x operation time x \$0.3/kWh (Australian Energy Council, 2016) for EC and \$50/kg (Sigma-Aldrich, 2016) for ion exchange resin). This calculation did not include labour, material and equipment costs. In the integrated system most of the nitrate removal occurred due to adsorption. Also, the adsorbent cost is much higher than the cost of electricity in the integrated system. Therefore, although the EC cost was much higher at the higher current, the total cost of the integrated system was almost equal for both the current values in the integrated system values; they were \$10.28 and \$10.06 for 1 A and 0.2 A, respectively. In the integrated system, the amount of nitrate removal was 12% higher for the highest current (1 A) compared to the lowest current (0.2 A) (Table 6.4).

The ammonium concentration in the solution declined when the current increased, probably due to the elevated rate of OCl^- formation, which would have reacted with ammonia/ammonium ions to release N_2 gas.

Table 6.3. The amount of nitrate removed (mg N) with the change of current after 3 h at pH 7

Removal method	0.2 A (9V)	0.5 A (18V)	0.7 A (24 V)	1 A (30 V)
EC only	1.72	2.02	2.48	3.17
Adsorption only	9.06	9.06	9.06	9.06
EC-adsorption	10.56	10.93	11.99	12.36

Table 6.4. Percentage removal (%) of nitrate with the change of current after 3 h at pH 7

Removal method	0.2 A (9V)	0.5 A (18V)	0.7 A (24 V)	1 A (30 V)
EC only	8.7	10.1	13.9	16.6
Adsorption only	49.1	49.1	49.1	49.1
EC-adsorption	54.7	57.1	61.8	67.0

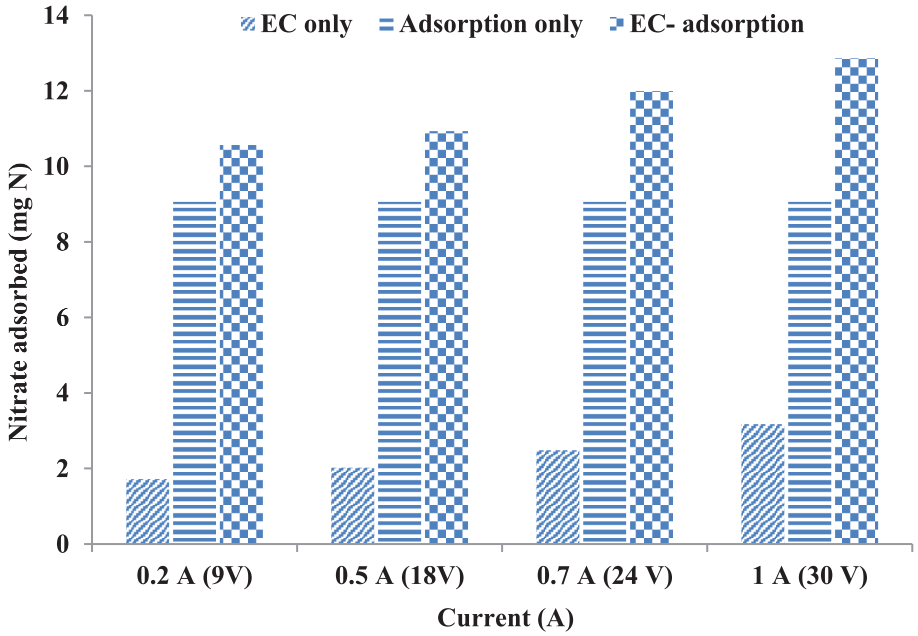


Figure 6.4. Amount of nitrate removed with change of current

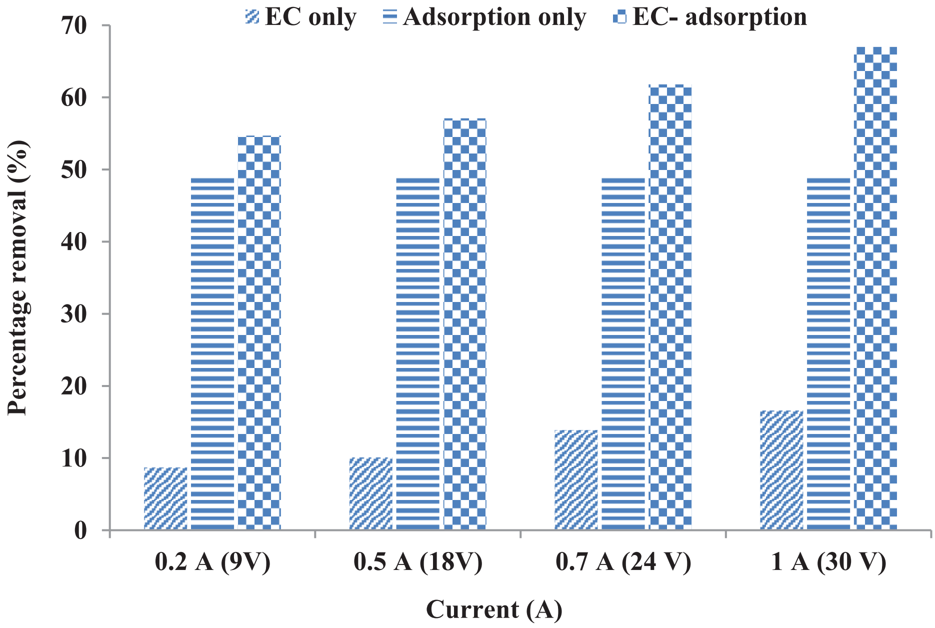


Figure 6.5. Percentage removal of nitrate with change of current

6.3.3. Effect of pH

The effect of pH on nitrate removal was investigated at pHs of 3, 5, 7, 9 and 11 with the conditions of 1 A and 25-30 V; results are presented in Tables 6.5 and 6.6 and Figures. 6.6 and 6.7. To adjust the pH, diluted hydrochloric acid (HCl) and diluted sodium hydroxide (NaOH) were used, and therefore the ionic concentration would have increased in the solution at low and high pHs, increasing the conductivity of the solution.

