9. ION EXCHANGE

9.1 Principles of Ion Exchange

Ion exchange is a process in which ions on the surface of a 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+}) that cause hardness of water:

$$H_2R + Ca^{2+} <=> CaR + 2H^+ \qquad (9.1)$$

where R represents a cation exchange resin.

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

$$SO_4^{2-} + R(OH)_2 = SO_4R + 2OH^- \qquad (9.2)$$

When all the exchange sites have been replaced with calcium or sulfate ions, the resin must be regenerated. The cation exchanger *can* be regenerated by passing a concentrated solution of sodium chloride or a strong acid 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 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 aluminum oxide to make a surface ion exchange should be mentioned. The natural clay mineral, *clinoptilolite,* can be used for waste water treatment as it has a high

selectivity for removal of ammonium ions; see also Section 5.8.

Synthetic ion exchange resins consist of a network 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 *sulfonic* $R\text{-}SO_3\text{-}H$ - *carboxylic,* R-COOH - *phenolic,* R-OH and *phosphonic,* $R\text{-}PO_3H_2$ (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 for acids generally.
Thus:

$$R\text{-}SO_3H = R\text{-}SO_3^- + H^+$$

$$\frac{[H^+] * [R\text{-}SO_3^-]}{[R\text{-}SO_3H]} = K \qquad pK = -\log K \qquad (9.3)$$

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

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 by using cellulose as a matrix, and due to the high porosity of this material it is possible to remove even high molecular weight ions such as proteins and polypeptides.

Preparation of cation exchange resin, using hydrocarbon molecules as a

matrix, is carried out by polymerization of such organic molecules as styrene and methacrylic acid. The degree of cross-linking in styrene is determined by the amount of divinylbenzene added to the polymerization. This can be illustrated by the example shown Fig. 9.1.

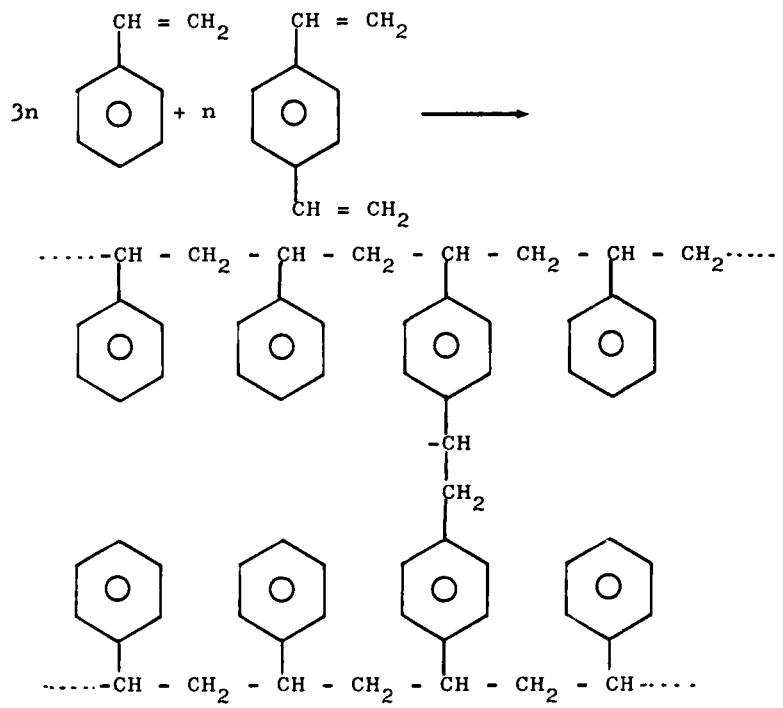


Figure 9.1. Polymerization of styrene and vinylbenzene to form polystyrene with degree of cross-linking.

It is characteristic that the exchange occurs on a chemical equivalent basis. The capacity of the ion exchanger is therefore usually expressed as equivalents per liter of bed volume.

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.

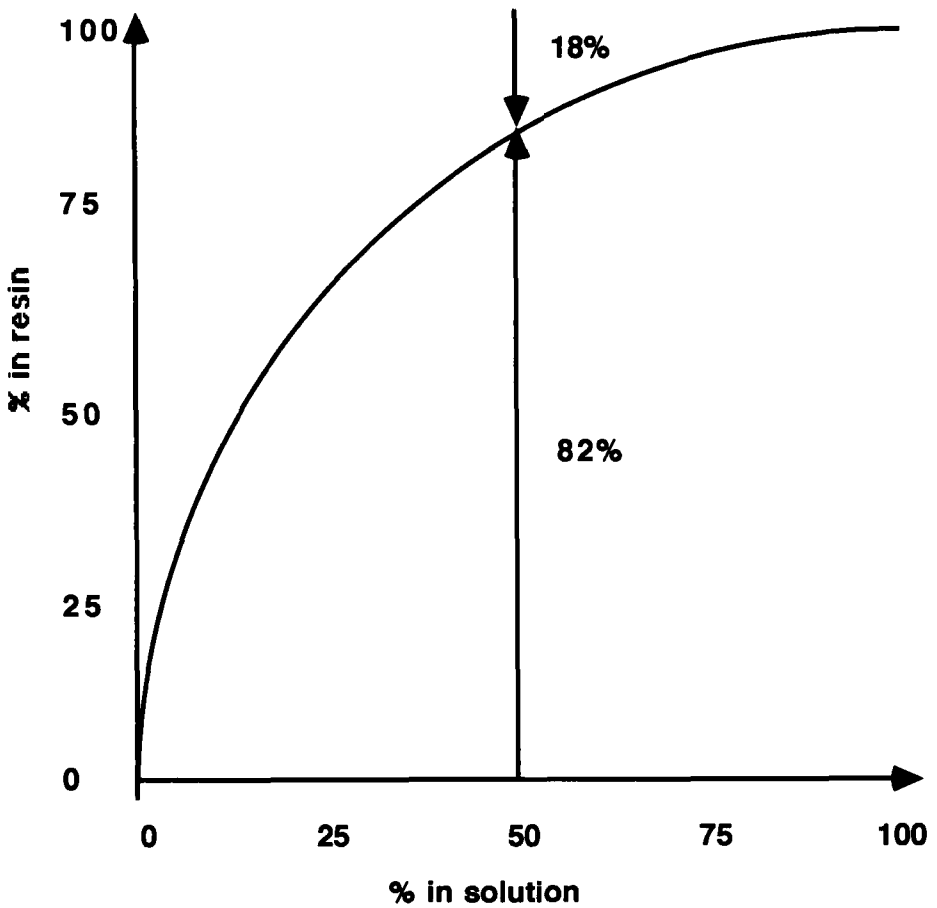


Figure 9.2. Illustration of the preference of an ion exchange resin for a particular ion. The selectivity coefficient at 50% in solution can be found from the diagram to be 82/ 18 = 4. 6.

Figure 9.2 illustrates the preference of an ion exchange resin for a particular ion. 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 = $a_{-50\%}$.

If we use concentration and not activity, it will involve, for monocharged ions:

$$C_B = C_A$$

$$a_{-50\%} = K_{AB,50\%} = \frac{C_{RA}}{C_{RB}} \qquad (9.4)$$

The plot in Fig. 9.2 can be used to read $a_{-50\%}$.

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:

$PO_4^{3-} > SO_4^{2-} > Cl^-$.

Similar for a series of cations:

$Al^{3+} > Ca^{2+} > Na^+$.

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, an effect 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.

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.

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:

$$A_n^+ + n(R^-)B^+ = nB^+ + (R^-)_nA^{n+} \qquad (9.5)$$

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 concentration of different counter ions in the resin will be different from the corresponding concentration ration in the solution.

