

CHAPTER 7

ION EXCHANGE

ION EXCHANGE PROCESSES

Ion exchange is a process in which ions on the surface of the solid are exchanged for ions of a similar charge in a solution with which the solid is in contact.

Ion exchange can be used to remove undesirable ions from waste water. Cations (positive ions) are exchanged for hydrogen or sodium and anions (negative ions) for hydroxide or chloride ions. The cation exchange on a hydrogen cycle can be illustrated by the following reaction; using in this example the removal of calcium ions, which are one of the ions (Ca^{2+} and Mg^{2+}) which cause hardness of water:



where, R, represents the resin.

The anion exchange can be similarly illustrated by the following reactions:



When all the exchange sites have been replaced with calcium or sulphate ions, the resin must be regenerated. The cation exchanger can be regenerated by passing a concentrated solution of sodium chloride through the bed, while the anion exchanger which in this case is of hydroxide form, must be treated by a solution of hydroxide ions, e.g. sodium hydroxide.

Ion exchange material

Ion exchange is known to occur with a number of natural solids, such as soil, humus, metallic minerals and clay. Clay, and in some instances other natural materials, can be used for demineralization of drinking water. In the context of adsorption, the ability of aluminium oxide to make a surface ion exchange has already been mentioned, but also the natural clay mineral, clinoptilolite, can be used for waste water treatment as it has a high selectivity for removal of ammonium ions.

Today mostly synthetic ion exchange resins are used. They consist of a net-work of compounds of high molecular weight to which ionic functional groups are attached. The molecules are cross-linked in a three-dimensional matrix and the degree of the cross-linking determines the internal pore structure of the resin. Since ions must diffuse into and out of the resin, ions larger than a given size may be excluded from the interaction through a selection dependent upon the degree of cross-linking. However, the nature of the groups attached to the matrix also determines the ion selectivity and thereby the equilibrium constant for the ion exchange process.

The cation exchangers contain functional groups such as sulphonic $R-SO_3H$ - carboxylic, $R-COOH$ - phenolic, $R-OH$ and phosphonic, $R-PO_3H_2$ (R represents the matrix). It is possible to distinguish between strongly acidic cation exchangers derived from a strong acid such as H_2SO_4 and weakly acidic ones derived from a weak acid such as H_2CO_3 . It is also possible to determine a pK -value for the cation exchangers in the same way as it is for acids generally.

This means:



$$\frac{[H^+] \cdot [R - SO_3^-]}{[R - SO_3H]} = K \quad pK = -\log K \quad (7.4)$$

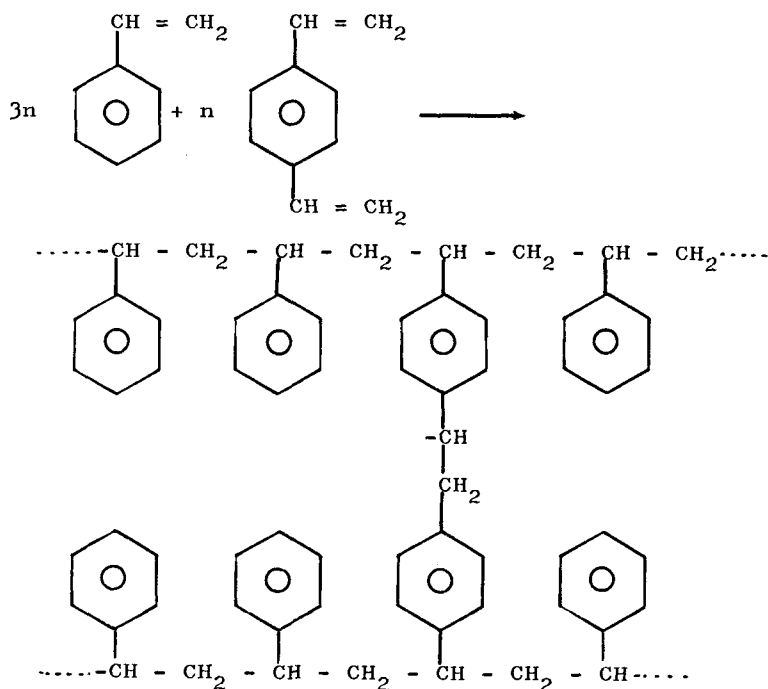
Anion exchange resins contain such functional groups as primary amine, $R-NH_2$, secondary amine, $R-R_1NH$, and tertiary amine $R-R_1-R_2N$ groups and the quaternary ammonium group $R-R_1R_2R_3N^+OH^-$.

