REACTIVATION OF ION EXCHANGE RESINS FOR WATER TREATMENT APPLICATION

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REACTIVATION OF ION EXCHANGE RESINS FOR WATER TREATMENT APPLICATION

by

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DECLARATION

I hereby declared that I have conducted, completed the research work and written the dissertation entitled: " **Reactivation of Ion Exchange Resins for Water Treatment Application**". I also declared that it has not been previously submitted for the award for any degree or diploma or other similar tittle of this for any other examining body or University.

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LIST OF SYMBOLS

%	Percentage
µm	micrometer
℃	Degree Celsius
g	gram
K	Kelvin
ml	milliliter
mV	milliVolt
nm	nanometer
ppb	part-per-billion
ppm	part-per-million
µS/cm	microSiemen per centimeter

LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectrometry
CD	Cross-linking Density
DC	Direct Current
DI	Deionized
DOC	Dissolved Organic Carbon
DVB	Divinylbenzene
EDBM	Electrodialysis with Bipolar Membranes
FTIR	Fourier Transform Infrared Spectroscopy
HCl	Hydrochloric Acid
IX	Ion Exchange
MCA	Moisture Content Analysis
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
ORP	Oxidation Reduction Potential
PSA	Particle Size Analysis
SAC	Strong Acid Cation Exchange Resins
SBA	Strong Base Anion Exchange Resins
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TOC	Total Dissolve Carbon
UC	Uniformity Coefficient
WAC	Weak Acid Cation Exchange Resins
WBA	Weak Base Anion Exchange Resins

PENGAKTIFAN SEMULA RESIN PERTUKARAN ION UNTUK APLIKASI RAWATAN AIR

ABSTRAK

Resin penukar ion atau resin IX ialah penukar ion polimer sintetik yang telah digunakan secara meluas dalam proses penulenan air untuk membuang bahan cemar dalam air seperti ion kekerasan melalui penyahmineralan. Dalam proses penulenan air, resin SAC (bentuk H ion) dan SBA (bentuk OH ion) IX biasanya digunakan. Selepas beberapa kitaran servis, resin IX menjadi letih dan perlu dijana semula untuk digunakan semula. Beberapa masalah yang dihadapi semasa penjanaan adalah kekotoran resin, kecekapan penjanaan semula yang rendah dan penggunaan bahan kimia yang tinggi. Tujuan penyelidikan ini adalah untuk menambah baik proses penjanaan semula resin. Untuk mencapai matlamat, rojek ini telah membangunkan proses pengasinan dengan parameter yang dioptimumkan, serta ciri-ciri dan membandingkan prestasi penulenan air bagi resin IX yang tidak dirawat dan resin IX pra-rawatan melalui proses penyahmineralan. Natrium klorida (NaCl) telah digunakan sebagai kimia pengasinan dan parameter kesan brining diuji menggunakan kaedah kelompok. Projek ini menunjukkan bahawa pengoptimuman proses brining dicapai dengan proses brining dalam keadaan kering dengan larutan air garam 5% dan nisbah isipadu 1:1 pada suhu brining 55 ℃. Spektrum FTIR resin menunjukkan bahawa pengasinan boleh membersihkan kekotoran seperti karbon organik (DOC) terlarut pada resin. Proses penyahmineralan menunjukkan pengasinan boleh memanjangkan hayat perkhidmatan resin. ICP-MS telah menunjukkan penggunaan kimia dalam penjanaan semula kimia boleh dikurangkan dengan membuang sebahagian ion kekerasan daripada resin yang dibelanjakan dengan secukupnya dalam pra-rawatan.

REACTIVATION OF ION EXCHANGE RESINS FOR WATER TREATMENT APPLICATION

ABSTRACT

Ion exchange resin or IX resin is a synthetic polymeric ion exchanger that has been extensively used in water purification process to remove soluble ionized contaminant in water such as hardness ions (E.g., Ca, Mg). In water purification process, SAC (H-form) and SBA (OH-form) IX resins are commonly used. After several service cycle, the IX resins become spent and need to be regenerated so that is can be reused in the next service cycle. Several problems encountered during resins regeneration, which are resin fouling, low regeneration efficiency and high chemical consumption. The purpose of this research is to improve the resin regeneration process. To achieve the goal, the project has developed a brining process with optimized parameters for IX resin regeneration, as well as characterized properties and compare the water purification performance of the untreated IX resin and the pre-treated IX resin by demineralization process. Sodium chloride (NaCl) is selected to use as brining regenerant and the effect brining parameters are tested using batch method. This project shows that optimization of brining process is achieved by brining process in dried state with 5% brine solution and volumetric ratio of 1:1 at brining temperature of 55°C. From the result, brining is able to remove some impurities on the spent resins, increase the regeneration efficiency by partially remove hardness prior to regeneration and reduce chemical consumption by improving hardness removal capacity of low concentration regenerant (4% HCl). In demineralization, regeneration without brining will produce water with higher purity but regeneration with brining provide longer service life of resins.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Ion exchange (IX) resin is a type of synthetic polymeric ion exchanger that can perform ion exchange in the aqueous phase. It consists of functional groups that can be neutralized by ions or counterions in the aqueous phase. It is commonly synthesized with polystyrene matrix and cross-linked with divinyl-benzene (DVB) to produce the framework. Figure 1.1 shows the general constituent of strong acid cation resins. The figure shows that the framework of traditional gel-type IX resins consists of 3D cross-linked polymer skeleton that held together covalently, the functional groups that covalently bonded to the skeleton and the mobile exchanging ions with opposite charges to the functional group (SenGupta, 2017).

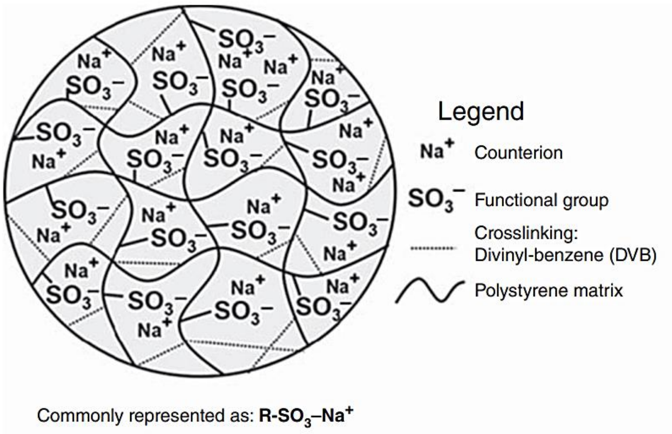


Figure 1.1: Schematic illustration of a strong acid cation (SAC) IX resin (SenGupta, 2017).

IX resin can either be cation or anion. Cation exchangers are those that interchange cations while anion exchangers are those that exchange anions. Negatively charge functional group such as sulphate, carboxylate, phosphate and benzoate are covalently bonded to matrix of cation IX resin, allowing diffusion of cations and rejecting diffusion of anions through the cation resin. Positively charged functional group such as amino group, alkyl substituted phosphine (PR_3^+) and alkyl substituted sulphides (SR_2^+) are covalently bonded to matrix of anion IX resin, allowing diffusion of anions and rejecting diffusion of cations through the anion resin (Kumar & Jain, 2013).