According to the law of mass action, the equilibrium relationship for reaction (9.5) will give:

$$K_{AB} = \frac{a_{Bn} * a_{RA}}{a_A * a_{RBn}} \qquad (9.6)$$

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. Note that the activities are used, which means that the activity coefficients should be calculated as shown in Section 7.1.

As mentioned above the clay mineral, clinoptilolite, can take up ammonium ions with a high selectivity. This process is used for the removal of ammonium from municipal waste water in the U.S.A., where good quality clinoptilolite occurs. Clinoptilolite has less capacity than the synthetic ion exchanger, but its high

selectivity for ammonium justifies its use for ammonium removal. The best quality clinoptilolite has a capacity of 1 eqv. or slightly more per liter. This means that 1 liter of ion exchange material can remove 14 g ammonium -N from waste water, provided all the capacity is occupied by ammonium ions. Municipal waste water contains approximately 28 g (2 eqv.) per m^3, which means that 1 m^3 of ion exchange material can treat 500 m^3 waste water (which represents a capacity of 500 bed volumes). The practical capacity is, however, considerably less - 150-250 bed volumes - due to the presence of other ions that are taken up by the ion exchange material, although the selectivity is higher for ammonium that for the other ions present in the waste water. The concentration of sodium, potassium and calcium ions might be several eqv. per liter, compared with only 2 meqv. per liter of ammonium ions.

Clinoptilolite is less resistant to acids or bases than synthetic ion exchangers. A good elution is obtained by use of sodium hydroxide, but as the material is dissolved by sodium hydroxide a very diluted solution should be used for elution to minimize the loss of material. A mixture of sodium chloride and lime is also suggested as alternative elution solution.

The flow rate through the ion exchange column is generally smaller for clinoptilolite than for synthetic material resin - 10 m/h as against 20-25 m/h.

The elution liquid can be recovered by air stripping, as mentioned in Section 7.6. The preconcentration on the ion exchanger makes this process attractive - the sludge problem is diminished and the cost of chemicals is reduced considerably. For further details about this method of recovery, see Jørgensen (1973 and 1975).

Another ion exchanger selective for nitrogen compounds is the above mentioned cellulose ion exchanger. It has a capacity of about 1 eqv./ l. of which at least 50% is highly selective for proteins and other high molecular nitrogen organics. It makes the application of this ion exchanger attractive for industrial waste water with high concentrations of proteins and where recovery of the proteins is desirable.

A combination of chemical precipitation and ion exchange has developed as an alternative to the mechanical-biological-chemical treatment method. A flowchart of such a plant is shown in Fig. 9.3. After the chemical precipitation the waste water

is treated on two ion exchangers (which, however, could be in one mixed bed column). The first ion exchanger is cellulose-based for removing proteins and reducing BOD_5. The nitrogen concentration is here typically reduced from total N 30 mg/l to total N 15-20 mg/l due to the high selectivity of the cellulose-based ion exchanger for organic nitrogen compounds. The second column could be either clinoptilolite and/or activated alumina. A plant using this process has been in operation since 1973 in Sweden, giving results comparable with or even better than the generally applied 3 steps treatment (see Table 9.1).

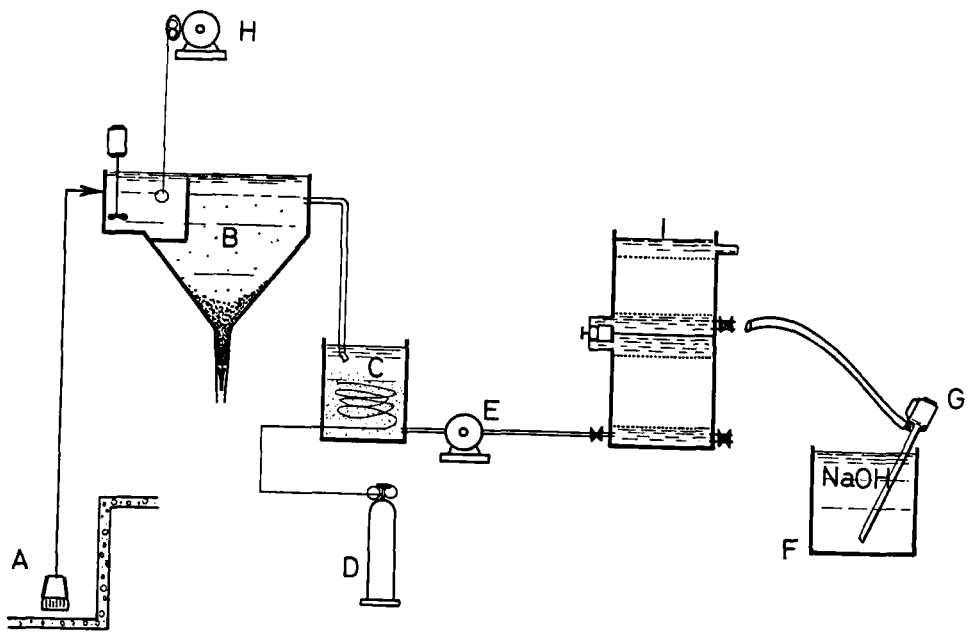


Figure 9.3. Flowchart of a combination of chemical precipitation and ion exchange. (A) a submersible pump, (B) the settling basin, (C) an intermediate vessel, where carbon dioxide is added, (D) a carbon dioxide container (50 atm., 25 liters.), (E) a pump feeding the ion exchangers, (F) elution liquid, (G) a hand-pump, (H) a dosing pump.

The capital cost and operating costs are approximately the same as for a three-steps plant. However, the plant produces 2-4 times less sludge than the normal 3 step plant, giving a correspondingly lower sludge treatment cost.

TABLE 9.1

Analysis (mg l^{-1}) of municipal waste water after chemical precipitation in combination with ion exchange (flowchart see Fig. 9.3)

BOD_5	10 - 18
COD	30 - 45
P	< 0.1 if activated alumina is used, otherwise 2-4 mg/l
N	< 1 if clinoptilolite is used, otherwise 10-15 mg/l

9.2. Process Variables

The pH value is crucial for the ion exchange process, as the form of the ion exchanger is dependent on pH, see equations (9.1) - (9.3), unless the ion exchanger is a strong acid or base, and as the form of the ions to be taken up is dependent on pH.

Optimum ammonium exchange by clinoptilolite occurs within an influent pH range of 4 to 8. If the pH drops below this range, hydrogen ions begin to compete with ammonium for the available ion exchange capacity. As the pH increase above 8, a shift in the ammonia-ammonium equilibrium toward ammonia begins. Consequently, operation outside the pH range 4 to 8 results in a pronounced decrease of exchange capacity.

The rate of exchange increases with decreasing clinoptilolite size. However, the improved rate of exchange is accompanied by disadvantage of higher head loss. A suitable flow rate in practice is 8-10 bed volume / hr, providing that the influent is clarified secondary waste water with less than 30 mg / l suspended matter. Biological growth which occurs is adequately removed by the regeneration.

The break through is determined by the desired concentration of ammonium

in the effluent. A typical break through curve is shown in Fig. 9.4. The corresponding utilization of the ion exchange capacity as a function of the column depth is illustrated in Fig. 9.5. The transition zone will have a certain depth, dependent on the flow rate but independent of the depth of the column; see Fig. 9.6, which is reproduced from Jørgensen et al., (1978).

It implies that a shallow bed utilizes less than a deeper bed, although the flow rate expressed in bed volume per unit of time will mean a smaller actual flow for the shallow bed. A deeper bed, on the other hand, will mean a higher head loss. A compromise between the head loss and the utilization has to be found and a bed depth of 1.5-2 meters is recommended in practice; see Koon and Kaufman (1971) and Suhr and Kepple (1974).