It can be seen that the anion exchanger can be divided into weakly basic and strongly basic ion exchangers derived from quaternary ammonium compounds.

It is also possible to introduce ionic groups onto natural material. This is done with cellulose as a matrix and due to the high porosity of this material it is possible to remove even high molecular weight ions.

Preparation of cation exchange resin, using hydrocarbon molecules as a matrix, is carried out by polymerization of such organic molecules as styrene and metacrylic acid.

The degree of cross-linking is determined by the amount of divinylbenzene added to the polymerization. This can be illustrated by the following examples:



It is characteristic that the exchange occurs on an equivalent basis. The capacity of the ion exchanger is usually expressed as equivalent per litre of bed volume. However, when the ion exchange process is used for reduction of hardness, the capacity can also be expressed as kg of calcium carbonate per m^3 of bed volume. Since the exchange occurs on an equivalent basis, the capacity can be found based either on the number of ions removed or the number of ions released. Also the quantity of regenerant required can be calculated from the capacity. However, neither the resin nor the regeneration process can be utilized with 100% efficiency.

The resin utilization is defined as the ratio of the quantity of ions removed during the actual treatment to the total quantity of ions that could be removed at 100% efficiency; this is the theoretical capacity. The regeneration efficiency is the quantity of ions removed from the resins compared to the quantity of ions present in the volume of the regenerant used.

Weak base resin has a significant potential for removing certain organic compounds from water, but the efficiency is highly dependent upon the pH.

It seems reasonable to hypothesize that an adsorption is taking place by the formation of a hydrogen bond between the free amino groups of the resin and hydroxyl groups of the organic substance taken up. As pH decreases, so that the amino groups are converted to their acidic form, the adsorption capacity significantly decreases.

Equilibrium

The exchange reaction between ions in solution and ions attached to the resin matrix is generally reversible. The exchange can be treated as a simple stoichiometric reaction. For cation exchange the equation is:



The ion exchange reaction is selective, so that the ions attached to the fixed resin matrix will have preference for one counter ion over another. Therefore the concentrations of different counter ions in the resin will be different from the corresponding concentration ratio in the solution.

According to the law of mass action, the equilibrium relationship for reaction (7.5) will give:

$$K_{AB} = \frac{a_B^n \cdot a_{RA}}{a_A \cdot a_{RB}^n} \quad (7.6)$$

where a_B and a_A are the activity of the ions B^{+} and A^{n+} in the solution and correspondingly a_{RB} and a_{RA} are the activities of the resin in B- and A-form, respectively.

Ion exchange component: Phenol.
Ion exchangers: Lewatit.

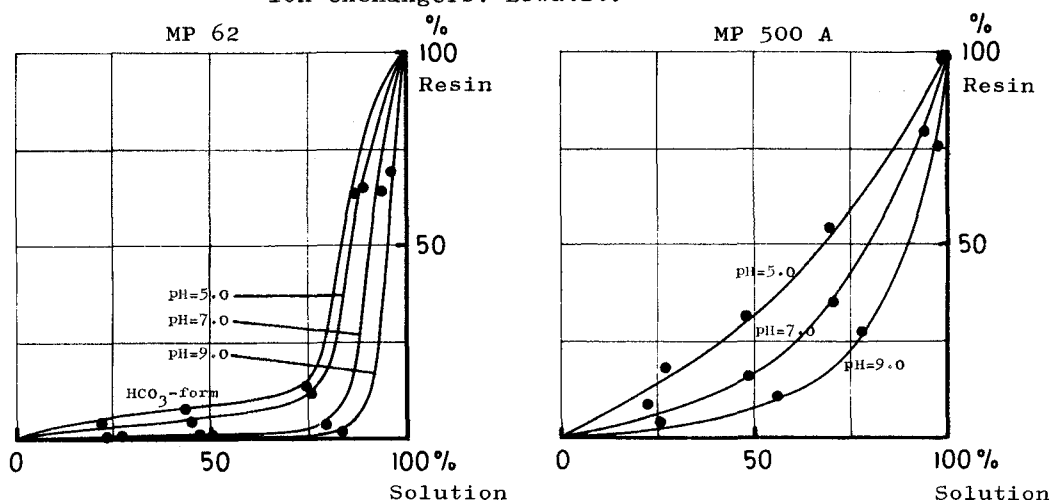


Fig. 7.1. Illustration of the preference of an ion exchange resin for a particular ion.