The nitrate removal by Dowex was slightly high at low pH due to the protonation of the Dowex surface and above 7 it decreased due to the repulsion of nitrate ions by the negatively charged surface of Dowex and competition from increased OH^- for adsorption. In the EC system the removal of nitrate was low and nearly the same at all pH levels. The integrated system percentage for nitrate removal was equal to the sum of adsorption and EC systems percentage removal for pH 7- 11; it was, however, lower than the sum for pH less than 7. This may be due to the competition of OH^- produced at low pH as a result of increased hydrogen evolution with nitrate for adsorption on Dowex (Eq 6.1). Li et al. (2010) also reported that hydrogen evolution increased with decreasing pH resulting in release more OH^- ions in the EC system which comprised of Fe cathode and Ti/IrO_2-Pt anode.

The ammonium ion concentration in the solution after 3 h was in the range of 0.1- 0.5 mg/L for the EC system and 0.01-0.05 mg/L for the integrated system for all pHs. This is probably due to the release of Cl^- from Dowex during NO_3^- adsorption in the integrated system and the released Cl^- being converted to OCl^-, which oxidised the ammonium (Eq 6.10-6.12).

Table 6.5. Amount of nitrate removed (mg N) with change of pH after 3 h at 1 A and 25-30 V

Removal method	3	5	7	9	11
EC only	3.6	3.5	3.2	2.1	2.7
Adsorption only	10.4	9.7	9.1	8.6	5.9
EC-adsorption	11.9	11.8	12.4	11	8.9

Table 6.6. Percentage removal (%) of nitrate with change of pH after 3 h at 1 A and 25-30 V

Removal method	3	5	7	9	11
EC only	17.9	18.8	16.6	13.2	14.1
Adsorption only	51.9	49.3	49.1	45.1	31.0
EC- adsorption	59.0	60.0	67.0	57.4	46.4

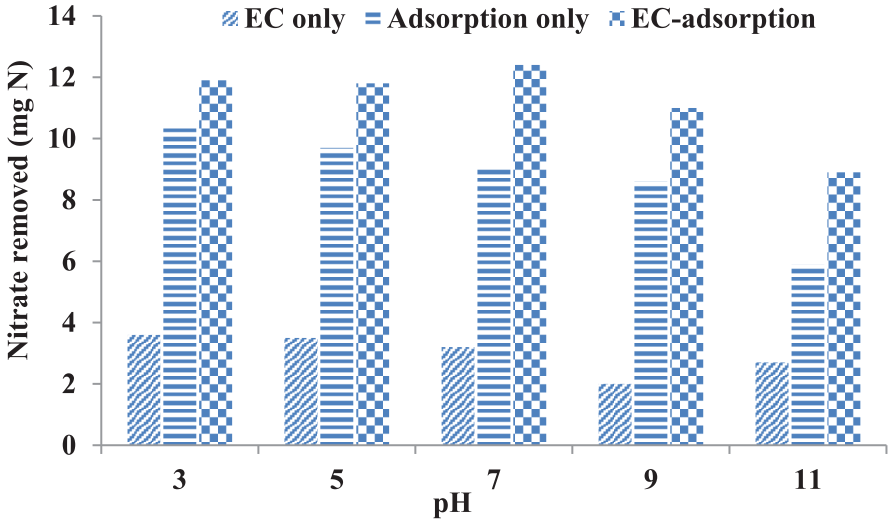


Figure 6.6. Amount of nitrate removed with change of pH

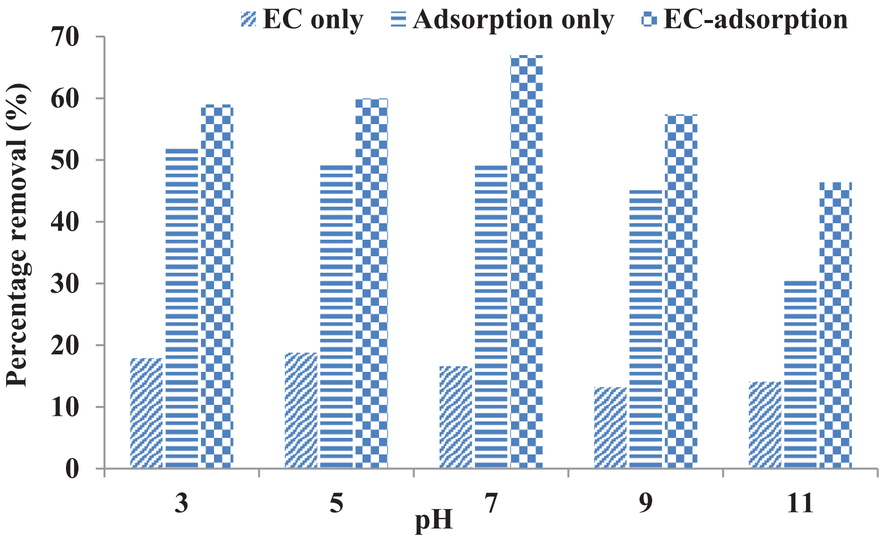


Figure 6.7. Percentage removal of nitrate with change of pH

6.3.4. Effect of time

The kinetics study was conducted at the optimum conditions of nitrate removal of pH 7, 1 cm distance between the electrodes, 1 A and 30 V. Figure 6.8 illustrates the cumulative nitrate removal increasing as time also increased. The rate of nitrate removal was faster at the start but slowed down after 1 h, due to the passivation of the Cu electrode in the EC system. The formation of CuH or CuH_2 on the surface of the Cu electrode curtailed the performance after some time (Paider et al., 1999). In the adsorption system, the number of vacant adsorption sites decreased with increased time resulting in a reduced rate of adsorption. In the integrated system, both the electrode passivation and reduction in adsorption sites occurred with increased time causing a reduced adsorption rate.

The integrated system percentage removal was almost equal to the addition of individual batch adsorption and EC system at all times. The ammonium ion concentration was measured every 1 h interval and it was observed that, for the EC system, it increased continuously and reached 0.26 mg/L at 3 h. For the integrated system it remained almost the same in the 0.01-0.02 mg/L range. The lower ammonium concentration in the integrated system might be due to the conversion of Cl^- ions released from the adsorbent during nitrate adsorption to hypochlorite, which reacted with ammonia/ammonium ions to produce N_2 gas. Therefore it suppressed the ammonia/ammonium ions concentration increment in the solution.