IX resin can be further divided into Strong Acid Cation (SAC), Strong Base Anion (SBA), Weak Acid Cation (WAC) and Weak Base Anion (WBA). SAC IX resin consist of sulfonic acid groups (HSO_3^-) as its functional group. It is commonly existed in form of hydrogen ($R-SO_3H$) or sodium ($R-SO_3Na$). SBA IX resin derive its functionality with quaternary ammonium functional groups, which can be further classified as Type I and Type II. Type I SBA resin have three methyl groups connected to the polymer matrix while Type II SBA resin have two methyl groups with one ethanol group connected to the polymer matrix. Type I SBA resin is commonly uses in selective ions removal such as removal of nitrates (NO^{3-}), sulphates (SO^{3-}) and perchlorate (CIO^{4-}). Type II SBA resins are commonly used for total removal of anions (Sharma, et al., 2018). WAC resin consist of carboxylic group (-COOH) as its functional group which is commonly available in hydrogen form (R-COOH). WBA resins exhibit minimum exchange capacity above pH 7 and it does not have an OH ion form (Vijay, 2014).

Hard water can be understood as the water that contain high minerals level such as high amount of calcium, magnesium and other minerals. In contrast, soft water is defined as water that contain higher concentration of sodium or salt relative to calcium, magnesium and other minerals. The hardness of water can be understood as the overall content of polyvalent ions in the water. In general, the higher the mineral level, the higher the hardness of water. In application, IX resins have been used in water purification process for many years. In water purification, it is used to remove the hardness of the water. The IX Resin will exchange the hardness ions from the hard water until it is spent, meaning that the ion exchange sites on the resin are fully occupied. Table 1.1 shows the general properties of a type of mix resins used in mixed bed system while Figure 1.2 shows a general water purification chart. Based on the chart, the application of IX resins is used in the production of ultrapure water through water purification process.

Table 1.1: The general properties of a type of SAC resins (Amberlite IR 120 in H^+ form) and a type of SBA resins (Amberlite IRA 402 in Cl^- form) that used in mixed bed system (Chandrasekara, et al., 2017).

Properties	**Amberlite IR 120**	**Amberlite IRA 402**
Functional group	Sulfonic acid	Quaternary amine
Matrix	Styrene-DVB (gel-type)	Styrene-DVB (gel-type)
Particle size (μm)	620-830	600-750
Moisture content (%)	53-58	49-60
Capacity (meq/ml, wet bed volume)	1.8	1.2
Cross-linkage (%)	8	6
Operating pH	0-14	0-14

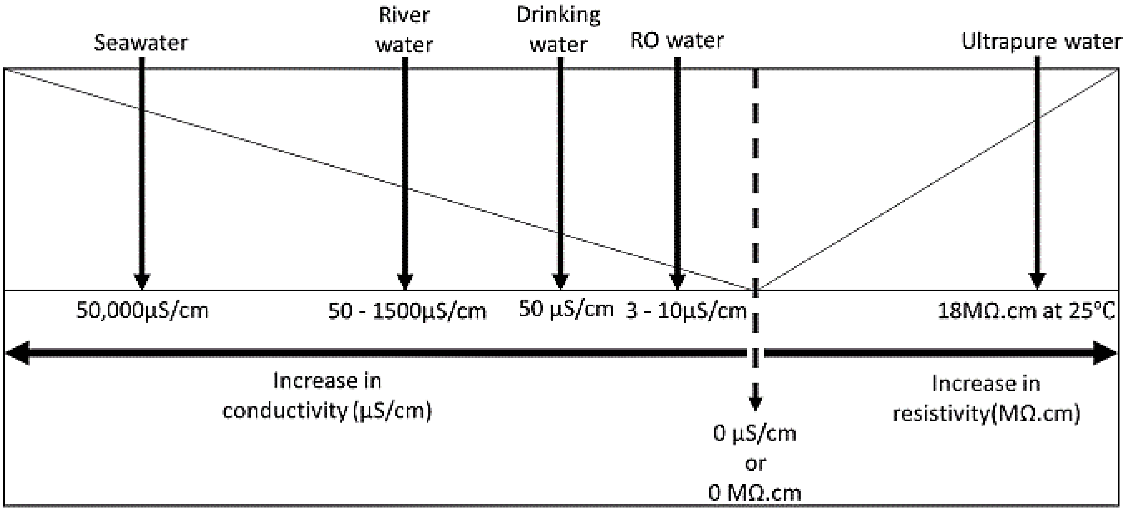


Figure 1.2: General water purification chart.

Figure 1.3 shows the schematic of the water purification process in a fixed-bed system. In general, IX resins undergo reversible ion exchange process between IX resin bed and the hardness contaminant ions in the aqueous phase. The input water with high hardness level passes through the SAC IX resins column follow by SBA IX resins column during the process. As water passed through the cation fixed bed system, all cations are exchanged, releasing equivalent amount of hydrogen ions (SenGupta, 2017):

$$RH + M^+ + N^- \rightarrow R^-M^+ + H^+ + N^- \quad \text{(Eq. 1.1)}$$

The output water produced in this stage is a dilute acid containing all the anions (N^-) which balanced by equivalent H^+cations. After the output water passed through the anion fixed bed column, all anions (N^-) are exchanged for hydroxyl (OH^-), which then bonded with H^+, producing pure water (H_2O):

$$ROH + H^+ + N^- \rightarrow R^+N^- + H^+ + OH^- \quad \text{(Eq. 1.2)}$$

$$H^+ + OH^- \rightarrow H_2O \quad \text{(Eq. 1.3)}$$

Thus, the overall reaction is:

$$RH + ROH + M^+ + N^- \rightarrow R^-M^+ + R^+N^- + H_2O \quad \text{(Eq. 1.4)}$$

As the process continue, the resin beds become spent or saturated with the contaminant ions. The resins need to be regenerated or the contaminant ions need to be removed so that the resins can be use in the next service cycle (Al-Asheh, et al., 2021). The regeneration reaction is a reverse reaction of the above reaction. An acid (HCl or H_2SO_4) is used to regenerate the cation IX resins, whereas a base (NaOH) is used to regenerate the anion IX resins.

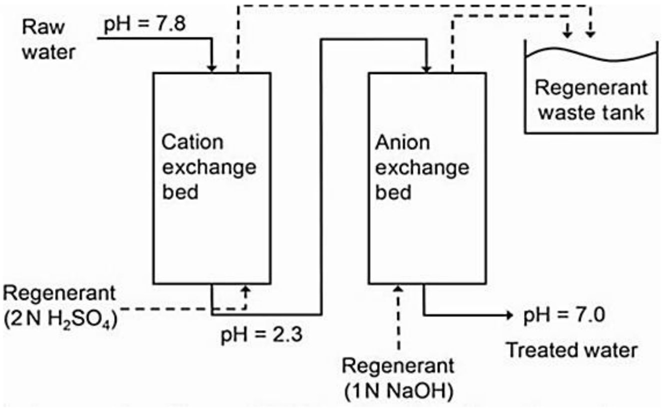


Figure 1.3: A schematic of the water purification process in a fixed-bed system (SenGupta, 2017).