The Fig. 7.1 plot is often used as an illustration of the preference of an ion exchange resin for a particular ion. As seen, the percentage in the resin is plotted against the percentage in solution.

The selectivity coefficient, K_{AB} , is not actually constant, but is dependent upon experimental conditions. A selectivity coefficient of 50% in solution is often used, $\alpha_{50\%}$.

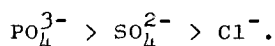
If we use concentration and not activity, it will involve, for $n = 1$:

$$C_B = C_A \quad (7.7)$$

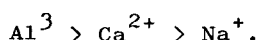
$$\alpha_{50\%} = K_{AB,50\%} = \frac{C_{RA}}{C_{RB}} \quad (7.8)$$

The plot Fig. 7.1 can be used to read $\alpha_{50\%}$.

The selectivity of the resin for the exchange of ions is dependent upon the ionic charge and the ionic size. An ion exchange resin generally prefers counter ions of high valence. Thus, for a series of typical anions of interest in waste water treatment one would expect the following order of selectivity:



Similarly for a series of cations:



But this is under circumstances where the internal pore structure of the resin does not exclude the ions mentioned from reaction. Organic ions are often too large to penetrate the matrix of an ion exchange, which is of course more pronounced, when the resins considered have a high degree of cross-linking. As most kinds of water and waste water contain several types of ions besides those which must be removed it is naturally a great advantage to have a resin with a high selectivity for the ions to be removed during the ion exchange process. Successful removal of uranium from low grade ores has been accomplished through the development of an ion exchanger that accepts uranium ions selectively from solution (Osborn, 1961).

Separation of rare earth metal ions has been achieved by taking advantage of their different complexing characteristics in solution.

Complexation might cause difficulties by removal of iron, manganese, copper or zinc by an ion exchange process. Natural waters often contain chelating agent and chelation drastically changes the behaviour of a metal ion in water. Manahan et al. (1973) have found a copper equivalent chelating capacity of 0-3.5 mg/l in several water and waste water samples.

Cellulose ion exchangers that preferentially accept high molecular weight ions have recently been developed (Jørgensen, 1970, 1972 and 1974).

Rate of exchange

The kinetic processes involved in the ion exchange reaction are similar to those involved in adsorption of substances from a solution by an adsorbent. For a batch reactor, where the rate is controlled by a film diffusion mechanism, the rate of exchange would be:

$$-\frac{dC}{dt} = k_f \cdot \frac{a}{V} (C - C^+) \quad (7.9)$$

where

C = the actual concentration in solution

k_f = the film transfer coefficient

V = the volume of solution

a = the effective area

C^+ = the equilibrium concentration

If, on the other hand, the pore diffusion is rate limiting, a diffusion model based on Fick's second law can be utilized to describe the reaction. The general expression for this type of reaction can be set up as follows:

$$\frac{\partial c}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \cdot D \cdot \frac{\partial c}{\partial r} \right) - \frac{\partial q^+}{\partial t} \quad (7.10)$$

where

r = the resin particle radius

D = the diffusion coefficient

q^+ = the concentration of exchanged ions of the resin in equilibrium with the concentration C

The effect of cross-linking on the rate of exchange is illustrated in Tables 7.1 and 7.2 (Bonner et al., 1956); (Gregor et al., 1954).

The rate of the actual exchange process can also control the overall exchange process, but generally this step is so rapid that it can be neglected as a significant rate factor.