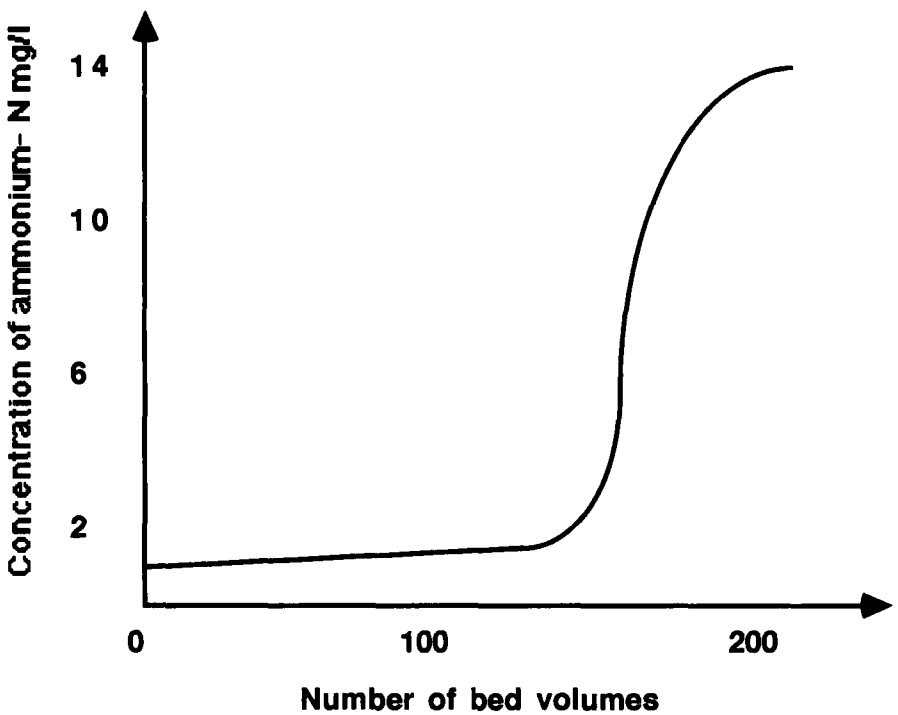


Figure 9.4. An ammonium break through curve is shown. The ammonium-N concentration in the effluent is plotted versus the number of bed volumes treated.

Furthermore, it is recommended to use two or more columns in series, because this makes it possible to utilize the entire capacity of the first column and

let the second column provide the required concentration of ammonium-N in the final effluent. After regeneration of the first column at saturation, the second column becomes the first and the freshly regenerated column number two in the series. Thereby it becomes possible simultaneously to achieve a low concentration in the effluent and a full utilization of the ion exchange capacity.

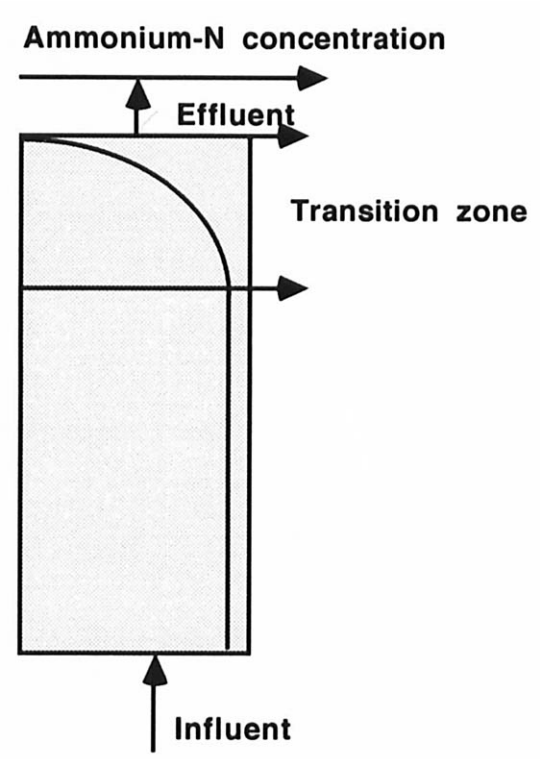


Figure 9.5. The concentration of ammonium-N in the ion exchanger is shown as a function of the depth at ammonium breakthrough. The ion exchanger is saturated up to the transition zone, where the capacity is not used entirely. The depth of the transition zone is dependent on the flow rate (m/h), but not on the total depth of the column.

Although clinoptilolite prefers ammonium ions to other cations, it is not absolutely selective and other ions do compete for the available ion exchange capacity. The ion exchange equilibria for the exchange of ammonium versus sodium, potassium, calcium and magnesium are available in the literature. Figure

9.7 gives the selectivity coefficients versus concentration ratios of sodium, potassium, calcium and magnesium respectively. These curves illustrate that clinoptilolite is selective for ammonium relative to all the examined ions except for potassium. It is possible from such curves to predict the ammonium capacity of clinoptilolite in the presence of various concentrations of other cations.

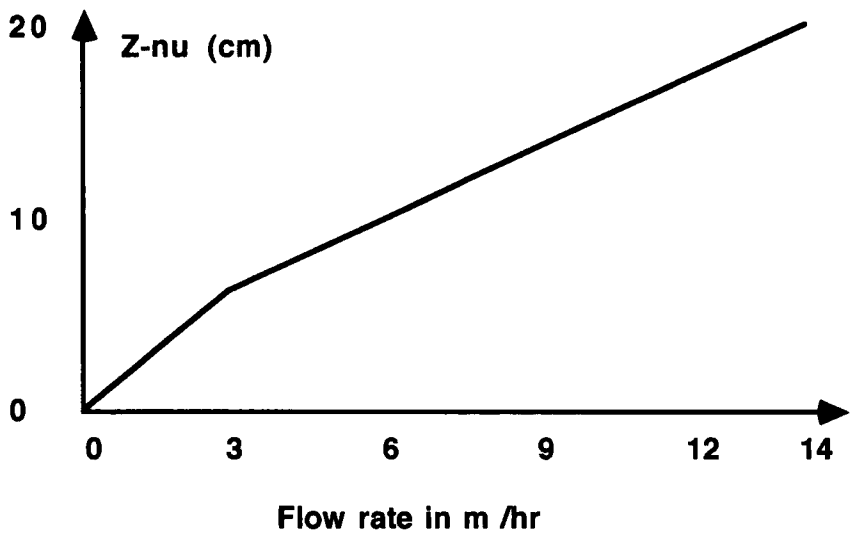


Figure 9.6 Z-nu, the layer not used is plotted versus the flow rate. Z-nu is independent of the height of the column, but as shown on the figure dependent upon the flow rate.

Clinoptilolite is available in different purities, dependent on the geological formation of this clay mineral. The clinoptilolite from California has a purity of 85-95%, while a Hungarian type from Tokaj has a purity of only 60-70%. The capacity is roughly proportional to the purity.

Investigations of the latter type of clinoptilolite, see Jørgensen et al (1975) and (1978), have demonstrated that a treatment of the clay mineral by sodium hydroxide or sodium carbonate, before use, will improve the uptake of ammonium. The results are expressed by use of the following equation:

$$K = (Q/C) * (C_0 - C)^n / (Q_0 - Q) \qquad (9.7)$$

where C is the equilibrium concentration of ammonium ions in solution, meqv /l, C_0 is the total initial concentration of ammonium ions in solution, meqv /l, Q is the ammonium ions taken up by clinoptilolite meqv /g, Q_0 is the total ion exchange capacity of the sorbent, meqv/g, while K and n are characteristic constants, which can be found by use of a logarithmic plot of equilibria data. The equation can be used for all types of waste waters and clinoptilolites. In each case equilibria data must be used to find K, n and Q_0.