1.2 Problem Statement

IX resins have been used in water purification process for many years. In water purification, the IX Resin will exchange the hardness ions from the hard water until it is spent, meaning that the ion exchange sites on the resin are fully occupied. The spent resins need to be regenerated or the contaminant ions need to be removed so that the resins can be reused in the next service cycle. There are several problems encountered during resins regeneration, which are resin fouling, low regeneration efficiency and high chemical consumption. Resin fouling will cause increased in resin sensitivity to flow rate and temperature, increased treated water conductivity, as well as decrease resin operating capacity in water purification process. Low regeneration efficiency will lead to low profitability to the water treatment plant while high chemical consumption will cause negative impact to the environment upon disposal. High chemical consumption also will lead to high operating cost which is uneconomic. Therefore, water purification process by IX resins technology needs to be improved by overcoming these problems.

1.3 Objective

The purpose of this research is to improve the resin regeneration process. To achieve the goal, the project carried the following objectives:

(i) To develop a brining process with optimized parameters for IX resin regeneration.

(ii) To characterize properties and compare the water purification performance of the untreated regenerated IX resin and the pre-treated regenerated IX resin by brining process.

1.4 Hypothesis

Brining process is a pre-treatment process that can prevent resin fouling by remove impurities from exhausted resins prior to regeneration; increase regeneration efficiency and decrease chemical consumption by partially remove hardness ions prior to chemical regeneration. The brining parameters that required to be study included pretreatment mode, brine concentration, resin-to-regenerant ratio and brining temperature. Brining mode will affect the ion exchange path during brining while brine concentration affects the diffusion process of ions during brining. Resin-to-regenerant volumetric ratio is able to affect performance of brining process. Temperature can alter selectivity of resins towards hardness ions removal. Thus, effectiveness of brining process can be improved by applying optimum pretreatment mode, brine concentration, brine-to-regenerant ratio and brining temperature.

1.5 Thesis Outline

There are five chapters in this paper which are: introduction (chapter 1), literature review (chapter 2), methodology (chapter 3), result and discussion (chapter 4) and conclusion (chapter 5). The research background, problem statement, objective and hypothesis are described in chapter 1. The literature review on the research as well as the research gap are discussed in chapter 2. This chapter review the previous studies on the IX resins regeneration process. In chapter 3, methodology used in this research is described using flow chart and schematic diagrams. The results of this research are presented and discussed in chapter 4. All results on brining parameters testing are evaluated and discussed extensively. In chapter 5, the finding of the research is summarized and several future works are suggested. Figure 1.4 shows the general process flow chart of this research.

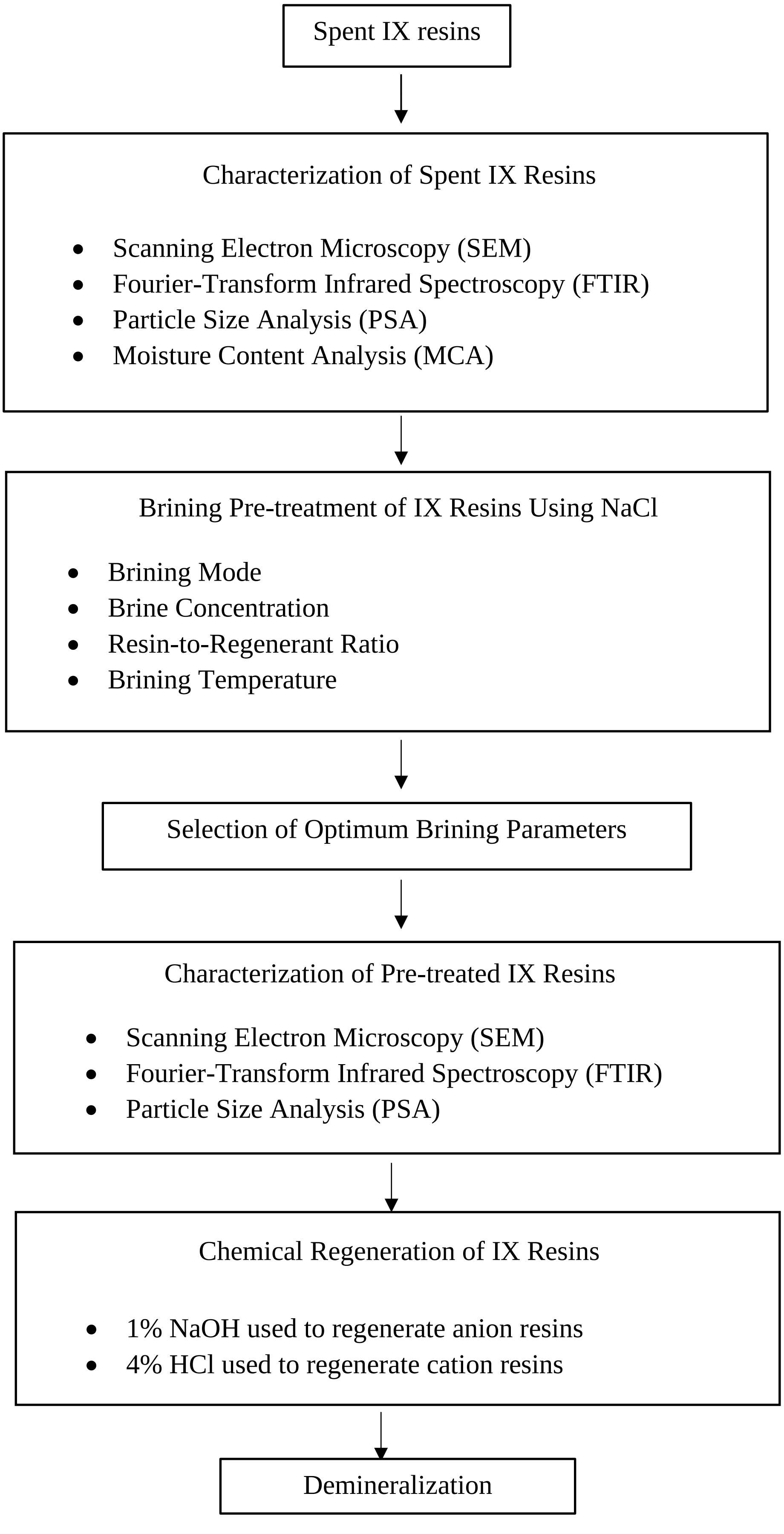


Figure 1.4: General process flow chart of research.