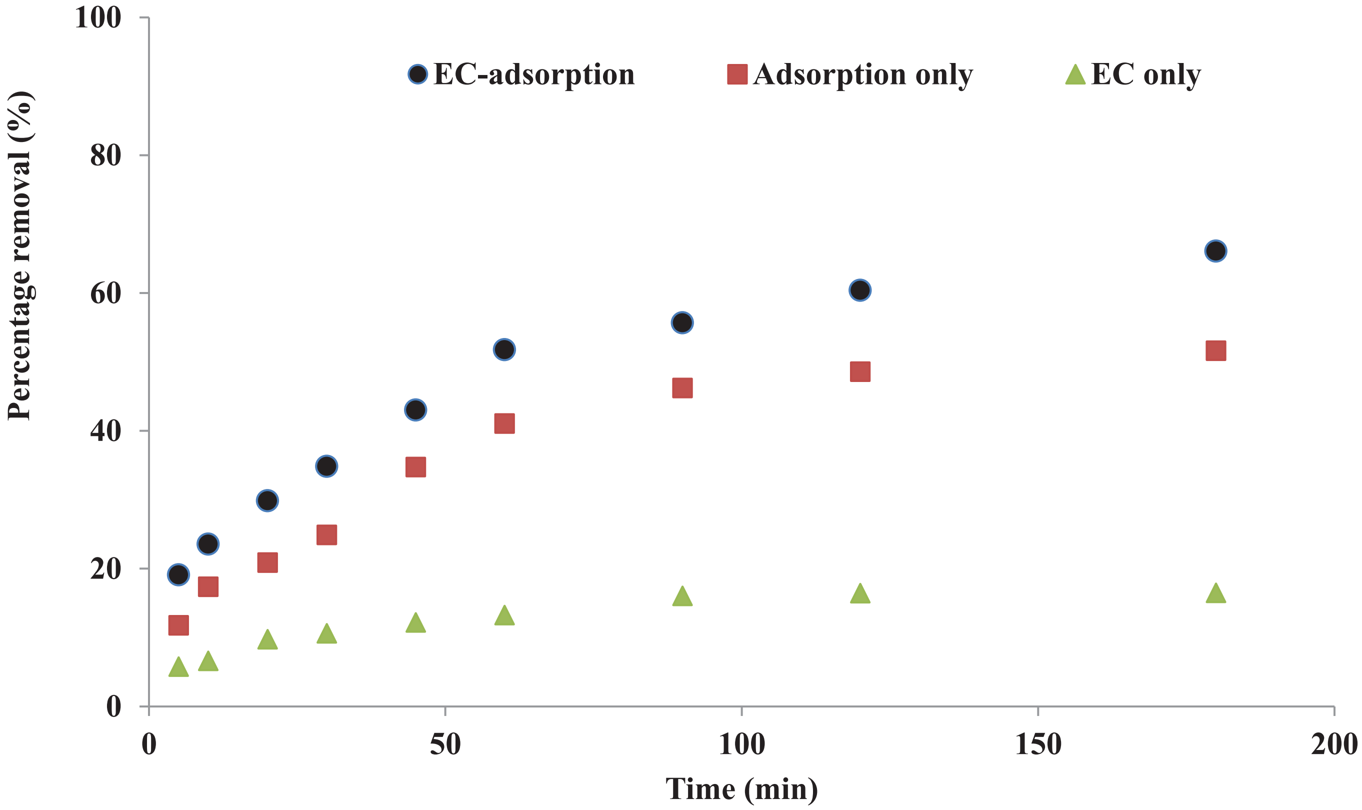


Figure 6.8. Percentage removal of nitrate over time for the three nitrate removal systems

6.3.5. Effect of complementary ions

6.3.5.1. Effect of phosphate

Phosphate's effect on nitrate removal was conducted with 20 mg N/L and 5 mg P/L at pH 7 and with the conditions of 1 A, and 28 V; the results are presented in Tables 6.7 and 6.8 and Figures. 6.9 and 6.10. Lower concentration of phosphate than nitrate was used in the experiment to mimic the concentration differences of these ions normally found in surface and ground water. The nitrate removal percentage fell slightly in the presence of phosphate ions for all three systems. The previous batch and column adsorption experimental results also revealed that nitrate removal was reduced slightly in the presence of phosphate due to competition of phosphate with nitrate for adsorption. The reduction in nitrate removal in the EC system may be because of electrode passivation from phosphate adsorbing on the anode or precipitating as $FePO_4$ on the anode surface. The Fe ions in the solution responsible for the precipitation would have been produced by the dissolution of the stainless steel sieve anode. The concentration of Fe ions in the solution was found to be 1.25 mg/L after 3 h. The oxidation of Fe^{2+} ions occurs above pH 5 and therefore this oxidation is highly likely at pH 7 where the experiment was conducted (Sasson et al., 2009). Lacasa et al. (2011) reported that in their EC system, Fe^{2+} ions were rapidly oxidised to Fe^{3+} ions. Assuming that the measured Fe concentrations were that of Fe^{3+} and converting the concentrations in mg/L to mol/L unit, a calculation was made to determine whether precipitation of $FePO_4$ occurred or not using the measured Fe and P concentrations as follows:

$$[Fe^{3+}]\,[PO_4^{3-}] = [2.23 \times 10^{-5}][1.61 \times 10^{-4}]$$

$$= 3.59 \times 10^{-9}$$

The solubility product of the $FePO_4$ at 25 ^{0}C is 1.3×10^{-22} $mol^5\,dm^{-15}$ (Rana et al., 2014). Therefore $[Fe^{3+}]\,[PO_4^{3-}]$ in the experimental solution was > Ksp which demonstrates that the phosphate was capable of precipitating in the experiment as $FePO_4$ in solution or on the electrode surface.

Phosphate removal by EC is more than double that by adsorption whereas nitrate removal was four times higher in adsorption than EC. This difference between nitrate and phosphate removals supports the reasoning that phosphate was removed by precipitation assisted by the EC process where Fe dissolute from the electrode reacted with phosphate.

