1 Introduction

1.1 Background

The interactions between soil, water and nutrients are important factors to predict the fate of nutrients in soils (Evangelou, 1998). Synthetic ion exchange resins commonly known as resins have been used in soil sciences for a long time. These resins are made from polymerization of styrene molecules with the reinforcement of divinylbenzene and ionogenic groups (Skogely and Dobermann, 1996).

These resins vary in their affinity towards different nutrients. The overall efficiency of the resins depends upon size and structure of resin particles, purity of the reagents, the concentration and the size of the applied ions.

An ion exchange reaction is the reversible interchange of ions between a solid phase and a solution phase in which the ion exchanger is insoluble. The ions which are exchanged from the exchangers are named ‘counter-ions’ while the ions that are not taken to the exchanger due to same charge are termed as ‘co-ion’s (Harland, 1994).

An ideal exchanger is characterised by a rapid rate of exchange, chemical stability, effective ion exchange capacity, mechanical strength and effective surface area (Harland, 1994). The movement of pollutants in ground water, water retention and movement in soils are governed by hydrophobicity, cohesion and adhesion (Evangelou, 1998).

Organic resins possess high mechanical and chemical stability, high ion-exchange capacity and fast exchange rates. Inorganic ion exchange gels also possess high capacities and fast exchange rates, but lacks mechanical and chemical stability.

1.2 General applications of ion exchange resins

Ion exchange is a universal phenomenal occurring in living organisms, rocks, sands and soils (Helfferich, 1995). Today, ion exchange governs processes such as filtration, distillation and adsorption (Table 1). They are widely used in water purification (Bratek et al., 2002), water softening (Anupkumar et al., 2001; Skipton et al., 2008), metal separation (Matsubara et al., 2000) and sugar manufacturing (Elmidaoui et al., 2002). The first commercial application of resin-in-pulp (RIP) was for gold recovery in mines (Lukey et al., 2000).

Since 1950`s, there has been a sharp increase in scientific literature dealing with the use of ion exchangers.

Ion exchangers are also used for isotope separation in nuclear industry. But their most important use is for purification of water. Many of the manufacturers of ion exchange resins are not interested in other application of these exchangers, because they are considered secondary (Zagorodni, 2007).

The advantages of ion exchange technology consist of the possibility to remove highly diluted contaminants and their insensitivity to variations in flow and concentration. Ion exchange resins are chemically active and highly stable in their physical and chemical structure. Due to these specific properties, they will not contaminate products (Zagorodni, 2007).

Table 1. Applications of ion exchange materials (Zagorodni, 2007).

Field of application	Various uses in detail
Water preparation	Water softening, production of ultra pure deionised water
Nuclear industry	Separation of uranium isotopes and condensate polishing
Pulp and paper industry	Removal of inorganic salts and detoxification of by-products
Purification of sugars	Separation of monosaccharides, purification of fructose and different kinds of sugar
Food industry	Deacidification of fruit juices, recovery of glutamic acids and removing off tasters
Dairy	Extraction of lactoferrin and purification of casein
Winery	Stabilisation of wine and adsorption of wine proteins
Biotechnology	Separation of lactic acid, production of L-glutamine, production of citric acid and organic acids
Pharmaceutics and medicine	Antibiotics, vitamins and tablet disintegration
Soil science	Evaluation of soil properties, artificial soils and remediation of contaminated soils

The main application of ion exchange resins is the separation of dissolved ions. These separation processes can be classified as

1) Purification of a solvent: When the solvent is the desired product and dissolved ions are considered to be contaminants
2) Purification of a solution: Here the product is a solution and the raw material is of a similar constitution but contains an undesirable solute
3) Extraction: When the dissolved compounds were taken from a solution and the exhausted solution has no significant value
4) Separation: Several ions of interest are obtained as different products