CHAPTER 2

LITERATURE REVIEW

2.1 Spent IX Resins Regeneration Techniques

IX resins regeneration or reactivation is the process of removing the contaminant ions that bonded onto the functional groups of resins upon water purification process. Several IX resins regeneration process have been studied and developed such as chemical regeneration, thermal regeneration, chemical-thermal regeneration as well as electrochemical regeneration. The process of these techniques as well as the differences between different regeneration techniques are discussed in this section. The focus of this study is on chemical regeneration as it is the most established and widely used regeneration technique.

2.1.1 Chemical Regeneration

Chemical regeneration is conducted with three main steps which are backwashing, regeneration and rinsing process. Backwashing is done by passing tap water upward through the exhausted resins column, allowing the anion and cation spent IX resins to separate into layers based on their density differences. The cation resins fall and settle at the bottom of the column while anion resins rise and settle at the top of the column. A this mix layers will be present in between the anion layers and cation layers which will be removed. Once separation is accomplished, the anion and cation resins will be transfer to two different vessels to be regenerated separately. Regeneration of cation resins is performed by running hydrochloric acid (HCl) solution as regenerant downward through the resins bed while regeneration of spent anion resins is performed the same way except the regenerant used is sodium hydroxide (NaOH) solution.

A study by Al-Asheh et al. (2021) shows that at room temperature, 1-vol% NaOH and 5-vol% HCl prepared with distilled water are sufficient to regenerate SBA and SAC resin, respectively. In this paper, regeneration efficiency is evaluated by conductivity of effluent water as the conductivity is proportional to the hardness of the effluent water (Al-Asheh, et al., 2021). In another study, Víctor-Ortega, et al. (2017) found that gel-type SAC and SBA can also be sufficiently regenerated with 4%HCl and 4%NaOH at 298K, respectively. They also found that the regeneration of SAC and SBA resins has no significant differences between regeneration efficiencies at 298 K and 308 K (both achieve almost 100% regeneration efficiency). Table 2.1 shows the optimum parameters values for regeneration of the selected WAC (Dowex MAC 3), SAC (Dowex Marathon C), WBA (Amberlite IRA-67) and SBA (Amberlyst A26) resins studied by Víctor-Ortega, et al. (2017). In rinsing, the regenerated resins are washed with deionized water. For a mixed bed system, the regenerated resins will undergo mixing in an agitator before return to the ion exchange column for another service cycle (Scherer, et al., 1978).

Table 2.1: Optimum parameters values for regeneration of the selected WAC (Dowex MAC 3), SAC (Dowex Marathon C), WBA (Amberlite IRA-67) and SBA (Amberlyst A26) resins (Víctor-Ortega, et al., 2017).

Resin Type	**Dowex MAC 3**	**Dowex Marathon C**	**Amberlite IRA-67**	**Amberlyst A26**
Mature of regenerant	H_2SO_4	HCl	NaOH	NaOH
Concentration	2% (v:v)	4% (v:v)	2% (v:v)	4% (v:v)
Regenerant volume	0.8L	0.6L	1L	0.7L
Rinse volume	0.8L	1L	0.8L	1.3L
Temperature	308K	298K	298K	298K
Flow rate	$2.5Lh^{-1}$	$2.5Lh^{-1}$	$2.5Lh^{-1}$	$2.5Lh^{-1}$

2.1.2 Thermal Regeneration

In 1978 a special kind of IX resins known as Sirotherm IX resins have been developed in Australia to partially purify water (Bolto, et al., 1978). Once it become spent or saturated with hardness ions, it needs to be regenerated. A regeneration that uses thermal energy to regenerate the Sirotherm IX resins have been developed, known as thermal regeneration. Thermal regeneration of Sirotherm IX resins is achieved with hot water rather than with chemical regenerants and the heat required for thermal regeneration is very little. Thus, the process is very economic as it does not involve chemical consumption cost and the little heat needed can be readily obtained using solar energy (Bolto, et al., 1978). The Sirotherm process uses WBA and WAC resins mixed bed system for the removal of salts from aqueous phase by altering the process temperature. In general, the process allows sorption at the ambient temperature and desorption at a higher temperature with the following equation (Chanda, et al., 2009):

$$R_A H + R_B + NaCl \leftrightarrow R_A Na + R_B . HCl \qquad \text{(Eq. 2.1)}$$

where R_AH is WAC resin and R_B is a WBA resin. The forward reaction take place at a lower temperature while the reverse reaction take place at higher temperature.

2.1.3 Chemical-Thermal Regeneration

Although the use of Sirotherm resins for water purification is economical due to zero chemical consumption in thermal regeneration process, the ion exchange capacity of Sirotherm IX resins reduce by 8 factors when the temperature incline from 30 °C to 80 °C (Chanda et al., 2010), indicating the partial regeneration of IX resins by this regeneration technique. In 2015, the efficiency of thermal regeneration has been improved by Chandrasekara and Pashley, who perform thermal regeneration of mixed bead Sirotherm resin by using ammonium bicarbonate. Their result has shown that ammonium bicarbonate could be thermally recycled upon regeneration. In general, ammonium bicarbonate solution (2 M) is used to regenerate IX resins by soaking them in the chemical at 20 °C for 15 hours, follow by heating the resins to 80 °C for 1 hour to decompose ammonium bicarbonate while returning the resins to their initial form such as tertiary amine and carboxylic acid form. Carbon dioxide and ammonia gases produced in the process were recovered and used as regenerant for subsequent regeneration. However, this process is not well established and still in development. Further study on the feasibility of this regeneration technique in pilot scale is required as it is needed to prove the feasibility of carbon dioxide and ammonia gas recovery in pilot scale (Liu, et al., 2021).

2.1.4 Electrodialytical Regeneration

Electrodialytical regeneration, also known as electrodialysis or electrochemical regeneration has been given a lot of attention. Some studied have use electrodialysis with bipolar membranes (EDBM) to produce acid or base solutions for the on-site regeneration of IX resins. This method was successfully tested for cation IX resins and anion IX resins in full-scale applications (Liu, et al., 2021). Due to high demand and high selling price of raw materials and environmental issue caused by disposal of industrial waste water, electrodialytic regeneration might again become an interest to researcher (Strathmann, et al., 1982). The principle of electrolytic regeneration is shown schematically in Figure 2.1. A cation IX resins which is charged with metal-ions is placed within cation-exchange membranes and two electrodes. The electrode compartments contain electrolyte solutions to provide the conductivity (Strathmann, et al., 1982). When apply direct current (DC), anode will generate hydrogen ions and the hydrogen ions will move into the resins bed by passing through the bipolar membranes (EDBM). The hydrogen ions will then replace the metal ions which move through the membrane and migrate towards the cathode. At cathode, the metal ions are reduced and cathode is the location for formation of solid metal precipitate. The process continued until equilibrium is achieved. Ideally, the electric current applied to the cathode is carried by the metal-ions yielding a current utilization for the regeneration process of 100% capacity recovery (Strathmann, et al., 1982).