Table 6.7. Amount of nitrate and phosphate removal (mg) from the solution containing nitrate and phosphate after 3 h at 1 A, 28 V, pH 7

Removal method	N removal with P	N removal without P	P removal
EC only	2.2	3.2	2.3
Adsorption only	8.9	9.1	1.5
EC-adsorption	12.1	12.9	3.7

Table 6.8. Percentage removal (%) of nitrate and phosphate from the solution which contained nitrate and phosphate after 3 h at 1 A, 28 V, pH 7

Removal method	N removal with P	N removal without P	P removal
EC only	12.1	16.6	48.6
Adsorption only	47.8	49.1	22.4
EC-adsorption	61.4	67.0	68.8

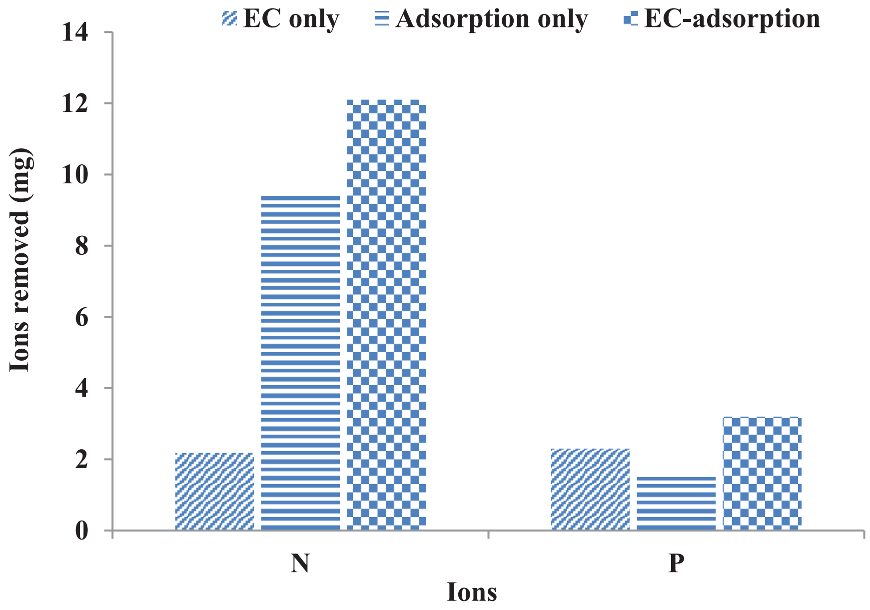


Figure 6.9. Amount of nitrate and phosphate removed from the solution containing nitrate (20 mg N/L) and phosphate (5 mg P/L)

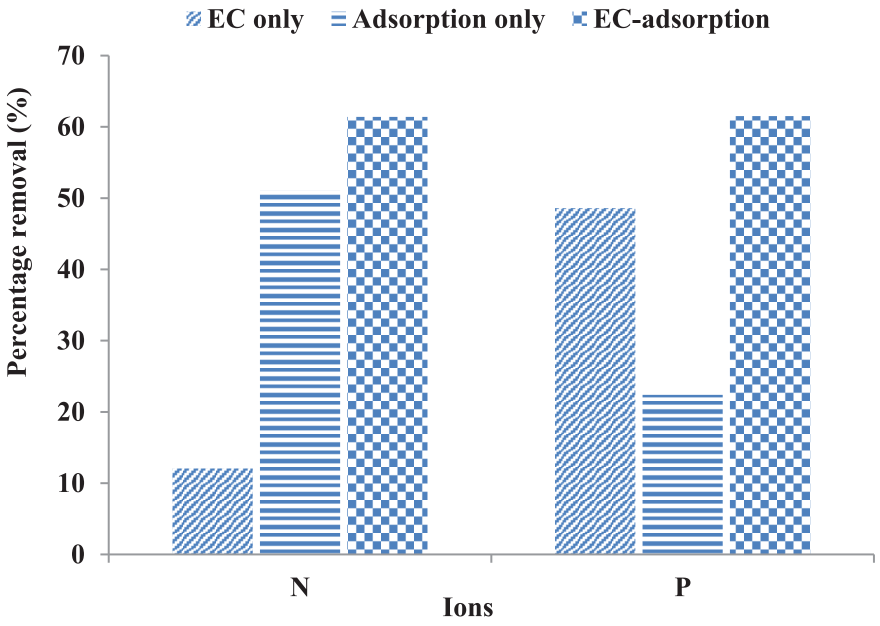


Figure 6.10. Percentage removal of nitrate and phosphate from the solution which contained nitrate (20 mg N/L) and phosphate (5 mg P/L)

6.3.5.2. Effect of sulphate

Sulphate's effect on nitrate removal was investigated in the presence of 50 mg S/L with 20 mg N/L at pH 7. The current was maintained at 1 A and the voltage fell from 30 V to 20 V due to the increased concentration of ions as a result of adding sulphate ions (Tables 6.9 and 6.10 and Figures. 6.11 and 6.12). The increasing ionic concentration decreased the resistance between the electrodes and increased the electrical conductivity of the solution; therefore a higher current was achieved at lower voltage. The nitrate removal was not affected by the addition of sulphate ions in the EC system. However, adding sulphate reduced the removal of nitrate in the adsorption system and integrated system. The previous batch and column adsorption studies indicated that the sulphate ion intensively competed with nitrate due to its higher valence (two negative charges) than nitrate (one negative charge) ions. The amount of nitrate removed in the integrated system is approximately equal to the sum of the nitrate removed in the adsorption and EC systems.

Table 6.9. Amount of nitrate and sulphate removed (mg) from the solution containing nitrate and sulphate after 3 h at 1 A, 20 V, pH 7

Removal method	N	S
EC only	3.2	1.95
Adsorption only	5.0	19.3
EC-adsorption	7.8	22.9

Table 6.10. Percentage removal of nitrate and sulphate from the solution which contained nitrate and sulphate after 3 h at 1 A, 20 V, pH 7

Removal method	N	S
EC only	16.4	4.0
Adsorption only	25.4	39.8
EC-adsorption	39.5	47.1