1.2.1 Applications in soil and environmental sides

Ion exchange resins were found to be extremely useful in the studies of nutrient dynamics in soil (Yang and Skogley, 1992; Wyland and Jackson, 1993; Lehmann et al., 2001; Siemens and Kaupenjohann, 2004), nutrient availability (Sibbesen, 1976; Lajtha, 1988) trace element release (Agbenin et al., 1999; Lang and Kaupenjohann, 2004), nitrogen fixation (Veluci et al., 2006), nitrogen mineralization (Eghball, 2000; Friedel et al., 2000; Hanselman et al., 2004), medium of plant growth (Skogley and Dawson, 1963; Skogley, 1966; Harper and Nicholas, 1976), soil testing (Sharpley et al., 1987; Li et al., 1993; Dobermann et al., 1994; Johns and Skogley, 1994), nutrient runoff (Agbenin and Raij, 2001; Uusitalo and Ekholm, 2003) and heavy metal contamination (Tack and Verloo, 1995; Brower et al., 1997; Rengaraj et al., 2002). In environmental sciences, ion exchange resins were successfully used in measuring eutrophication (Uusitalo and Ekholm, 2003), water purification (Tiravanti et al., 1997; Dąbrowski et al., 2004), removal of organics, (DeSilva, 1997), and heavy metal removal (Beatty et al., 1999; Chiarle et al., 2000).

1.3 Stages involved in the process of ion exchange

The ion exchange separation process is affected by the scale of the separation process, economical aspects and environmental safety (Zagorodni, 2007). The process in which the ions attach to the ion exchanger is called sorption. When sorption is completed, the ions must be harvested from the exchanger by elution. This process is also called ‘desorption’ ‘recovery’ or ‘stripping’. Then the material is reconverted into its original state for the next ion exchange cycle; this is known as ‘regeneration’ (Figure1). Elution and regeneration are processes just opposite to sorption; as regeneration allows an ion exchanger to regain its initial form (Zagorodni, 2007). If more than one product has to be eluted from the exchanger, several elution steps will have to be performed.

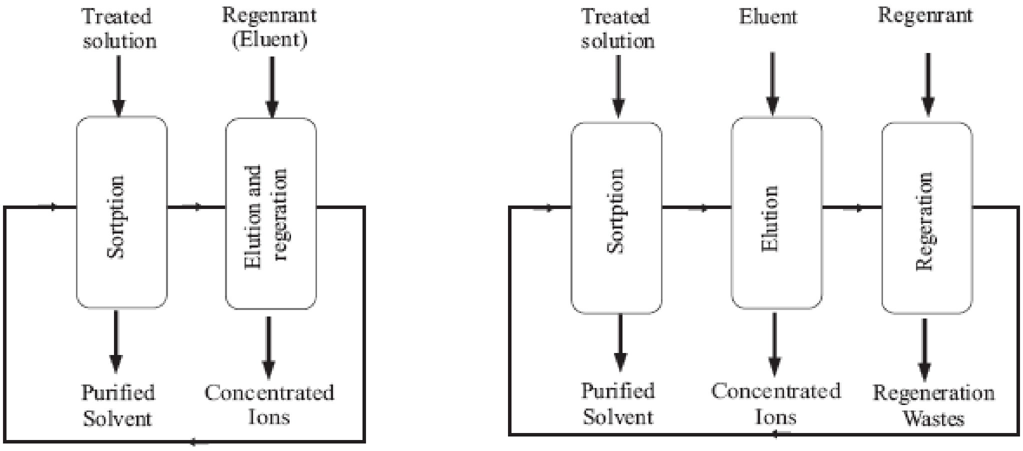

Figure 1. Simplified diagram of an ion exchange separation: two-step process combining elution and regeneration (left) and three-step process with separate elution and regeneration procedures (right; Zagorodni, 2007).

1.4 Water usage and associated problems

Environmentally, the protection of ground water resources is of high priority, but often source and effects of contaminations are difficult to measure (Alley, 1993). Recycling of waste water reduces the increasing pressure on water resources, conserves the supply of fresh water and protects the environment (Judd, 2003). At present, the industry uses almost a quarter of the total water consumptions (Table 2). Much of this water is taken from public water supplies and should be of high standard according to specifications of the industry (Table 3).

Table 2. Water demand of various industrial sectors (Judd, 2003).

Industry	Water demand
Paper	29 m^3/t paper produced
Brewing	10-15 m^3/m^3 beer
Dairy	140 m^3/m^3 milk
Sugar	8 m^3/t sugar
Dying	100 m^3/t fabric produced
Soap	2 m^3/t soap produced

Table 3. Generalised industrial water quality standards (Judd, 2003).