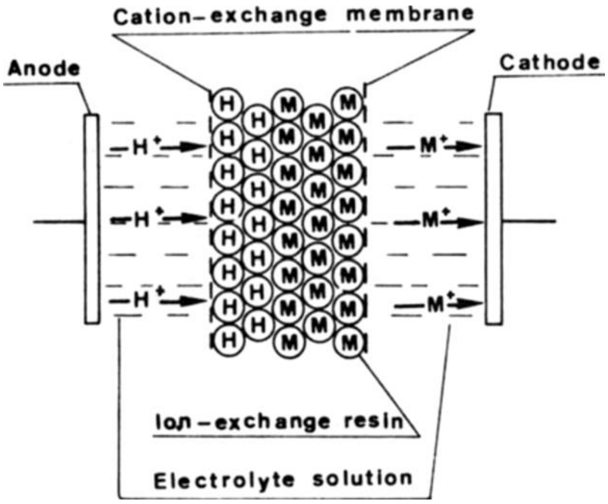


Figure 2.1: Schematic diagram of the electrolytic regeneration of a metal-ion charged cation-exchange resin (Strathmann, et al., 1982).

A study by Donald, et al. (1952) has shown that the most promising method of complete removal of both anion and cation from the mixed IX resins is the combination of an acid wash with electrodialysis because acid wash makes possible a complete exchange of hydrogen for the cation of the resins, while electrodialysis remove anions from the resins. The disadvantage of this additional step is the added cost from the acid wash (Chessmore, 1952).

2.1.5 Comparison Between Regeneration Techniques

The main difference between electrodialytical and conventional chemical regeneration is that H^+ ions are exchanged from an aqueous solution into IX resins under the driving force of a chemical potential gradient in chemical regeneration, while in electrodialytical generation the H^+ ions are forced into the resin under an electrical potential gradient, leading to a virtually effluent-free regeneration (Strathmann, et al., 1982). A study by Chen et al. (2016) that use electrodialysis with bipolar membranes

(EDBM) has shown that the energy required to produce the acid and the base was an order of magnitude lower than that required to purchase the chemical. Although chemicals are still needed in electrodialysis, the chemical consumption is significantly reduced compared to conventional chemical regeneration (Liu, et al., 2021).

Thermal regeneration is less expensive than chemical regeneration as regenerant is not required. It also avoids disposal of spent regenerants to the environment. In term of regeneration efficiency, chemical-thermal regeneration is able to achieve complete regeneration (100% recover capacity) by using ammonium bicarbonate with aid of temperature to regenerate the mixed bed Sirotherm resin. Electrodialysis is able to achieve complete regeneration (100% recover capacity) of mixed resins if electrodialysis is used in combination with acid wash. Conventional chemical regeneration and thermal regeneration can recover capacity of IX resins up to 80%. Thermal and electrodialytical regeneration are chemical-free regeneration while chemical and chemical-thermal regeneration are not. In economic view point, chemical regeneration is the most expensive method, follow by chemical-thermal regeneration, electrodialysis and thermal regeneration. Thermal regeneration is the most economic technique since its chemical-free and the thermal energy can be obtained with solar energy. Among the techniques, chemical regeneration is the most well established with the least operational skill requirement whereas electrodialysis required the most extensive operation skill. Thus, chemical regeneration is widely used in water treatment industries.

2.2 Limitation of Chemical Regeneration

The traditional regenerant used in chemical regeneration can be divided into salts, acids and alkalis. The examples of salt used are sodium chloride (NaCl), potassium chloride (KCl) and ammonium chloride (NH_4Cl). The examples of acid used are hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3). The example of alkali used are sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonia (NH_3). The traditional regenerant have low regeneration efficiency and required high chemical consumption, which lead to high operational cost. In sustainability view point, chemical regeneration can lead to severe environmental pollution as high concentration of acid and base are used and discharge to the environment as waste (Xu, 2014). Furthermore, if rinsing process is not sufficiently done, some residue compound might leach off the resins and passing into the treated water in the next service cycle, which is known as leakage phenomenon (Al-Asheh, et al., 2021). This will cause decrease in quality of treated water or cause increase in conductivity of the treated water.

Ion exchange or adsorption of chemical elements that are not easily removed by normal regeneration will cause gradual resin fouling that led to loss of resin ion exchange capacity. There are several types of resins fouling, which are microbial fouling, iron and magnesium fouling, organic fouling and oil fouling (Purolite, 2021). Type of resins fouling depends on input water quality in the water treatment process. Common form of foreign matter that cause fouling includes corrosion products, organic acids, bacteria, iron and oil. According to a reputed resin manufacturer of India (Ion Exchange India Ltd.), high iron and heavy metal concentration in input water and excessive use of polyelectrolytes (high molecular weight organic substances) can cause irreversible fouling of the cation and/or anion resins (Bagchi, 2014).

Figure 2.2 shows an example of SEM micrograph of microbial fouling of resin. Bacterial contamination in the hard water or the input water in water purification process will leads to microbial fouling as the bacteria adhere onto the resins surface. When contamination of resin beds is observed, disinfection need to be done. Peracetic acid is commonly used as disinfectant because of its wide spectrum of attack. However, there are some shortcomings of this pre-treatment process such as the treatment may slightly break down the cross-linked matrix of the resin (Purolite, 2021).

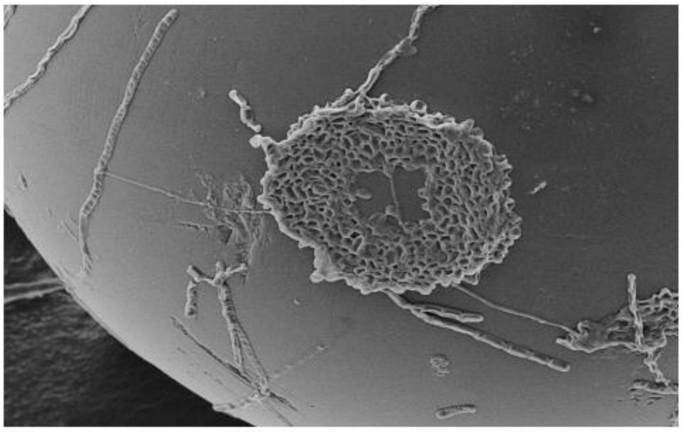


Figure 2.2: SEM microstructure of microbial fouling of resin (Purolite, 2021).

Iron exists in water in different form, such as ferrous form (Fe^{2+}), oxidised ferric form (Fe^{3+}) and anionic complex that held together with organic matter. Normally, iron present in the ferric state (Fe^{3+}) is removed by cation resin operated in either the sodium or hydrogen forms. In water softening, the IX cation resin removes the iron from the water. Consequently, the iron accumulates on the resin and leads to progressive iron fouling. When iron exist in organic iron complex form, the complex is present as an anion and is removed from the solution by the anion IX resins. In this case, hydrochloric acid (HCl) can be used to wash the resins as a pre-treatment process to remove the iron. Figure 2.3 shows an example of iron fouling.