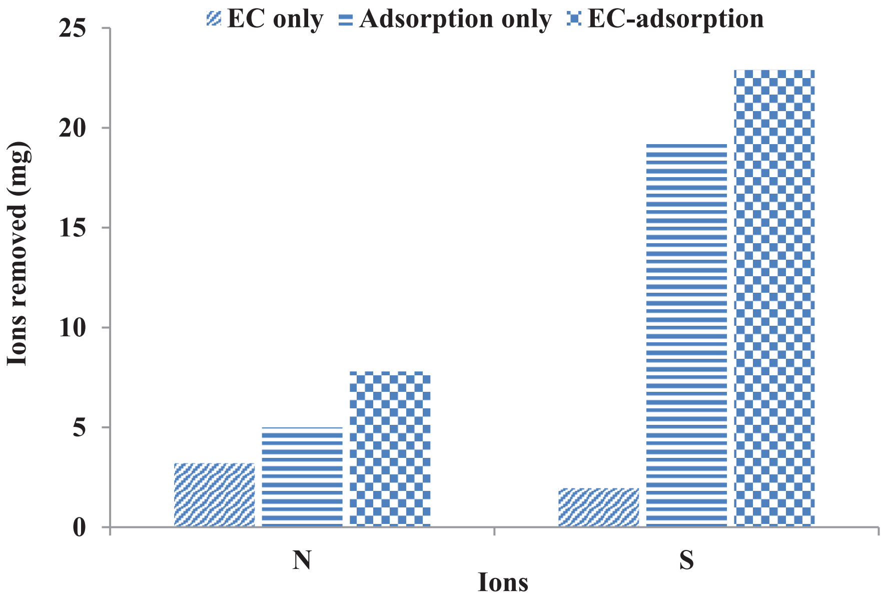


Figure 6.11. Amounts of nitrate and sulphate removed from the solution containing nitrate (20 mg N/L) and sulphate (50 mg S/L)

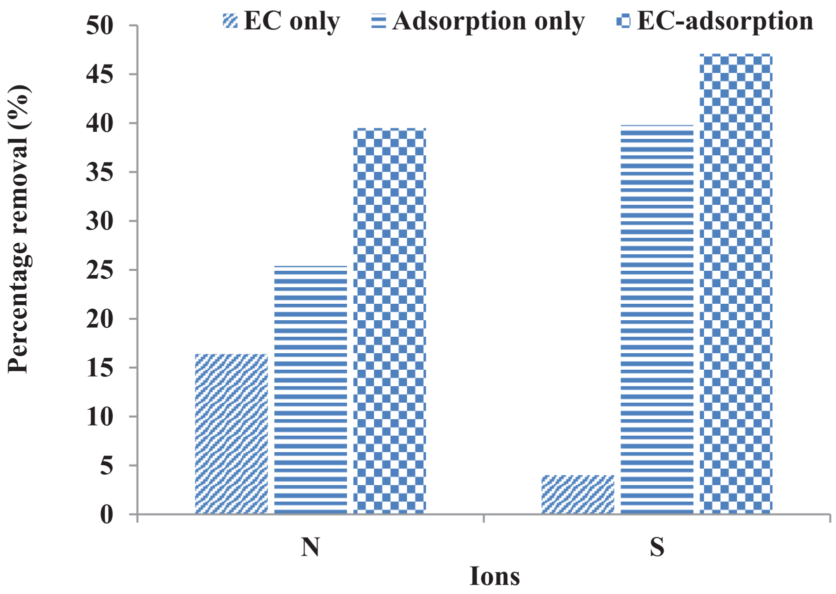


Figure 6.12. Percentage removal of nitrate and sulphate from the solution which contained nitrate (20 mg N/L) and sulphate (50 mg S/L)

6.3.5.3. Effect of Phosphate and Sulphate

In this experiment the phosphate and sulphate ions’ competition with nitrate removal was tested in the presence of 5 mg P/L phosphate and 50 mg S/L sulphate in a solution. This solution contained 20 mg N/L of nitrate with the following conditions: 1 cm between electrodes, 1 A and 18 V (Tables 6.11 and 6.12 and Figures. 6.13 and 6.14). In the presence of these co-ions the EC system’s nitrate removal efficiency was not affected. However, the amount of nitrate removed by adsorption on Dowex was reduced by these co-ions especially by the sulphate (compared to removals in the presence of P (Table 6.7) and S (Table 6.9)). Consistent with this data the sulphate adsorption was many times higher than phosphate adsorption (Table 6.11). The phosphate removal was higher in this N+P+S solution (Table 6.11) compared to the N+P solution (Table 6.7). This may be due to the increase in iron concentration in the solution when sulphate was present. The iron concentration rose from 1.25 mg/L to 8 mg/L when the sulphate ion was added to N+P solution. The phosphate ions formed $FePO_4$ precipitate in solution/or surface precipitation at the surface of the stainless steel electrode as discussed in sub-section 6.3.5.1. The reason for the higher Fe concentration in the N+P+S solution was due to higher electrical conductivity that was produced by the higher N+P+S ion concentration. No notable change occurred in the sulphate removal for this solution compared to the N+S solution.

Table 6.11. Amount of NO_3^-, PO_4^{3-} and SO_4^{2-} removed (mg) from the solution containing nitrate, phosphate and sulphate after 3 h at 1 A, 18 V, pH 7.

Removal method	N	P	S
EC only	3.0	4.4	2.1
Adsorption only	4.8	0.9	21.9
EC-adsorption	7.0	4.7	23.7

Table 6.12. Percentage removal (%) of NO_3^-, PO_4^{3-} and SO_4^{2-} from the solution which contained nitrate, phosphate and sulphate after 3 h at 1 A, 18 V, pH 7.

Removal method	N	P	S
EC only	17.1	85.5	4.1
Adsorption only	24.6	9.3	43.5
EC-adsorption	40.7	95.1	49.9

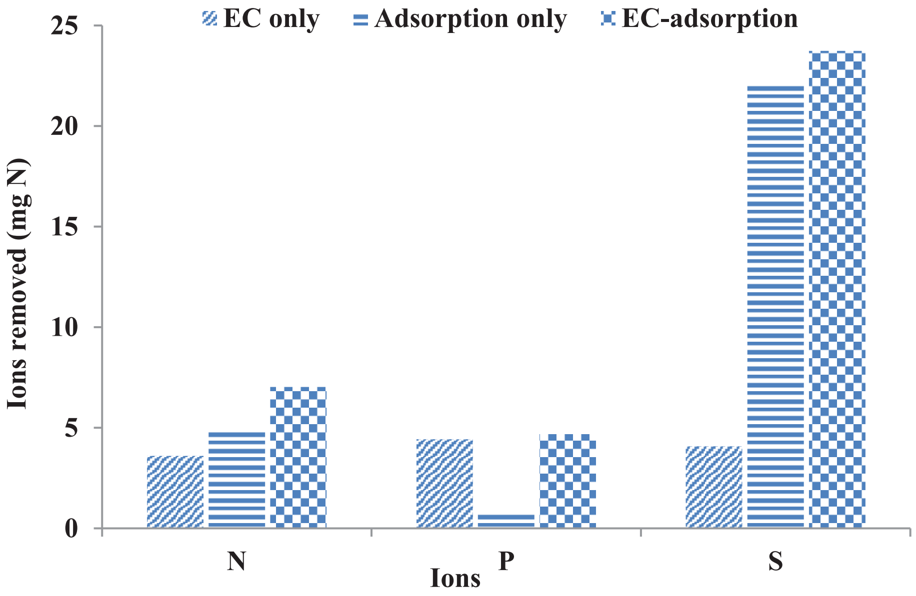


Figure 6.13. Amount of NO_3^-, PO_4^{3-} and SO_4^{2-} removed from the solution containing nitrate (20 mg N/L), phosphate (5 mg P/L) and sulphate (50 mg S/L)