TABLE 7.1

Ion exchange selectivity coefficients for polystyrene resins, sulphonic acid cation exchanger, at 20°C

Cations	Cross-linking			—
	4%	8%	16%	
Li ⁺	1.0	1.0	1.0	
H ⁺	1.3	1.3	1.5	
Na ⁺	1.6	2.0	2.4	
K ⁺	2.3	2.9	4.5	
Cs ⁺	2.7	3.3	4.7	
As ⁺	4.7	8.5	22.9	
Tl ⁺	6.7	12.4	28.5	
Mg ²⁺	3.0	3.3	3.5	
Ca ²⁺	4.2	5.2	7.3	
Ba ²⁺	7.5	11.5	20.8	
Pb ²⁺	6.6	9.9	18.0	

TABLE 7.2

Ion exchange selectivity coefficient for polystyrene resins, Quarternary base anion exchanger, at 25°C

Anions	Cross-linking	
	4%	8%
Cl ⁻	1.0	1.0
OH ⁻	0.8	0.5
F ⁻		0.08
Br ⁻	2.7	3.5
I ⁻	9.0	18.5
NO ₃ ⁻		3.0
SCN ⁻	6.0	4.3
ClO ⁻	9.0	10.0

Design of ion exchange column

As mentioned above the exchange process occurs in essentially three steps: the movement of the exchangeable ions through liquid films surrounding the resins, the diffusion of the ions in the porous resin and the actual exchange process.

The resistance of the first two can be combined in an overall mass transfer term as in adsorption.

Equation (6.31) can be used directly:

$$SdY = K_t \cdot a (Y - Y^x)dz \quad (7.11)$$

The symbols are the same as indicated p. 74.

It might be convenient to modify the equations as follows:

$$N_t = \int_{Y_B}^{Y_E} \frac{dY}{Y - Y^x} = \frac{Z_a}{H_t} = \frac{Z_a}{S/K_t \cdot a} \quad (7.12)$$

As seen, the design can be carried out along the same lines as those given by the adsorption method and this is illustrated in example 7.1.

Laboratory experiments

It is often necessary to operate a laboratory ion exchange unit to develop the necessary design data. It is possible to find the flowrate, column height, pH and type of counter ion on the capacity and efficiency. The equilibrium data might be obtained from a column, but it is also possible to equilibrate a sample of the ion exchanger in one single batch with a known volume of solution of known composition.

The advantages of using batch techniques are that less time and solution are required for the experiments. There are, however, several disadvantages. The solution composition which changes in the course of equilibration cannot be fixed beforehand and, furthermore, the solution and the ion exchanger must be analysed unless the swelling changes and the electrolyte sorption are known to be negligible. From the experiments and laboratory experiments in general it should be possible to get the necessary data for the ion exchange process, including a plot of the type shown in Fig. 6.9. The break-point curve may also come as a result of laboratory experiments.

Ion exchange systems

A complete demineralization involves a cation exchanger followed by a weak base, anion exchanger. A schematic diagram of this arrangement is given in Fig. 7.2.

If the cation resin is of H^+ -form and the anion exchanger resin is of OH^- -form, the ions removed will be replaced by water. All ionic material except carbon dioxide and silica will be removed with this arrangement.

By the use of highly basic resins it will also be possible to remove carbon dioxide and silica.

It is also possible to use a mixed resins exchange operation. This operation is shown in Fig. 7.3.

In recent years devices for continuous countercurrent contact of an ion exchange resin and water have been developed, but they are not yet generally applied in industrial waste water treatment, where mainly a fixed bed operation is used.

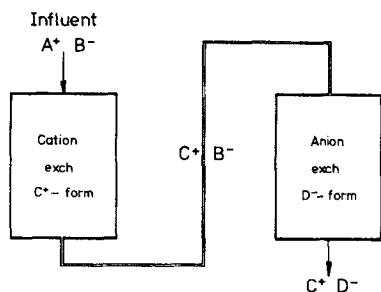


Fig. 7.2. Cation and anion exchanger in series.

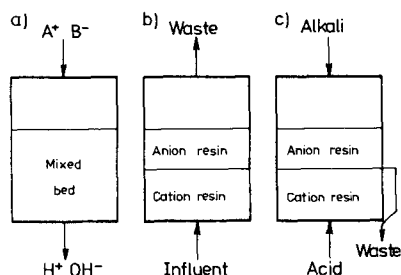


Fig. 7.3. Operation - mixed bed ion exchanger.