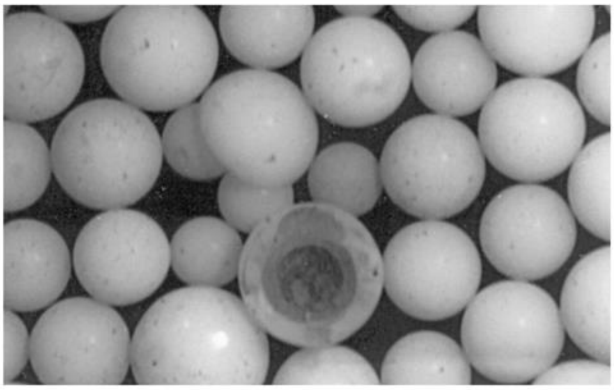


Figure 2.3: Anion IX resins iron fouling (Purolite, 2021).

Organic fouling is fouling of IX resins caused by organic substances in a feed water. Organic fouling can result in increased rinse requirement, increased sensitivity to flow rate and temperature, deterioration in effluent quality as well as decrease in operating capacity (Abrams, 1982). Noted that increases in rinse requirement can be cause by oxidation of the resin too and organic fouling occur more often to weak-base resins than to strong-base resins. A simple testing can be applied to differentiate between organic fouling and oxidation. When an organic fouled resin is being put through reflux with 6N HCl for 24 hours, a significant reduction in its rinse requirement indicates that the foulant has been removed. An oxidized resin would not shows decrease in rinse requirement (Abrams, 1982). When organic substances are not sufficiently removed from IX resins, increase in flow rate and decrease in temperature will cause decrease in ion exchange capacity. This will lead to increase the chance for leakage to happen and also decreased the operating capacity (Abrams, 1982).

Figure 2.4 shows oil fouled resin which can be cause by oil present in feed water or regeneration solution. When oil coats on surface of resin, it will be difficult for ions to penetrate through the oil layer into the exchange sites of the resins to perform ion exchange reaction. Thus, oil fouling results in declining of resin kinetics and drop in treated water quality as well as reduced operating capacity (Purolite, 2021). If resin is heavily oil fouled, it may be impossible to clean them. For lightly oil fouled resins, it can be pre-treated with a low foaming, non-ionic surfactant or detergent. Anionic detergent is use for cation exchangers and non-ionic or cationic detergent is use for anion exchangers in the oil cleaning process (Abrams, 1982). The treatment is most effective if the solution is being controlled at approximately 40°C during the pre-treatment process to produce considerable foaming (Purolite, 2021).

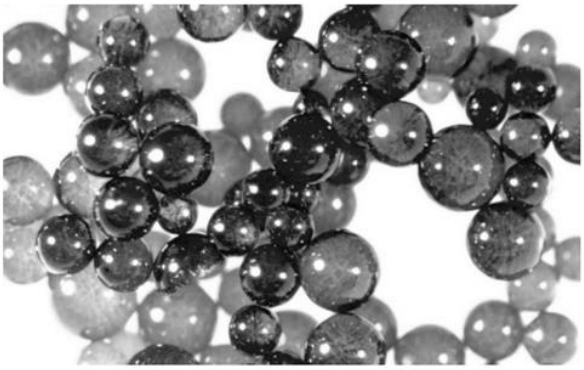


Figure 2.4: Oil Fouled resin (Purolite, 2021).

2.3 Function of Brining Process

Brining process is a pre-treatment process that prevent resin fouling by removing impurities such as dissolve organic carbon (DOC) from exhausted resins; increase regeneration efficiency and decrease chemical consumption by partially remove hardness prior to regeneration. SBA resins are very effective for removing organics from natural waters as it can remove over 90% of the river water DOC (Semmens, et al., 1983). However, the DOC is hard to be removed in regeneration process which can lead to organic fouling of resins. Thus, brining is an important pre-treatment process that needs to be applied prior to chemical regeneration. The DOC adsorbed onto the spent SBA resins can be regenerated effectively with sodium chloride (NaCl) brine solution (Semmens, et al., 1983). Although an organic fouled SBA resins can be effectively restored by brining, there is a risk of resin fragmentation due to “osmotic shock” cause by sequential change of regenerant when the resins undergo brining follow by regeneration (Abrams, 1982).

A study by Schulz, et al. (2017) show that three different compositions of brine, which are: (i)brine (100 g NaCl/l), (ii)caustic soda with brine (20g NaOH/l + 100g NaCl/l), and (iii)pre-disinfection with caustic and brine (0.1% peracetic acid before 20g NaOH/l + 100g NaCl/l) are able to partially regenerate the spent SAC resins with same recovered capacities. NaCl is normally used to regenerate SAC resins in the softening process. In environmental aspect, NaCl is a good conventional regenerant relative to other traditional regenerant as it produces less negative impact to the environment upon disposal. This is because part of the spent NaCl can be reduce and recover back to pure form to be reused for regeneration of IX resin through nanofiltration process. Vaudevire, et al. (2013) has proven that by implementing nanofiltration, 80% of brine recovery can be achieved, leading to less volume of spent brine disposal. However, the possibility of using lower concentration of brine still needs to be study as there are still 20% of brine being disposed into the environment as waste.

2.4 Factors Affect Brining Process

The factors affecting brining pre-treatment efficiency in mixed bed system are resins morphology, particle size of resin, ion exchange osmosis, brine concentration, resin-to-regenerant ratio, brining temperature and contact time between IX resins and liquid phase during brining. Resin with different morphology such as the pore structure on the resins will affect the ion exchange process in brining. The particle size of resins will affect the rate of ions release from mixed spent resins. Ion exchange osmosis is depending on cross-linking density (CD) of the resins and the cross -linking density will affect ion exchange kinetics. Brine concentration affect the diffusion process in brining while resin-to-regenerant ratio will affect the chemical consumption and operating cost of brining. Brining temperature will affect the selectivity of resins while flow rate affects contact time between resins and the aqueous phase during brining.

2.4.1 Morphology

The surface area that available for ion exchange reaction of IX resins is determined by their morphology. Ion exchange resins with different morphology are distinguished by their different in gel density distribution as shows in Figure 2.5. For a traditional gel type resin, the gel density or polymer density is uniformly distributed across the bead. Gel type resin does not consist of well-defined pore structure. However, the nano-scale open area in the polymer chain is described as pore. When the gel resin is in swollen state, the solvent will fill in the pore. When the gel resins are in dried state, the pore will cave in and virtually does not exist (Zagorodni, 2007). Isoporous resins also have uniform or homogeneous hydrocarbon chain distribution across the bead. The different between gel resins and isoporous resins is that the isoporous resins have more uniform micropore structure. Macroporous resins have a heterogeneous (at both the nano- and macro-scale) structure with two phases, which are dense polymer chains and macroscopic permanent pores with pore size range from 20nm to 200nm on its surface (Zagorodni, 2007). One of the special features of the microporous resins is its relative consistency shape. When the material loses water, the macropores do not collapse.