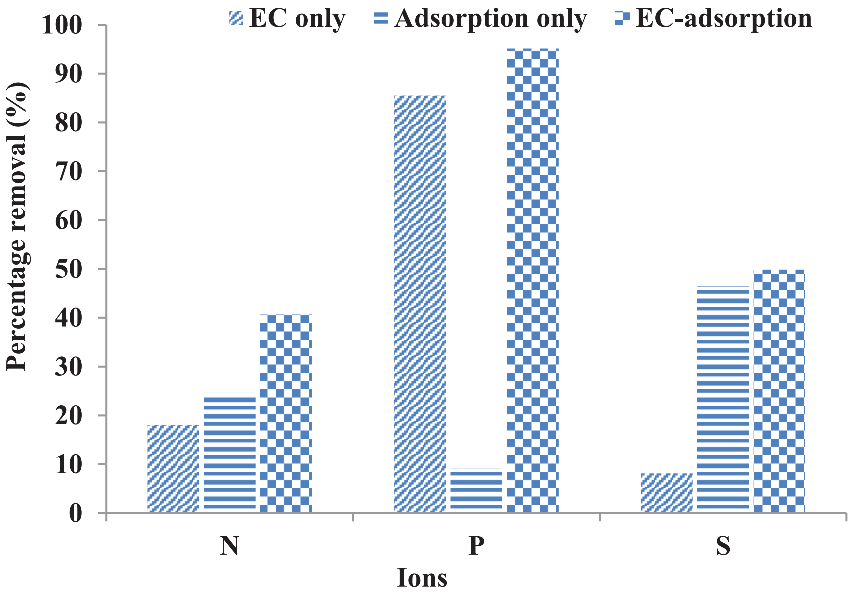


Figure 6.14. Percentage removal of NO_3^-, PO_4^{3-} and SO_4^{2-} from the solution which contained nitrate (20 mg N/L), phosphate (5 mg P/L) and sulphate (50 mg S/L)

6.3.6. Different adsorbents

The nitrate removal efficiency and the amount of nitrate removed in the integrated system, individual EC system and adsorption system using four adsorbents such as Dowex, Dowex-Fe, AG corn cob and AG coconut copra are shown in Tables 6.13 and 6.14 and Figures. 6.15 and 6.16. This study was conducted with 20 mg N/L nitrate solution at pH 7. The distance between the electrodes was maintained at 1 cm with the electrical potential of 30 V and current of 1 A for 3 h. The nitrate removal efficiencies and the amounts of nitrate removed in the integrated system were higher than the individual batch adsorption and EC systems. When the adsorbents were added into the EC system, the nitrate removal efficiencies increased to 67%, 79%, 56%, and 51% from the EC system's lone value of 16.6% for Dowex, Dowex-Fe, AG coconut copra and AG corn cob, respectively. The nitrate removal percentages in the integrated system were approximately the sum of the percentages of those in the EC system and the adsorption system. The order of decreasing nitrate removals was the same as that in the adsorption system alone (Dowex-Fe > Dowex > AG coconut copra > AG corn cob).

The ammonium concentration in the final solution was less than 0.1 mg/L for all the adsorbents and nitrite was not detected. This indicates that nitrate from the solution was adsorbed by the adsorbents and also reduced to N_2 gas as the major product in the EC process. The solution used in the experiment was prepared from tap water and it contained 30 mg/L of Cl^- ions. Also, when nitrate adsorption occurred the adsorbents released Cl^- ions. The Cl^- ions helped to reduce the concentration of ammonium ions in the solution by the processes described previously.

Table 6.13. Amount of nitrate removed (mg N) by the four adsorbents after 3 h at 1 A, 30 V, pH 7

Removal method	Dowex	Dowex-Fe	AG coconut	AG corn cob
EC only	3.17	3.17	3.17	3.17
Adsorption only	9.06	13.41	8.12	7.82
EC-adsorption	12.36	15.79	10.84	10.7

Table 6.14. Percentage removal (%) of nitrate using the four adsorbents after 3 h at 1 A, 30 V, pH 7

Removal method	Dowex	Dowex-Fe	AG coconut	AG corn cob
EC only	16.6	16.6	16.6	16.6
Adsorption only	49.1	62.7	39.0	37.6
EC-adsorption	67.0	79.0	55.8	51.4