Application

One important application of the ion exchange process in waste water treatment is for the recovery of valuable metals from industrial waste water. Chromate, CrO_4^{2-} , from electroplating waste water is a major example. In this case even the treated water can be reused (Fagden, 1952; Paulson, 1952; Keating et al., 1954). A continuous belt ion exchanger has been developed for this purpose (Brown et al., 1976). Recovery of Cu^{2+} from different industries (Solt, 1973) and Ag^+ from the photo-chemical industry are also examples of possible recoveries.

Mercer et al. (1970) have reported a successful application of the specific ion exchanger, clinoptilolite, for removal of ammonium from waste water. Jørgensen (1975) has reported the possibility of recovering ammonium from industrial waste water.

For removal of dyestuffs from paint- and textile factory waste it is possible to use a cellulose anion exchanger as reported by Jørgensen (1978) and Gangneux et al. (1976).

Proteins can be recovered from slaughterhouses, fish filletting plants, dairies, etc. by the use of a cellulose cation exchanger (Jørgensen, 1970, 1971, 1973).

Xanthate ion exchangers are used for recovery and removal of cadmium. Small concentrations of mercury can be eliminated and recovered by means of a selective ion exchanger (Kanczor, 1975).

Mercury can be removed from waste water by the use of wool and other protein-containing substances in accordance with Friedmann et al., (1972a). The mechanism is probably the chemical binding of mercury ions to the protein (Kutat et al., 1973).

Tannery hair can be used as a cheap and effective protein-containing substance (Friedmann et al., 1972b). The use of tannery hair as an ion exchange material in a stirred tank system for removal of ionic mercury from waste water down to the low ppb range looks entirely feasible. The ionic mercury can be removed from the tannery hair by the use of hydrochloric acid or sodium chloride.

Table 7.3 gives a survey of the application of the ion exchange process in the treatment of industrial waste water.

TABLE 7.3

A survey of the application of the ion exchange process in the treatment of industrial waste water

Type of waste water	Components removed	Reference
Metal plating and finishing industry	Several metal ions incl. chromate	Schaufler, 1959 Spanier, 1969
Iron industry and mining	Iron	Jørgensen, 1971
Electrolytical industry	Mercury	Euxelins, 1970
Manufacturing of Glass- and stone wool	Phenol	Jørgensen, 1971
Fertilizer industry	Phosphate, Ammonium, Nitrate	Jørgensen, 1971
Food industry	Protein, Carbohydrates	Jørgensen, 1970
Textile industry	Dyes, Organic chemicals	Poulsen, 1970

Example 7.1

Fig. 7.4 illustrates the equilibrium data for protein uptake by a cellulose ion exchanger.

Waste water with a protein concentration of 200 mg/l is considered.

The break-point will be considered as the time at which the effluent has a protein concentration of 20 mg/l and the bed will be considered exhausted when the effluent has a protein concentration of 180 mg/l.

$$H_t = 0.05 \text{ m.}$$

The depth of the ion exchange bed is 0.5 m.

Find Z_a and the saturation in percentage.

Solution

The equilibrium data as indicated above are plotted in Fig. 7.4.

Table 7.4 lists the value of Y on the operating line between Y_B and Y_E , and the corresponding value of Y^+ .

In Table 7.2 $\frac{1}{Y - Y^+}$ has been computed. Column 4 in the table is based on Fig. 7.5 and column 5 indicates the corresponding values of $\frac{W - W_B}{W_A}$.

By means of column 6, which shows $\frac{Y}{Y_0}$, Fig. 7.6 is plotted.

The total number of transferred units is found in Table 7.4 to be 4.23.

Based on Fig. 7.6 it is now possible to find f , as: 0.64.