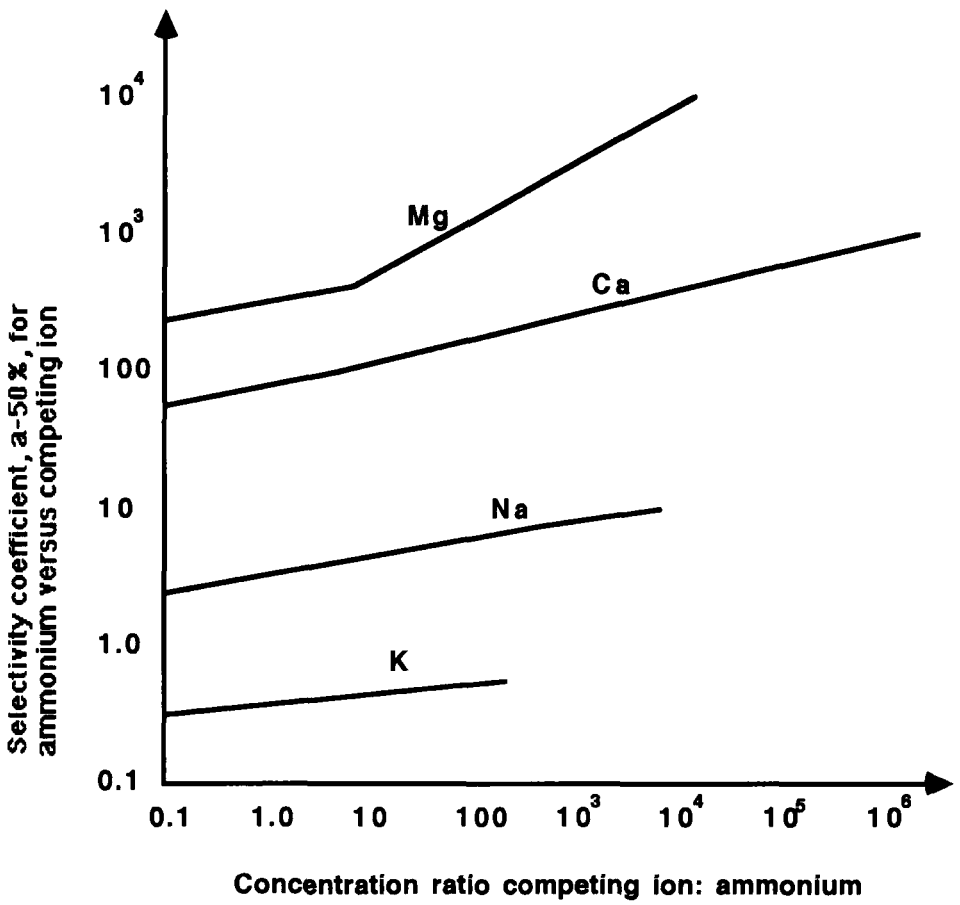


Figure 9.7. The selectivity coefficient a-50% of ammonium competing with potassium, sodium, calcium or magnesium versus concentration ratio of competing ion / ammonium. Note that the graph is double logarithmic.

Table 9.2 gives the results of investigations of treated (with sodium hydroxide or sodium carbonate) and untreated Hungarian clinoptilolite, using ammonium solutions in distilled water to find the equilibrium data.

The equilibrium curve, resulting from equation (9.7) can be used directly in the design of ion exchange columns as presented in Section 9.4. Note that the untreated clinoptilolite gives an equilibrium curve quite different from the treated one and that the treated clinoptilolite will give a far better uptake of ammonium; see Table 9.2.

The regeneration of the ion exchange material is carried out either by sodium or calcium ions by passing the regenerant through the clinoptilolite in the opposite flow direction of the normal service cycle. Lime-slurry was used for the first studies of this process. It was, however, found that elution with lime could be speeded up by the addition of sufficient sodium chloride (0.1M). Ammonium ions are converted to ammonia, so it can readily be removed from the regenerant, and the volume of regenerant required for complete regeneration decreases, with increasing pH of the regeneration liquid. Precipitation of calcium carbonate and magnesium hydroxide occurs, however, at high pH, which leads to clogging of the exchanger inlets and outlets.

Table 9.2.

The three parameters in equation (9.7) for untreated and treated clinoptilolite, originating from Tokaj, Hungary.

Parameter	Untreated	Treated
K	1.16	1.78
n	1.18	1.25
Q_0	0.65	0.76

Two large municipal waste water installations in California and in Virginia utilize a regenerant with a pH near neutral. The active portion of the regenerant is a 2 percent sodium chloride solution. A typical elution curve for ammonium with this type of regenerant is shown Fig. 9.8. It is seen that approximately 25-30 bed

volumes are required before the ammonium concentration reaches equilibrium, while 10-20 bed volumes are sufficient at high pH regeneration. If the regenerant is recovered, see below, the volume is not very critical. Variations in regenerant flow rates of 4-20 bed volumes / hr do not affect regenerant performance. Typical design values are 10 bed volumes / hr.

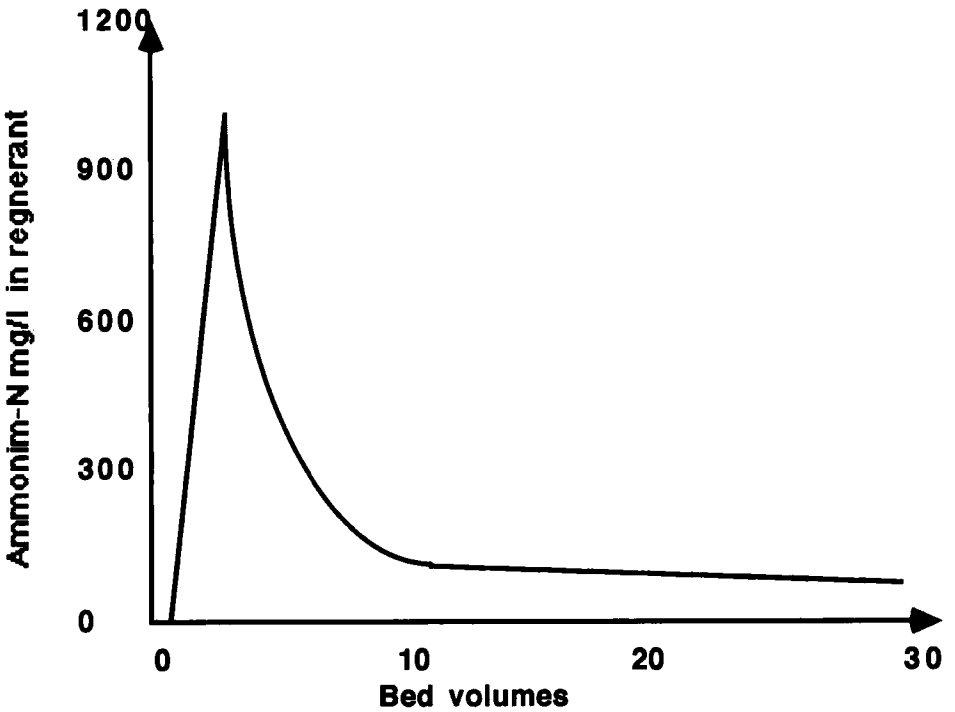


Figure 9.8. Ammonium elution with 2% sodium chloride. The concentration of ammonium-N, mg/l in regenerant is plotted versus the number of bed volumes used.

The regeneration cycle is usually followed by back washing with 2-4 bed volumes. The back wash water is mixed with the influent to remove the minor ammonium present. The regenerant may be recovered by either air or steam stripping. When the ammonia is removed by this process, the clinoptilolite is ready to be used again for next regeneration cycle.