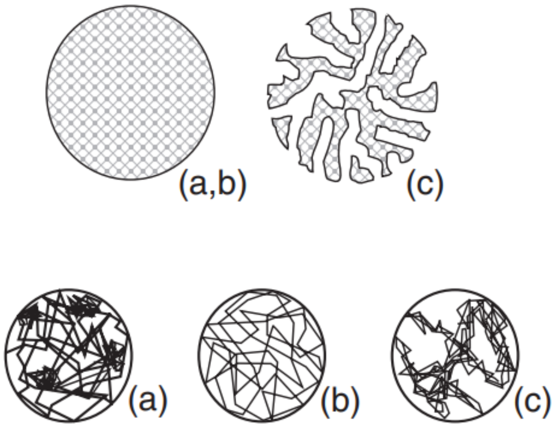
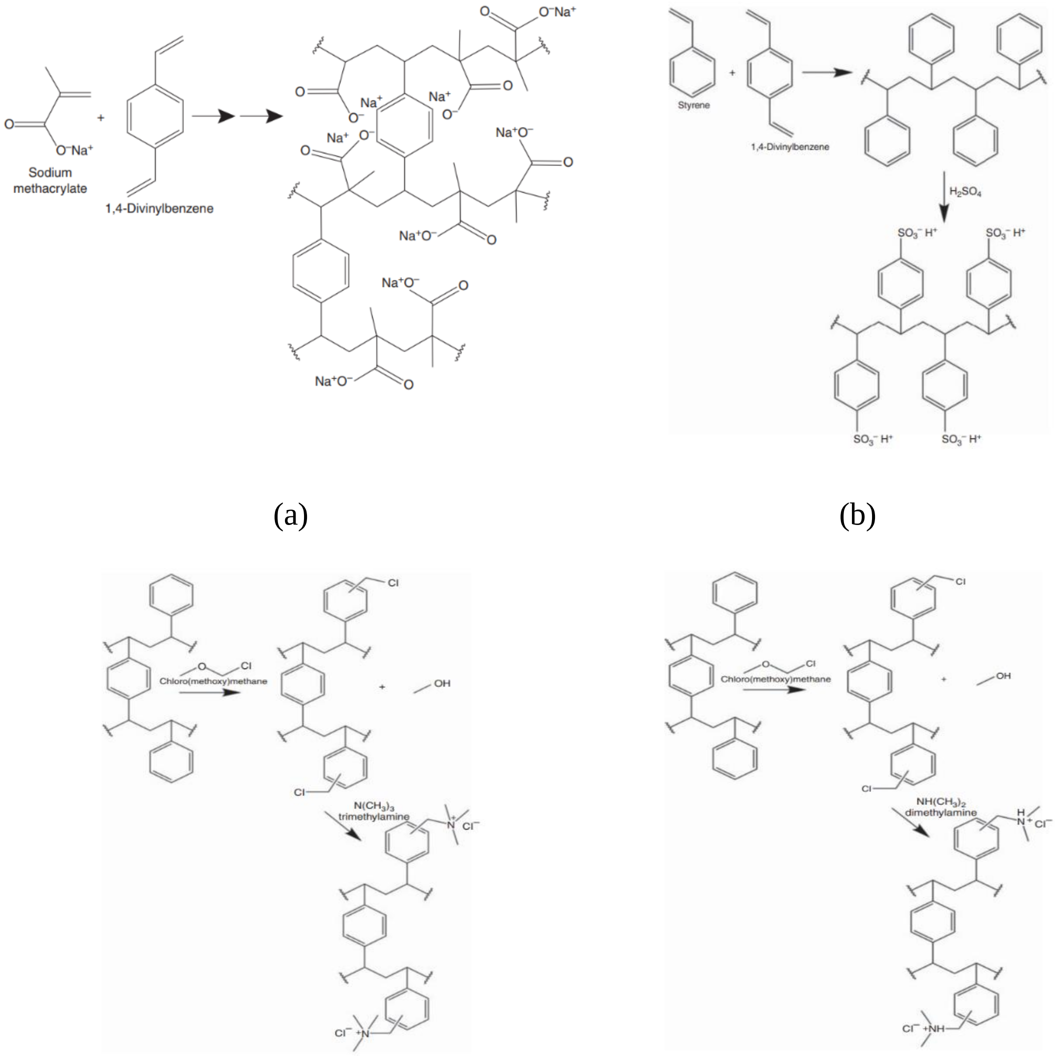


Figure 2.5: Morphology (upper row) and distribution of polymeric chains (bottom row) in ion exchangers: (a) gel resins; (b) isoporous resins; (c) macroporous resins (Zagorodni, 2007).

For macroporous resin, ion exchange takes place on the surface of macropores or in close proximity to the surface, thus the molecules do not enter the dense gel regions (Zagorodni, 2007). Based on Monika and Zbigniew, macroporous resins with high effective area facilitate the ion exchange process, give access to exchange larger ions, make more rigid beads, take up the solvent with little or no change in volume and can be used with almost any solvent (Wawrzkiewicz, et al., 2015). On the other hand, gel resins consist of smaller pores with 1 to 2 nm in hydrated form in the resin structure. Gel resins have higher initial exchange capacity and a lower price than macroporous resins of the same type. For gel resins, ions diffuse through the resins by interaction with the functional groups. Gel resins have several advantages such as less fragile and requiring less care in handling.

2.4.2 Type of IX resins

Figure 2.6 provide the step-wise preparation of the four most widely used IX resins. The four functional group are: carboxylic ($R\text{-}COO^-$), sulfonic ($R\text{-}SO^-_3$), tertiary amine ($R\text{-}N^+R_2H$) and quaternary ammonium ($R\text{-}N^+R_3$) for WAC, SAC, WBA and SBA, respectively. For WAC, the carboxylate ionogenic group exist readily in the methacrylic acid monomer prior to polymerization. DVB cross-linking is introduced to attain the 3D polymer network. For SAC, the styrene–DVB copolymer is synthesized first and then sulfonated to introduce the ionogenic group. Synthesis of WBA and SBA involve three consecutive steps; first is synthesis of styrene–DVB copolymer; second is chloromethylation of the copolymer; and third is amination of the chloromethylated copolymer, culminating in positively charged functional groups (SenGupta, 2017).



(a) (b)

(c) (d)

Figure 2.6: Synthesis of (a) weak-acid cation (WAC) (b) strong-acid cation (SAC) (c) strong-base anion (SBA) (d) styrenic weak-base anion (WBA) (SenGupta, 2017).