Class	Type	Uses
1	Natural, river	Fire fighting, irrigation
2	Potable	Drinking
3	Softened	Laundries, Steam raising and heat transfer
4	Deallocate	Steam raising and heat transfer
5	Deionised	Food, soft drinks, cosmetics
6	Purified	Pharmaceuticals, cosmetics
7	Apyrogenic	Pharmaceuticals
8	High purity	Laboratories
9	Ultrapure	Semiconductor

1.5 Composition of ion exchange resins

Differences in chemical and physical properties of ion exchange resins make them suitable for different applications. Adsorbents that are used for study of soil or environments are generally termed as synthetic ion exchange resins. These are manufactured from polymerized styrene molecules with divinylbenzene as cross-linking agents (Figure 2). The polymer chain cross-linkages influence the physical and chemical properties of ion exchange resins (Skogely and Dobermann, 1996).

Macroporous (macroreticular) ion exchange resins are widely used in soil studies. These resins are also called resins beads, which are spherical, opaque and possess a large internal surface area (Figure 3). Ion exchange membranes which are available in cation, anion or bi-polar forms are also used for soil and environmental studies (Skogely and Dobermann, 1996).

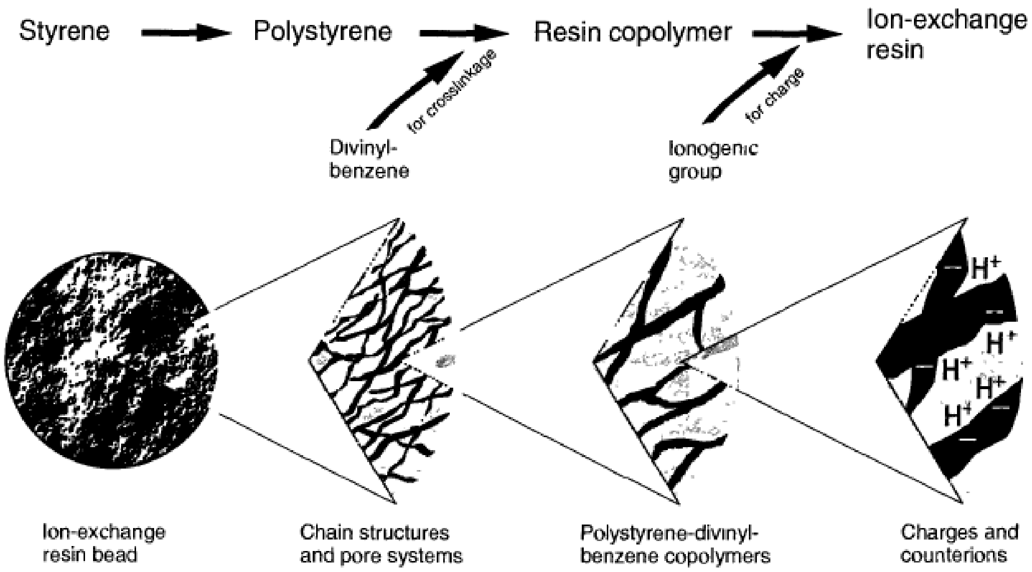

Figure 2. Schematic formation of ion exchange resins and properties of a macroporous resin bead (Skogely and Dobermann, 1996).