Cellulose ion exchangers are selective to proteins and offer a possibility for

protein recovery. The capacity is about 1 meqv / g , but with a low bulk weight , the capacity will only be roughly 0.2 eqv / l . As 50% of this capacity is selective for proteins and proteins have a high equivalent weight, the capacity on a weight to weight basis is still attractive, although it is strongly dependent on the source of protein, including how much time the proteins have had to decompose before the treatment. Due to the slow diffusion rate of proteins, the retention time of waste water in the cellulose ion exchanger is required to exceed 12-15 minutes. Regeneration can be carried out by sodium hydroxide, which expand the cellulose fibers, whereby the proteins are released. To ensure the presence of a sufficiently high sodium concentration and thereby obtain the sodium-form of the ion exchange material, elution by a mixture of sodium hydroxide and sodium chloride is recommended. Proteins dissolved in the elution liquid may be recovered for instance by precipitation; see also Section 11.1.

Figure 9.6 is also valid for this ion exchange process, for which a column height of about 1.5 m is recommended.

9.3. The Sequential and Continuous Ion Exchange Operation

The *sequential adsorption or ion exchange operation* is limited to treatment of solutions where the solute to be removed is adsorbed relatively strongly when compared with the remainder of the solution. This is often the case when colloidal substances are removed from aqueous solutions using carbon, as in the production of process water.

The method for dealing with the spent adsorbent or ion exchanger depends upon the system under consideration. If the material taken up is valuable (e.g., proteins), it might be desorbed by contact with a solvent other than water. If the removed component is volatile (e.g., ammonia), it may be desorbed by reduction of the partial pressure of the adsorbate over the solid by passing steam or air over the solid, i.e., air or steam stripping is applied; see also Section 9.2. In the case of most sequential operations in the context of waste water treatment, the adsorbate is of no value and it is not easily desorbed. The adsorbent may then be regenerated by burning off the adsorbate, followed by reactivation.

A mathematical treatment of the sequential operation distinguishes between *single-stage operations, multi-stage cocurrent operations and multi-stage*

countercurrent operations. The mathematical treatment does not distinguish adsorption from ion exchange - the basic equations are the same. A schematic flowchart for a *single-stage operation* is shown in Fig. 9.9.

As the amount of ion exchanger is usually very small compared with the amount of solution treated and since the solutes to be removed are taken up much more strongly than the other components present, the up take of the latter may be ignored. Furthermore, the ion exchanger is generally insoluble in the solution. If the water (see Fig. 9.9) to be treated contains S kg of unadsorbed substance (water) then the adsorbable solute concentration is reduced from Y_0 to Y_1 kg of solute per kg of solvent.

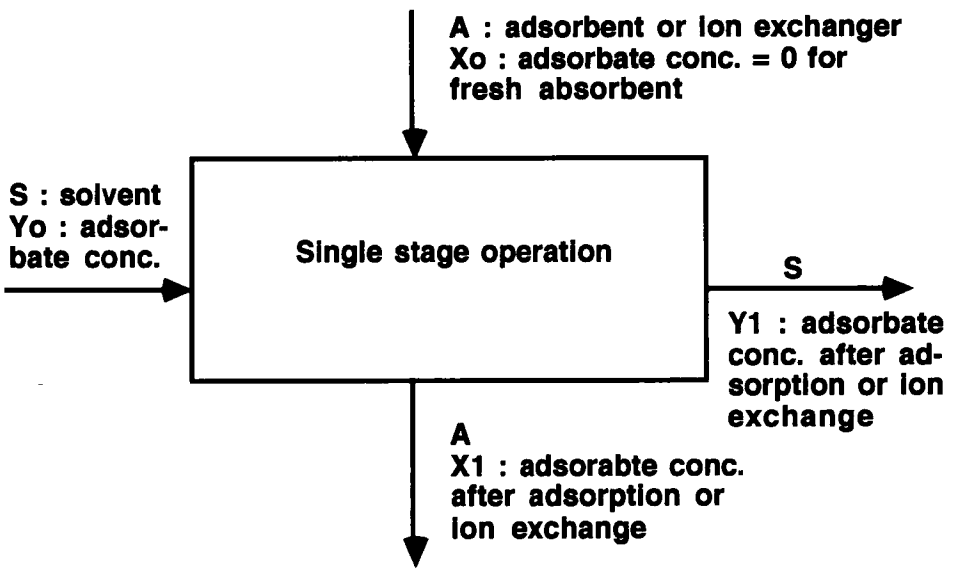


Figure 9.9 Flowsheet for the single-stage operation. Application of the mass conservation principle for the component removed from S to A leads to equation (9.8).

If the adsorbent (ion exchanger) added is A kg, then the solid adsorbate content increases from X_0 to X_1 kg of solid per kg of adsorbent. In most cases fresh adsorbent is used so that $X_0 = 0$. The mass balance of the solid removed is given by the following equation:

$$S(Y_0 - Y_1) = A(X_1 - X_0) \qquad (9.8)$$

This equation gives the so-called operating line, shown in Fig. 9.10 together with the equilibrium curve. This could be either Freundlich's or Langmuir's isotherm or equation (9.7), which may be considered a modified Freundlich's isotherm.

It is presumed in Fig. 9.9. that the solvent and adsorbent can be separated completely after the ion exchange process, which is not always the case in practice. The presence of solvent in the used ion exchanger may not to interfere with the further treatment of the adsorbent or it may be possible to remove the solvent by drying or other processes. It is under all circumstances important to consider this problem in the application of adsorption and ion exchange processes in practice.

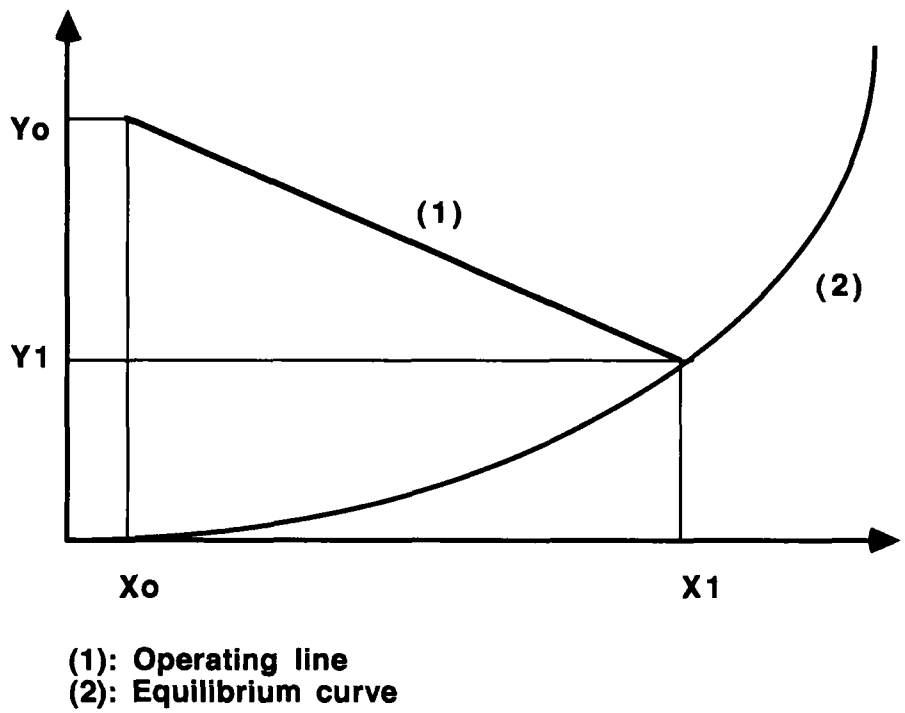


Figure 9.10. Operating line and equilibrium curve for a single-stage operation.

If sufficient time of contact is allowed, so that equilibrium is almost reached, the final liquid and solid concentration will correspond to a point (see Q, Fig. 9.10), which is quite close to the equilibrium curve.