$$Z_a = N \cdot H_t = 4.23 \cdot 0.05 = 0.21 \text{ m}$$

$$\text{Saturation (\%)} = \left(\frac{Z - (1 - f)Z_a}{Z} \right) 100 =$$

$$\frac{(0.5 - (1 - 0.64) \cdot 0.21)100}{0.5} = 85\%.$$

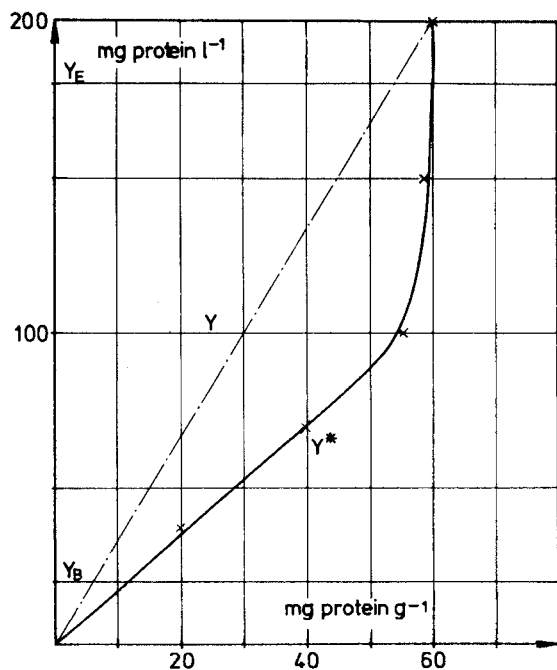


Fig. 7.4. Equilibrium line and operation line. (Example 7.1).

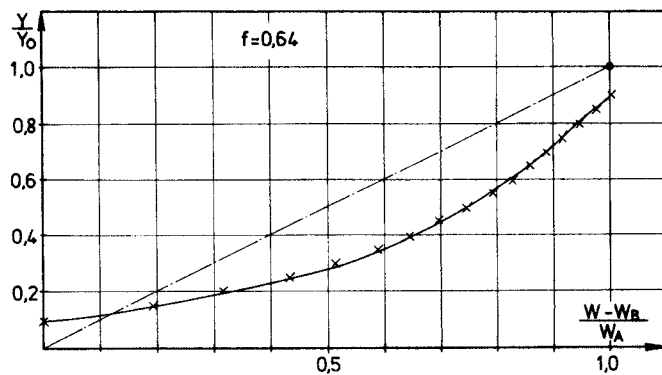


Fig. 7.5. $\frac{W - W_B}{W_A} = f\left(\frac{Y}{Y_0}\right)$. (Example 7.1).

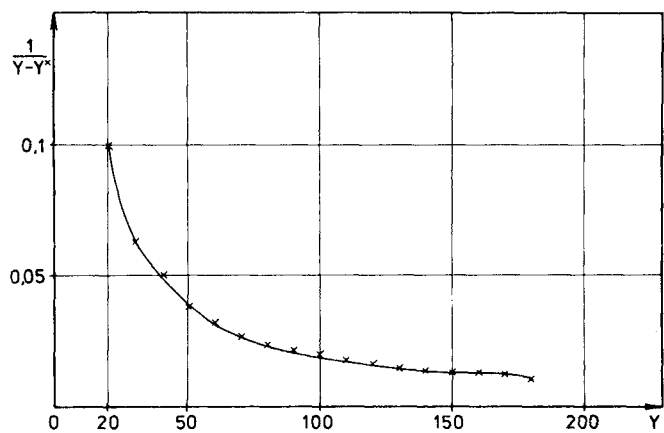


Fig. 7.6. $Y = f(\frac{1}{Y - Y^x})$. (Example 7.1).

TABLE 7.4

Theoretical column calculations

Y	Y^+	$\frac{1}{Y-Y^+}$	$\frac{dY}{Y-Y^+}$	$\frac{W-W_B}{W_a}$	$\frac{Y}{Y_o}$
20	10	0.100	0	0	0.1
30	14	0.063	0.8	0.189	0.15
40	20	0.050	1.35	0.319	0.20
50	24	0.038	1.81	0.428	0.25
60	29	0.032	2.16	0.510	0.30
70	33	0.027	2.47	0.584	0.35
80	39	0.024	2.72	0.643	0.40
90	44	0.022	2.94	0.695	0.45
100	49	0.020	3.14	0.742	0.50
110	53	0.018	3.32	0.785	0.55
120	58	0.016	3.48	0.823	0.60
130	64	0.015	3.63	0.858	0.65
140	68	0.014	3.74	0.884	0.70
150	74	0.013	3.87	0.915	0.75
160	80	0.013	4.00	0.946	0.80
170	85	0.012	4.12	0.974	0.85
180	93	0.010	4.23	1.000	0.90

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