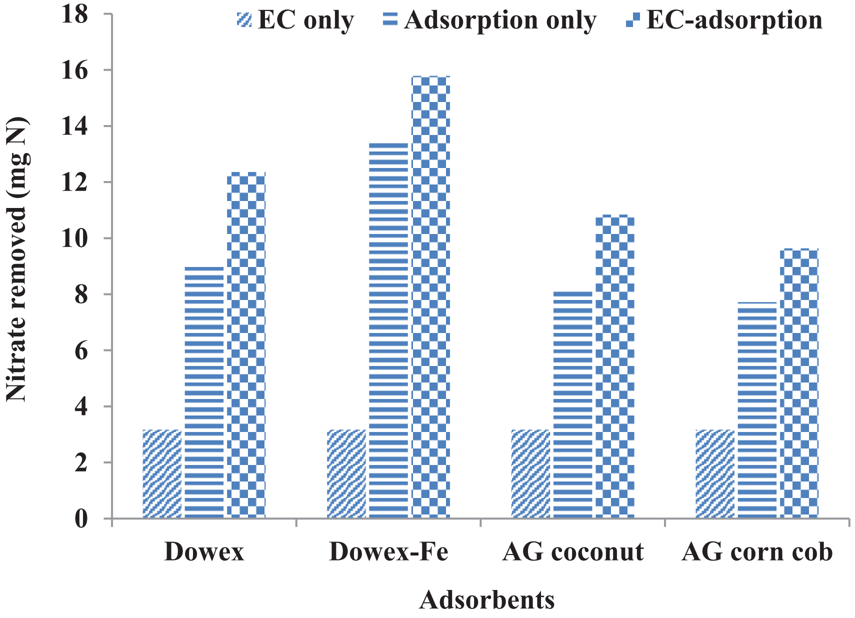


Figure 6.15. Amount of nitrate removed by four adsorbents

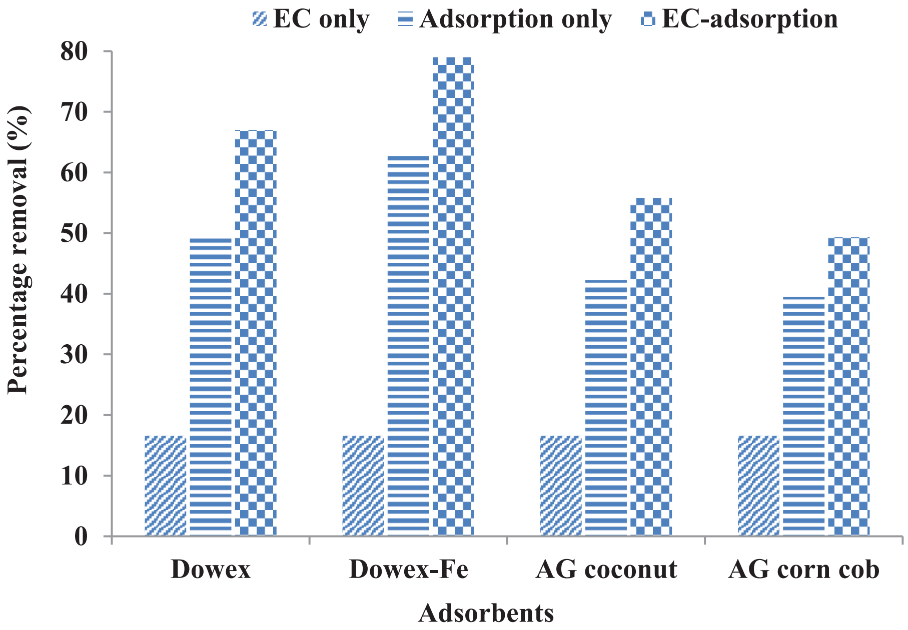


Figure 6.16. Percentage removal of nitrate by four adsorbents

6.3.7. Cost calculation

Cost is an important factor in the water treatment process and removing more pollutants at low cost is preferred. While it is difficult to compare the systems cost-wise, rough calculations of operational cost were made for the EC treatment system (EC), adsorption treatment system and integrated system (EC-adsorption) separately based on the experimental results. The cost of electricity in the EC system was assumed to be \$0.3 for 1 kWh (Australian Energy Council, 2016) and that of Dowex was \$50/ kg (Sigma-Aldrich, 2016). The costs of removing 1000 mg N from the nitrate solution were calculated and found to be \$8.52, \$11.04, and \$10.28 for EC, adsorption, and EC-adsorption, respectively. The EC system's removal efficiency was low compared to the adsorption system but the cost to remove 1000 mg N was less in the EC system. The cost in the adsorption system can be reduced if the resin is regenerated and repeatedly used. Similarly, the integrated system cost can be reduced if the resin is regenerated. The costs for removal of 1000 mg N as nitrate in the presence of sulphate and phosphate were \$ 5.33, 20.79, and 16.53 for EC, adsorption, and EC-adsorption systems, respectively. By adding these anions the current could be maintained to 1 A at a lower voltage in EC and EC-adsorption, and therefore less power would be consumed. Conversely, in the adsorption system the presence of phosphate and sulphate reduced nitrate adsorption. The EC system can be used to remove several other pollutants such as oil, COD, suspended solids, viruses, fluoride, phosphate, ammonia, and nitrite. Consequently, the overall treatment cost should be further reduced for the EC and EC-adsorption systems. A cost calculation was done for the removal of 1000 mg N in order to compare the processes, though it is difficult to remove 1000 mg N by the EC method using a single EC cell (one cathode/one anode). Multiple cells are required to achieve this amount of removal which will increase the operational costs. This suggests that adsorbent should be added to the EC system to achieve the higher removal of nitrate in a shorter period of time. Such an integrated process will reduce labour costs as well as energy costs for the treatment process. Overall, the EC-adsorption integrated system is an effective treatment strategy that will remove nitrate efficiently in terms of cost and operation time.

Table 6.15. Cost calculation for EC system only (1 kWh = $ 0.3)

Experiments	Current (A)	Voltage (V)	W	Time (h)	kWh	Cost ($)	N removed (mg)	Cost for 1000 mg N removal
N only	1	30	30	3	0.09	0.027	3.17	8.5
N+P+S	1	18	18	3	0.054	0.016	3.04	5.3

Table 6.16. Cost calculation for batch adsorption only (1 kg Dowex = $ 50)

Experiments	Adsorbent used (g)	Adsorbent cost ($)	N removed (mg N)	Cost for 1000 mg N removal
N only	2	0.1	9.06	11.0
N+P+S	2	0.1	4.81	20.8

Table 6.17. Cost calculation for integrated system

Experiments	Cost ($)	N removed (mg)	Cost for 1000 mg N removal
N only	0.13	12.36	10.3
N+P+S	0.12	7.03	16.5

6.4. Conclusions

The integrated EC-adsorption system removed more nitrate compared to the adsorption and EC systems operated separately. Of the four distances (0.5, 1, 2 and 3) between the electrodes, 1 cm was found to be the most cost-effective. The optimum nitrate removal (67% from solution containing 20 mg N/L) was achieved for the integrated system at pH 7 with the conditions where electrodes were 1 cm apart at 1 A, 30 V and 30 ^{0}C for Dowex. Of the four adsorbents tested (Dowex, Dowex-Fe, AG coconut copra and AG corn cob) the most amount of nitrate was removed when using Dowex-Fe adsorbent. There was no significant change in nitrate removal efficiency in the EC and integrated system in the presence of sulphate and phosphate. The highest phosphate removal achieved was 95% in integrated system which was much higher compared to batch adsorption and slightly higher compared to the EC system. The ammonia produced as a byproduct of the EC and integrated systems is low in the final solution because of the higher concentration of Cl^- that was in the tap water used in the experiment. The ammonium ion concentration was further reduced in the integrated system compared to the EC system due to the release of Cl^- ions from the adsorbents. A high rate of nitrate removal can be achieved in the integrated system in a short period of time at less cost and space compared to the other systems. This system can operate over the long-term by adding larger amounts of adsorbents initially and later frequently in the stainless steel electrode box. This study was conducted with a single cell (one cathode and one anode) to demonstrate the suitability of the integrated system for nitrate removal. It is recommended that future studies use multiple cells connected in series to continuously and more efficiently remove nitrate.