The mass balance assumes that the amount of liquid mechanically retained with the solid after filtration or settling is negligible. This is usually the case.

If Freundlich's isotherm can be used, we can, at the final equilibrium condition, set up the following equation:

$$Y_1 = k * X_{1n} \tag{9.9}$$

Since the adsorbent (ion exchanger) normally used contains no initial adsorbate, that is $X_0 = 0$, then the two equations yield:

$$\frac{A}{S} = \frac{Y_0 - Y_1}{(Y_1/k)^{1/n}} \tag{9.10}$$

As can be seen, this permits analytical calculation of the adsorbent solution ratio for a given change in solution concentration, provided that the constants in the equation system are known.

However, removal of a given amount of solutes may be accomplished by less adsorbent, if the solution is treated with separate small batches of ion exchanger rather than a single large batch. This method is *the multi-stage cocurrent operation*. The savings are greater the larger the number of batches, but the expense of equipment and even handling costs will increase with the number of stages. It is therefore rarely economical to use more than two or three stages. A schematic flowchart and operating diagram for two ideal stages of cocurrent adsorption are shown in Fig. 9.11. As seen, the same quantity is treated in each stage, but by two different amounts of adsorbent A_1 and A_2. The mathematical balances are given by the following equations:

$$S(Y_0 - Y_1) = A_1(X_1 - X_0) \tag{9.11}$$

$$S(Y_1 - Y_2) = A_2(X_2 - X_0) \tag{9.12}$$

These two equations provide the operation lines as shown in Fig. 9.12.

When Freundlich's expression is used as a description of the adsorption isotherm and fresh adsorbent is used in each stage, $X_0 = 0$, the two-stage system can be computed directly:

$$\frac{A_1}{S} = \frac{Y_0 - Y_1}{(Y_1/k)^{1/n}} \tag{9.13}$$

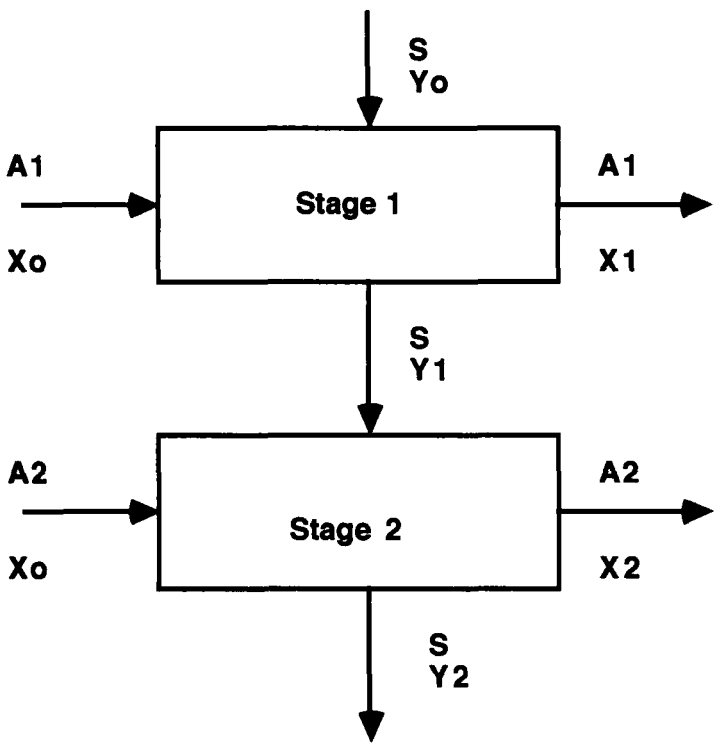
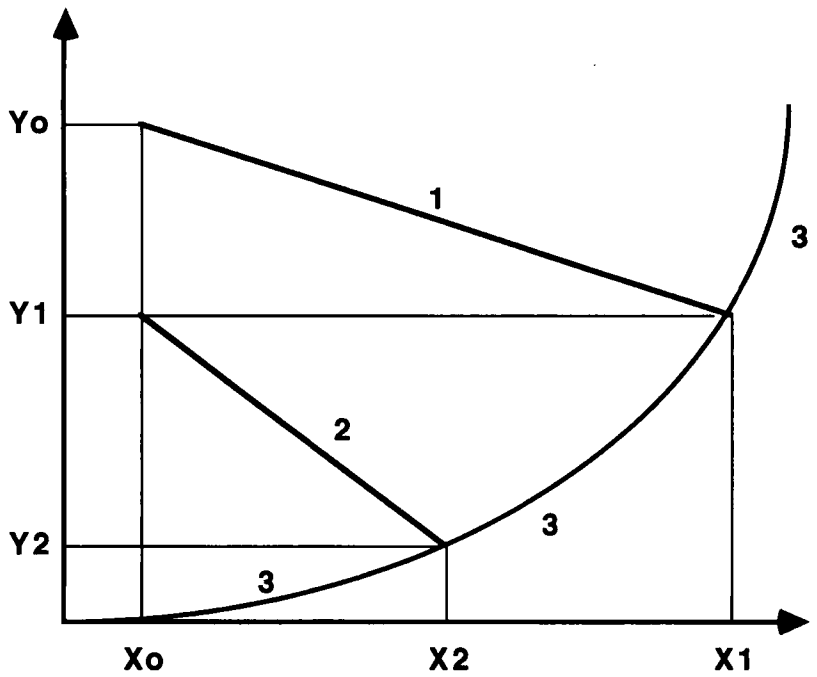


Figure 9.11. Flowchart for a two stages cocurrent operation.

$$\frac{A_2}{S} = \frac{Y_1 - Y_2}{(Y_2/k)^{1/n}} \tag{9.14}$$

or

$$\frac{A_1 + A_2}{S} = k^{1/n}\left(\frac{Y_0 - Y_1}{Y_1^{1/n}} + \frac{Y_1 - Y_2}{Y_1^{1/n}}\right) \qquad (9.14)$$



1: operating line 1
2: operating line 2
3: equilibrium curve

Figure 9.12 Operating diagram for two stages cocurrent ion exchange or adsorption.

The minimum total adsorbent is found by setting

$$\frac{d(A_1 + A_2)}{dY_1} = 0 \qquad (9.15)$$

This reduces to:

$$\left(\frac{Y_1}{Y_2}\right)^{1/n} - \frac{1}{n} * \left(\frac{Y_0}{Y_1}\right) = 1 - \frac{1}{n} \qquad (9.16)$$

Equation (9.16) can be solved for Y_1, and the adsorbed quantity can be found by equations (9.13) and (9.14).

Even greater economy in the use of adsorbent / ion exchanger can be achieved by *a countercurrent operation*. Figure 9.13 shows a diagram of this operation and Fig. 9.14 shows the operation line and equilibrium curve for this case. The operating line can be set up as follows:

$$S(Y_0 - Y_2) = A(X_0 - X_1) \tag{9.17}$$

and if Freundlich's adsorption isotherm can be used and $X_0 = 0$, then a combination of this equation and (9.17), provides the following expression:

$$\frac{S}{A} = \frac{Y_0 - Y_2}{(Y_1/k)^{1/n}} \tag{9.18}$$

An equation for calculating Y_1 can be found by eliminating S/A:

$$\frac{Y_0}{Y_2} - 1 = \left(\frac{Y_1}{Y_2}\right)^{1/n} \cdot \left(\frac{Y_1}{Y_2} - 1\right) \tag{9.19}$$

It is then possible to calculate S/A directly from (9.17).

If Freundlich's adsorption isotherm cannot be used, it is of course possible to use the diagram for the necessary calculation as shown in Fig. 9.14.