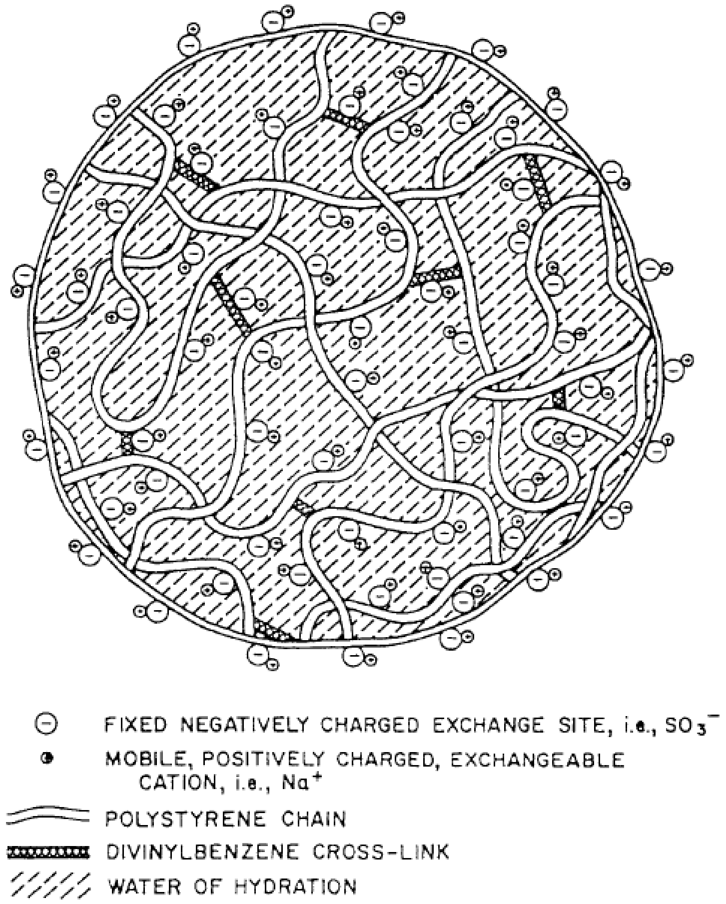

Figure 3. Expanded view of a polystyrene bead (Alchin, 2009)

Ion exchange resins can be divided into cation exchangers and anion exchangers. The cation exchangers possess negatively charged functional groups while anion exchangers possess positively charged functional groups. These active (ionogenic) groups are responsible for chemical properties of ion exchange resins (Table 4). Resins with one type of active group are termed as monofunctional resins.

Table 4. Active groups in ion exchange resins (Skogely and Dobermann 1996).

Name of resin	Active (ionogenic) group
Cation exchange resin	Sulfonic acid, carboxylic acid and hydroxide
Anion exchange resin	
Type I	Trimethylamine
Type II	Dimethyl-β-hydroxyethylamine

Cation exchange resins have either strongly acid or weakly acid properties, while anion exchange resins are either strong base or weak bases. Strongly acidic cation exchange resins have low affinity for H^+ ions and act as a sink for other cations, while, weakly acidic cation exchange resins have high affinity for H^+ ions (Skogely and Dobermann, 1996). Strong ion exchanger groups can be ionized in a wide range of pH, while weak ion exchanger groups are ionized in a narrower pH range (Choudhary and Horvath, 1996).

Maximum resin capacity measures the total number of exchangeable ions per unit mass of the resin and is commonly expressed in milliequivalents per gram (meq g^{-1}). The resin capacities can change depending on the type of active group, degree of cross linking and pH (Dobermann et al., 1994; Skogely and Dobermann, 1996; Richardson and Harker, 2002).

At low pH, H^+ ions present on the weak acid cation exchangers remain undissociated. On the other hand, NH_3^+ ions present on weak base anion exchangers form uncharged NH_2 ions at high pH. Thus, weakly acidic cation exchange resins are useful at pH 5 to 14 (Table 5), and weakly basic anion exchangers function effectively at pH 0 to 9 (Skogely and Dobermann, 1996; Richardson and Harker, 2002).

Table 5. Resin types, functional groups and useful pH ranges (Choudhary and Horvath, 1996; Skogely and Dobermann, 1996).

Resin	Type	Functional group	Affinity	pH range
Cation	Strongly acidic	Sulfonic acid	Low affinity for H$^+$ ions	0-14
	Weakly acidic	Carboxylic acid	High affinity for H$^+$ ions	5-14
Anion	Strongly basic	Quaternary ammonium compounds	High affinity for OH$^-$ ions	0-14
	Weakly basic	Primary, secondary or tertiary amines	Low affinity for OH$^-$ ions	0-9

Table 6. Trade names and manufactures of ion exchange resins (Helfferich, 1995).

Trade name	Manufacturer
Amberlite	Rohm & Haas Co., USA
De-Acidite	The Permutit Co. Ltd., England
Dowex	Dow Chemical Co., USA
Duolite	Chemical Process Co., USA
Imac	Industrieele Mij. Activit N.V., Netherlands
Ionac	Ionac Co. Ltd., USA
Nalcite	National Aluminate Corp., USA
Wofatit	VEB Farbenfabrick Wolfen, Germany
Zerolit	United Water Softeners, England

Owing to the wide diversity of resins, a good classification of properties and usages is needed. The ion exchange systems used in soil and environmental studies are based on the specificity of the resins and the manner of use (Skogely and Dobermann, 1996; Table 7).

Table 7. Classification scheme of resin systems used in soil and environmental studies (Skogely and Dobermann, 1996).