CHAPTER 7

Conclusions and recommendations for future studies

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CHAPTER 7

Conclusions and recommendations for future studies

7.1. Conclusions

For the plant-scale removal of nitrate from contaminated waters using the adsorption process, the adsorbent should have high adsorption capacity, high nitrate selectivity in the presence of other anions, low cost, good hydraulic conductivity when packed in columns, and able to be regenerated several times for repeated use without significant loss of adsorption capacity. One effective means of achieving some of these characteristics is to surface modify the adsorbent by providing new functional groups that can give additional positive charges to electrostatically adsorb the negatively charged nitrate. Unlike many previous studies, the research presented in this thesis was on the removal of nitrate from waters containing co-ions by surface modified adsorbents in both batch and column studies. Adsorbents in the columns were regenerated for repeated use.

7.1.1. Batch and column studies

The ion exchange resin Dowex was surface modified by incorporating Fe on the surface (Dowex-Fe). The agricultural wastes, coconut copra and corn cob were surface modified by incorporating amine groups (AG corn cob and AG coconut copra). The surface-modified adsorbents' adsorption capacities were very much higher than the unmodified adsorbents in both batch and column experiments due to the increase in the number of surface positive charges as confirmed by zeta potential measurements. The Langmuir adsorption capacities were in the order Dowex-Fe > AG coconut copra > AG corn cob > Dowex for the initial nitrate concentration of 20 mg N/L and different doses of adsorbents (solutions prepared in milli-Q) at pH 6.5. The column adsorption capacities were in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob for the initial nitrate concentration of 20 mg N/L (solutions prepared in tap water) at pH 6.5- 7.5 with the dry bed height of 15 cm and 5 m/h filtration velocity. The adsorption capacity reduced more for the agricultural wastes than ion exchange resin Dowex in the column experiments due to the presence of Cl^- ions in the tap water. Nitrate adsorption capacity was greatly reduced in the presence of sulphate ions for all the adsorbents. It was, however, slightly reduced in the presence of phosphate and chloride ions for Dowex and considerably reduced in AG wastes when using chloride.

The batch isotherm models, Langmuir, Freundlich, and Sips and batch kinetics models pseudo first-order, pseudo second-order, Elovich and HSDM satisfactorily fitted to the adsorption data for all adsorbents. The Thomas model fitted well to all the adsorption-desorption cycles of the column data for all adsorbents, yet the plug-flow model satisfactorily fitted to the data only for the first cycle. The nitrate adsorbed was effectively desorbed from the adsorbents using 1 M KCl (more than 85% desorption) for all the adsorbents. The adsorption capacity of the regenerated ion exchange resins fell slightly for each repeated adsorption-desorption cycle. The agricultural wastes' adsorption capacity declined by 30% for the second cycle and then marginally reduced for the 3rd and 4th cycles. The low-cost amine grafted agricultural wastes had adsorption capacities similar to that of the commercial anion exchange resins. The exhausted agricultural wastes can be used as fertiliser on agricultural lands and the solutions obtained from desorption which contained K and desorbed nitrate can be used for fertigation (N and K are nutrients) of plants.

7.1.2. Membrane adsorption hybrid system

The membrane adsorption hybrid system with frequent 10% adsorbent replacement used to continuously remove nitrate from an influent solution nitrate concentration of 20 mg/L was effective in maintaining the nitrate effluent concentration below the WHO limit of 11.3 mg N/L for a long operation period. Out of the four adsorbents, Dowex-Fe performed the best in terms of the amount of nitrate removed and the volume of water treated. This system can be utilised to obtain high quality and quantity of treated water by simultaneously removing nitrate and other pollutants such as micro-organisms, micro particles, suspended solids, colloids. It can also retain the adsorbents in the tank when the treated water flows through the membrane.

7.1.3. Electrochemical adsorption system

The EC system integrated with adsorption technology by adding adsorbent to the stainless steel anode box proved to be an effective method for nitrate removal. Nitrate removal in the integrated system was generally the sum of the removals in the EC and adsorption system used individually. The integrated system's nitrate removal functioned at its best when pH was neutral (pH 7) with distance between electrodes of 1 cm and at the current and voltage values of 1 A and 30 V, respectively. The integrated system reduced the concentration of the byproduct - ammonium ions in the solution - better than the EC system due to the release of chloride ions from the adsorbents during nitrate adsorption.

Overall, among the adsorbents used in the studies, Dowex-Fe performed the best out of four adsorbents. However, amine grafted agricultural wastes are cost effective adsorbents and can be used in developing countries. The methods used here cannot be compared with each other because each method has various advantages and disadvantages in terms of efficiency, cost, operation period, and simultaneous removal of other pollutants. However, if the raw water contains nitrate alone, column adsorption will be effective and low cost method with long term operation.

7.2. Recommendations for future studies

The following recommendations are proposed for future research work:

- Research needs to surface modify other low-cost adsorbents to produce adsorbents that are nitrate selective and have high nitrate adsorption capacities.
- Most of the adsorption experiments have been conducted in batch mode using synthetic water. Future studies should be conducted in column mode/submerged membrane hybrid adsorption system experiments with real surface, ground and Waste water, which contain several inorganic and organic constituents. This will enable the results to be applied directly to practical situations.
- The integrated adsorption-EC system used in this study showed promising results in the removal of nitrate. However a single cell containing one anode and one cathode was used. Research needs to be conducted using many such cells connected in series to continuously remove nitrate in a dynamic water flowing system. Adsorbents can be frequently added to the stainless steel box to maintain high adsorption capacity.
- Encouraging results obtained with the surface modified adsorbents in the laboratory scale experiments in this thesis need to be tested further in pilot-plant scale experiments where the conditions are closer to that of a real treatment plant.

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