In *the continuous operation* the water and the adsorbent / ion exchanger are in contact throughout the entire process without a periodic separation of the two phases. The operation can either be carried out in strictly continuous steady-state fashion by movement of the solid as well as the fluid or in a semi-continuous fashion characterized by moving fluid but stationary solid, the so-called fixed bed adsorption / ion exchange, which is widely used in waste water treatment, including by the removal of ammonium and proteins from waste waters. It is generally found more economical to use a stationary bed for waste water treatments due to the relatively high cost of continuously transporting solid particles. Only this case will therefore be treated mathematically.

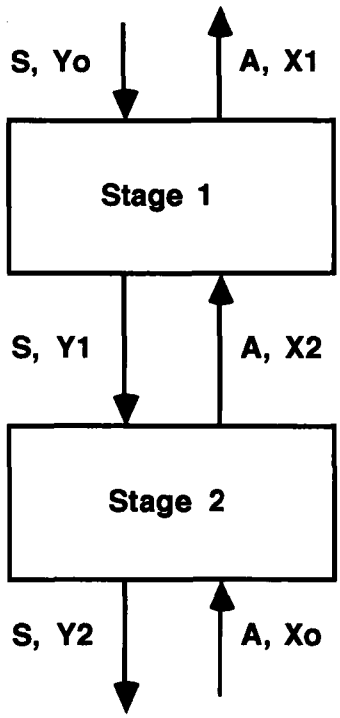


Figure 9.13. Flowsheet for a two stages countercurrent adsorption.

The design of a fixed bed ion exchanger and the prediction of the length of the cycle requires knowledge of the percentage approach to saturation at the break point. Figure 9.15 shows an idealized break-through curve.

Let us consider a case where the flow of water through an ion exchange bed is S kg/h m^2 - entering with an initial solute concentration of Y_o kg solute / kg solvent. The total, solute free, effluent after a given time is W kg/m^2 (see Fig. 9.15). The break-through curve should be steep and the solute concentration in the effluent rises rapidly from close to zero to that of the incoming water. Some low value Y_B is arbitrarily chosen as the break-point concentration and the column is considered exhausted when the effluent concentration has risen to some other arbitrarily chosen concentration of value Y_E, close to Y_o. The critical values are the quantity of effluent W_B and W_E (see Fig. 9.15).

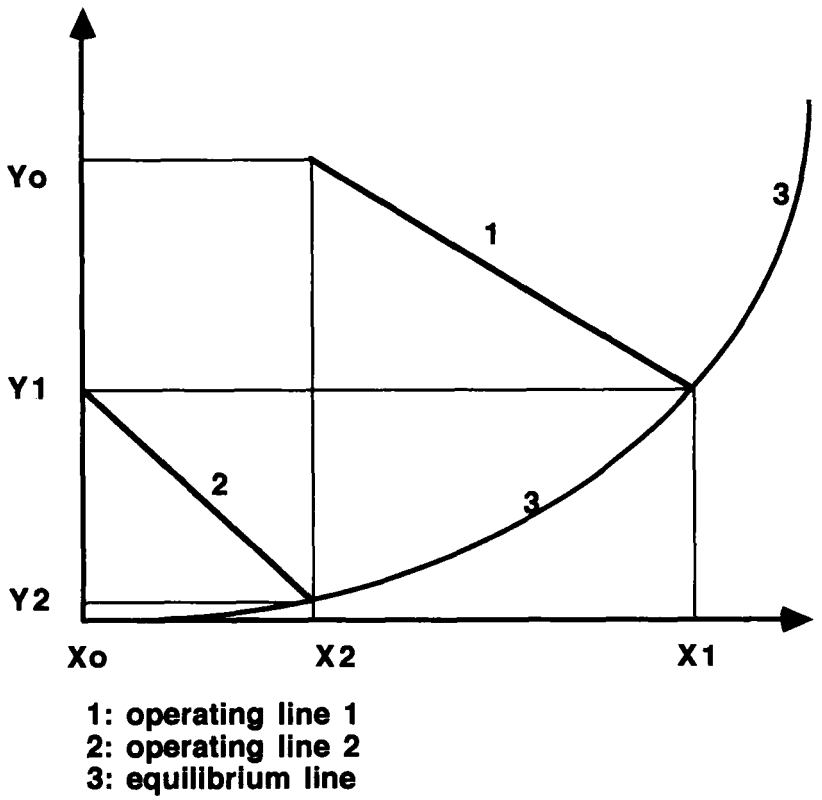


Figure 9.14. Operating diagram for two stages countercurrent adsorption.

The effluent accumulated during the occurrence of the break-through curve is:

$$W_A = W_E - W_B \qquad (9.20)$$

The adsorption or ion exchange zone, that part of the bed in which the concentration changes from Y_B to Y_E, is considered to have a constant height of Z_A m. If we use T_A for the time required for the adsorption zone to move its own height down the column after the zone has been established, then:

$$T_A = W_A / S \qquad (9.21)$$

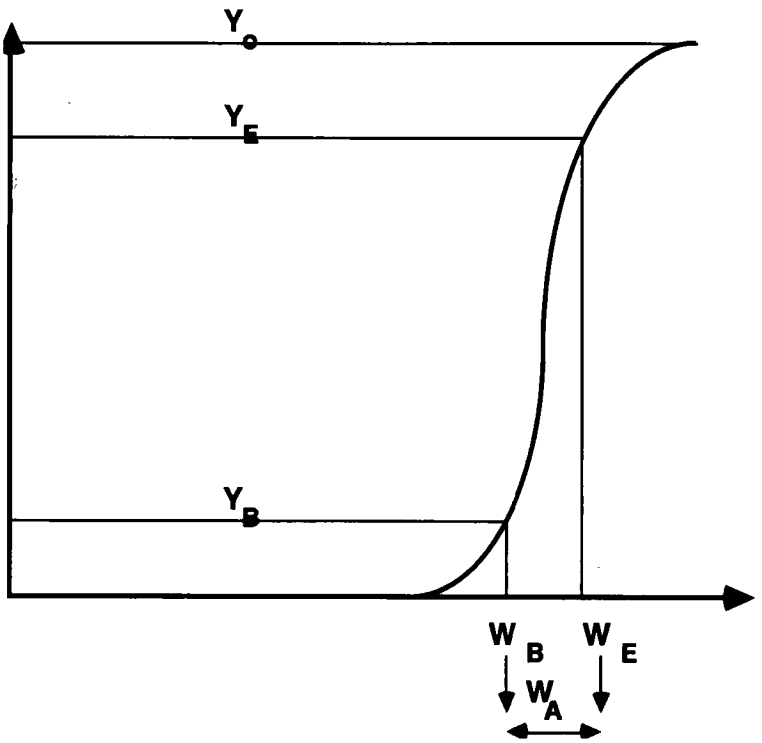


Figure 9.15 Idealized break-through curve.

Correspondingly we call the time required for the ion exchange zone to establish itself and move out the bed, T_E, which can then be calculated from:

$$T_E = \frac{W_E}{S} \qquad (9.22)$$

If we call the height of the entire ion exchange bed, Z(m), and, T_F, the time required for formation of the ion exchange zone, we get:

$$Z_A = Z \frac{T_A}{T_E - T_F} \qquad (9.23)$$

The quantity of solid removed from the water in the ion exchange zone from the break-point to exhaustion is U kg solid / m^2. This area is areas 1 and 2 in Fig. 9.15.

If all the ion exchanger in the zone was saturated with solute, it would contain $Y_o * W_A$ kg solute / m^2.

Consequently at the break-point, the zone is still within the column. The fractional ability, f, of the adsorbent in the zone still to adsorb is:

(9.24)

$$f = \frac{U}{Y_o * W_A} = \frac{\int_{W_B}^{W_E} (Y_o - Y)\, dW}{Y_o * W_A} = \int_{0.0}^{1.0} (1 - Y/Y_o)\, d\left(\frac{W - W_B}{W_A}\right)$$

If f = 0 it means that the ion exchanger in the zone is saturated, and the time of formation of the zone at the top of the bed, T_F, should be the same as the time required for the zone to travel a distance equal to its zone height, T_A. On the other hand, if f = 1.0 so that the solid in the zone has essentially not taken up anything of the component considered, the zone formation should be very short.