Level	Classification criterion	Classes
1	Function of the resin	Resin used as source and sink
2	Resin-medium contact	Batch and diffusion sensitive
3	Target ions	Anion, cation and both
4	Number of target ions	Single-ion and multi-ion
5	Rein physical form	Loose, bag, capsule and membranes
6	Counter-ion	The name of the ion

Resins exchanges the initial counter ions for the target ions in the medium and later the resins are analysed for amount of the target ions accumulated. The anion and cation exchange resins were used in batch or diffusion-sensitive modes. Mixed-bed systems uses anion and cation exchange resins, but the interpretations of these data is more complicated than of those from mono-bed systems (Skogely and Dobermann, 1996).

Batch resin systems are widely used. They differ in their operational and stripping methods. The shaking time varies from 1 hour (Lathwell et al., 1958) to 305 hours (Bache and Ireland, 1980). Mixed-bed resin systems are widely used for stimulating nutrient uptake by plants, ion leaching and transformations (Langlois et al., 2003).

For the proper quantification of the solute transport, direct field measurements of soil leaching are necessary. Tensiometer-controlled suction samplers, wick samplers and ion exchange resins allow measurement of nutrient fluxes in soils. For the first two methods, high cost and maintenance needs to limit the number of samplers which can be deployed in the field. (Siemens and Kaupenjohann, 2004).

The resin capsule method was found to be promising for the study of nutrient dynamics (Pampolino et al., 2000). The data from ion exchange resin extractions are expressed in weights or moles of desired nutrient per unit-weight or surface area of ion exchange resin (Skogley et al., 1996; Johnson et al., 2005). Ion exchange resins are placed in resin boxes or bags and installed in the soil. As the drainage water passes through the resins, the solutes are adsorbed by the ion exchange resins. Subsequently, the resins are removed and the solutes are harvested with appropriate stripping solutions such as KCl or NaCl (Simkin et al., 2003; Siemens and Kaupenjohann, 2004).

Ion exchange resin boxes are not suitable for studying short term nutrient leaching dynamics but their low price and easy maintenance allows to deploy a relatively large number of replicates in order to measure cumulative leaching data in heterogeneous environments (Lehmann et al., 2001). The efficiency of the ion exchange resins in capturing plant available nutrients especially nitrates can be hampered by competition of plant microbes and ion diffusion (Binkley, 1984; Skogley and Schaff, 1985; Hart and Firestone, 1988; Subler et al., 1995).

The resins used for the study described here were of industrial grade which are quite different from laboratory grade resins. Background contaminations of NH^+_4 and NO^-_3 ions in such resins were reported in Rexyn, Baker and Amberlite brands (Langlois et al., 2003) and call for the consistent use of blanks during analysis.

To eliminate the background contamination, ion exchange resins can be pre-treated. Pre-treatment of the above mentioned ion exchange resins with 2M KCl significantly reduced the background contamination of NO^-_3 ions. However, it was noticed that this increased the background contamination level of NH^+_4 (Langlois et al., 2003). Also such pre-treatment can significantly decrease ion absorption capacity. The recovery of dissolved inorganic phosphate (DIN) and dissolved organic phosphate (DOP) was also affected by pre-treatment (Langlois et al., 2003).

Ion exchange resins may also be sensitive to operating conditions and storage temperatures. In the case of the Amberjet 4200 Cl anion exchange resin, the manufacturer-recommended maximum operating temperature is 80°C (Table 9). After the capture of solutes, ion exchange resins are typically stored in deep freezers to avoid the loss and degradation of the solutes. Assuring cold storage during long-distance transport of the resins to an appropriate laboratory may be difficult.

1.6 Hypotheses

Hypothesis 1: Industrial grade ion exchange resins contains significant amount of ions that disturb subsequent analysis.

Hypothesis 2: The recovery rate of ion exchange resins is affected by the purity of the ion exchange resin, as well as the concentration and the flow rate of the applied nutrient solution.

Hypothesis 3: Storage conditions affect the amount of ions absorbed to the ion exchange resins.

1.7 Objectives

The main objectives of this study were to determine:

1) the background contamination of commercially available ion exchange resin Amberjet 4200 Cl anion exchange resin and Amberjet 1200 Na cation exchange resin;
2) effective pre-treatment (washing) methods for Amberjet 4200 Cl anion exchange resin and Amberjet 1200 Na cation exchange resin;
3) the efficiency of resins in capturing various nutrients applied at different concentrations, flow rates and purity conditions and;
4) the best methods for the storage of the resins