SBA resins can further be classified into Type I and Type II anion exchanger. SBA consist of quaternary amine functional groups (R_4N^+) and during the final stage of synthesis of an anion exchanger, the polymer is aminated with alkyl substituted amine. When the SBA polymer aminated with trimethylamine, (R-$N^+(CH_3)_3$) Type I SBA is produced as shown in Figure 2.7(a) in chloride form. When the SBA polymer aminated with dimethylethanolamine (R-$N^+(CH_3)_2(C_2H_4OH)$), Type II SBA is formed as shown in Figure 2.7(b). Type II anion exchange resins is more hydrophilic due to the presence of a methyl group with ethanol. Thus, the efficiency of regeneration with NaOH is significantly greater for Type II SBA resins compared to Type I (SenGupta, 2017).

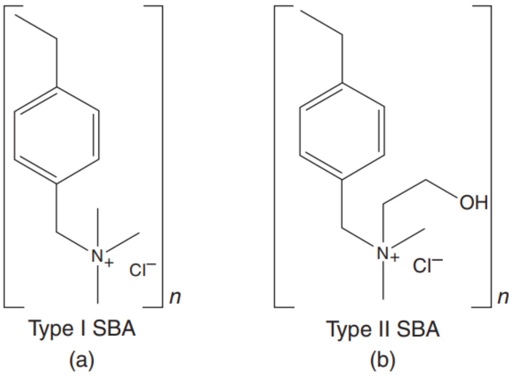


Figure 2.7: (a) Type I and (b) Type II functional groups of SBA resins (SenGupta, 2017).

2.4.3 Particle Size

A study conducted by Torrado and Valiente (2004) on the influence of resin particle sizes on the rate of ions release from mixed resins shows that small particles will affect the ion exchange kinetics by increase the rate of release of ions. Fine resins with relatively high surface area to volume ratio and low mass transfer resistance allows higher operation capacity by increasing contact surface between resins and ions, resulting increase in rate of release of ions. Coarse beads are frequently more sensitive to osmotic stress and have slower kinetics, thus giving a lower operating capacity. Noted that capacity of resins means the number of chemical equivalents of ions that can be taken up by a unit amount of the resin, where the unit amount of resin can be dry weight, wet weight or wet volume. Based on Sahu and Jaiswani (2018), large particle size results in a slow ion release pattern due to longer diffusion path length compare to smaller particles.

2.4.4 Ion Exchange Osmosis

When IX resin is introduced into an electrolyte, the resin will start swelling due to osmosis and ion exchange reaction will take place to redistribute ions between resins and the aqueous phase. At the same time, the trace amount of coions (E.g.: Cl^-) will enter the ion exchanger phase due to electrolyte penetration, which is known as Donnan coion invasion. All three of the phenomena will happen simultaneously until equilibrium is achieved. Figure 2.8 shows illustration of three of the phenomena using a conventional IX resin in sodium form and potassium chloride (KCl) as electrolyte (SenGupta, 2017). Most resins reach their maximum volume in solvent within an hour or less, nearly all resins reach this stage within 24 hours (Bodamer, et al., 1953).

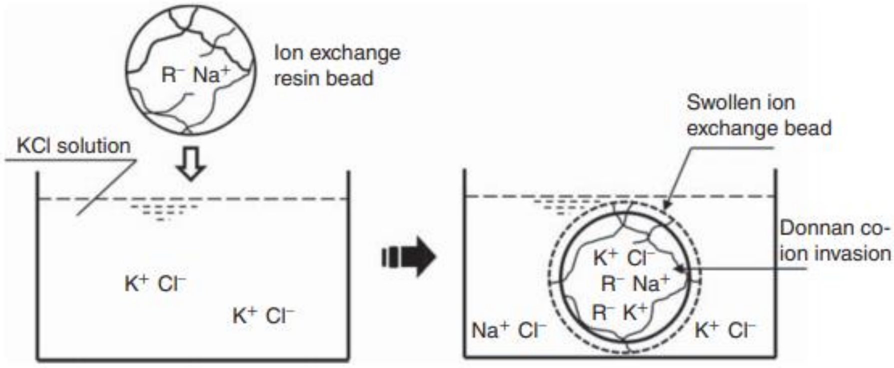


Figure 2.8: Illustration of an ion exchange process showing ion exchange, swelling and coion invasion (SenGupta, 2017).

IX resins consist of a hight amount of fixed functional groups with charges. Thus, the inner osmosis pressure of IX resin is very high. When put into water, the the covalent bonded functional groups with charges are unable to diffuse into water because of immobility. Although high difference in concentration is present, the charges cannot diffuse into the aqueous phase because it will cause electroneutrality imbalance. So, the

IX resin-water interface act as semi-permeable membrane. The water molecules will diffuse into IX resins to decrease the difference in osmosis pressure, meaning that osmosis is initiated, causing swelling of IX resins. The IX resins phase dilute itself, stretched and comes to equilibrium when the swelling pressure in resins balance out the osmosis gradient. This mechanical model was introduced by Gregor, which state that matrix of IX resins is a network of elastic springs on which the functional groups are attached (SenGupta, 2017). The illustration of Gregor's concept is presented in Figure 2.9.

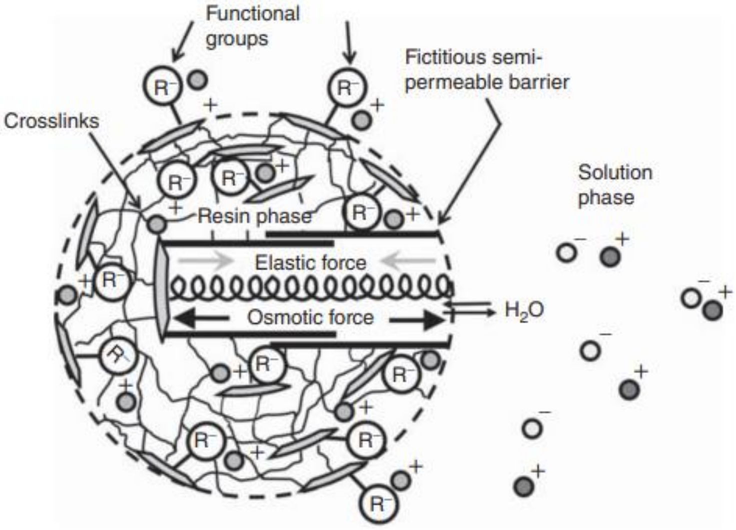


Figure 2.9: Schematic illustration of Gregor's concept on swelling and shrinking of ion exchange resin (SenGupta, 2017).

The swelling level of resins is directly related to water content while the water content is affected by degree of cross-linking of resins. Based on Ikkai, et al. (1996), a structure model which accounts for swelling behaviour of IX resins is presented as Figure 2.10. The circles represent the size of IX resins, the lattice represent polystyrene network while the dots represent crosslinking points of resins. In this structure model, some assumptions are made. First, the size of IX resin with high cross-linking density (CD) at swelling equilibrium is the same as IX resin with low CD. Second, the polymer concentrations are the same in both resins. Third, the resin with high CD should shrink less than resin with low CD because of topological constraints (Ikkai, et al., 1996). When