These limiting conditions are described by:

$$T_F = (1 - f)\, T_a \qquad (9.25)$$

Equations (9.23) and (9.25) provide:

$$Z_a = Z \frac{T_A}{T_E - (1 - f)\, T_A} = Z \frac{W_A}{W_E - (1 - f)\, W_A} \qquad (9.26)$$

The ion exchange column is Z m tall of unit cross sectional area, and contains Z * Q kg adsorbent, where Q is the apparent packed density of the solid in the bed. If the column was in complete equilibrium and saturated at an ion concentration of X_T kg / kg solid, the weight of the component taken up would be Z * Q * X_T kg. At the break-point the adsorption zone of height, Z_a, is at the bottom of the column, but the rest of the column, Z - Z_A (m), is substantially saturated. At the break-point therefore, the removed amount of the considered component is:

$$(Z - Z_A)\, Q * X_T + Z_A * Q * f * X_T \qquad (9.27)$$

The fractional saturation of the column at the break-point is:

$$\frac{(Z - Z_A) * Q * X_T + Z_A * Q * f * X_T}{Z * Q * X_T} = \frac{Z - (1 - f) * Z_A}{Z} \qquad (9.28)$$

In the fixed bed of ion exchange, the active zone moves through the solid in the flow direction as we have seen.

The operating line of the entire tower is:

$$S(Y_0 - 0) = A(X_T - 0) \qquad (9.29)$$

or

$$\frac{S}{A} = \frac{Y_0}{X_T} \qquad (9.30)$$

Since the operating line passes through (0,0) of Fig. 9.16 at any level in the column, the concentration of solute in the water, Y, and the removed component on the solid, X, are then related by the equation:

$$S * Y = A * X \qquad (9.31)$$

Over the differential height, dZ, the rate of ion exchange is:

$$SdY = K_t * a(Y - Y+)*dZ \qquad (9.32)$$

where K_t = the overall transfer coefficient, a = the outside surface area of the solid particles and Y+ = the equilibrium concentration.

For the entire ion exchange zone:

$$N_t = \int_{Y_B}^{Y_E} \frac{dY}{Y - Y+} = \frac{Z_a}{H_t} = \frac{Z_a}{S/K_t * a} \qquad (9.33)$$

where N_t = the overall number of transfer units in the ion exchange zone.

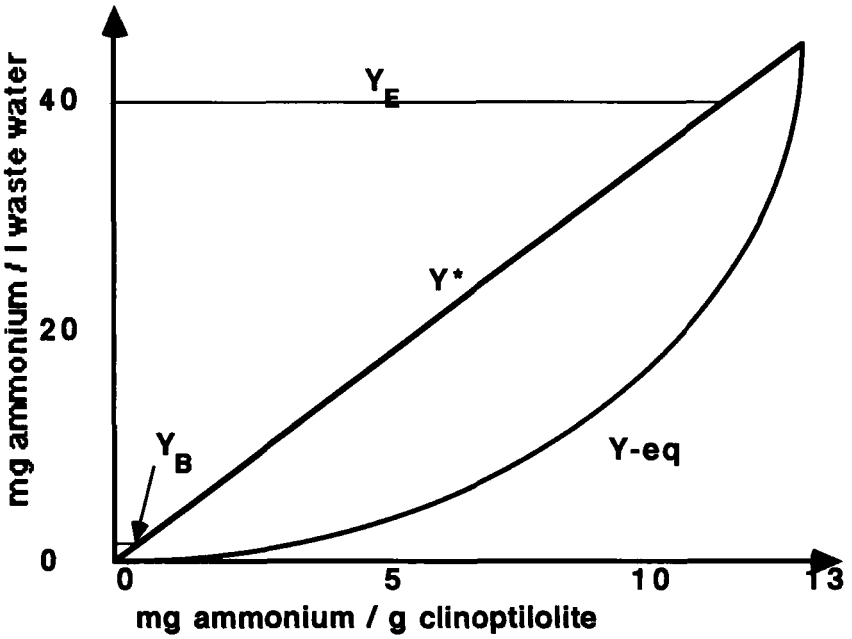


Figure 9.16. Y* is the operating line, Y-eq the equilibrium curve, Y_B is considered as break-point and the bed is saturated at Y_E.

The success of this analysis hinges upon the constancy of K_t or H_t for the concentration within the adsorption zone. This will of course depends upon the relative constancy of the resistance to mass transfer in the fluid and within the pores of the solid. An alternative method to determine Ht will be described below; see page 295.

The ion exchange rate can be limited by external diffusion, internal diffusion or by the actual ion exchange process. The external diffusion controls the transfer of solute from the water to the boundary layer of fluid immediately adjacent to the external surface of the ion exchanger. The external diffusion is governed by molecular diffusion and in a turbulent flow by eddy diffusion.

The process can be described by the following equation:

$$V_a = k_e * a (Y - Y+) \qquad (9.34)$$

where V_a = the rate of ion exchange; Y = the concentration of the ion in the fluid

and Y+ = the concentration of the ion in the fluid in equilibrium with the existing concentration in the ion exchanger. k_e is the external mass transfer coefficient.

Internal diffusion processes control the transfer of solid from the exterior of the ion exchanger to the internal surface. This condition is represented by the following equation:

$$V_a = k_i * a * \Sigma * (X_x - X) \tag{9.35}$$

where Σ = the interparticle void ratio; X_x = the concentration of the ion in the solid phase that is assumed to be in equilibrium with the coexisting liquid phase at concentration, Y; X = the actual concentration of ion in the solid phase.

If the internal and the external diffusions occur at comparable rates the respective mass transfer coefficients, measured individually, may be added (King, 1965):

$$\frac{1}{K} = \frac{1}{k_e} + \frac{1}{k_i} \tag{9.36}$$

The diffusion coefficient as used in the design of a practical column must be found in the literature or by determined experimentation. The internal diffusion can be found by equilibrium experiments by use of equation (9.34).

Ht may be found alternatively by a series of experiments, where the capacity (expressed as volume of water, which can be treated with a required efficiency, i.e., Y_B is given) is found for different flow rates. The values found are expressed as a percentage of the theoretical capacity, which gives the percentage of the total column "not used," which is equal to Z-nu = (1-f)*Za in Fig. 9.6. Equation (9.33) is used to find Nt by graphic integration. f is furthermore found by graphic integration of Y / Yo versus (W -WB), corresponding to equation (9.24). Hence Za can be found, since (1-f*Za) is known. Finally is Ht determined (see also the example in Appendix C2) as a function of the flow rate from equation (9.33): Ht = Za / Nt and can be used for design of full-scale columns. The method is published in Jørgensen et al. (1978) for the exchange ammonium-sodium on clinoptilolite. Ht as function of the flow rate may furthermore be used for an economic optimization of the ion exchange column. Higher flow rate means that the required column volume

is reduced but that the utilization of the column is also reduced, which in turn means, that a more frequent regeneration is required to obtain the same effluent quality. A lower flow rate, on the other hand, means that more ion exchange volume is needed, but the frequency of elution is decreased.

The design of an ion exchange column will be exemplified as mentioned above in Appendix C2. The steps to be followed may be summarized in 6 points:

1. Z-nu is determined in laboratory or pilot scale tests as function of the flow, i.e., for various S-values.
2. Hence (1-f)*Za is known, see equation (9.28)
3. Nt is determined by graphic integration of equation (9.33).
4. f is determined by graphic integration of equation (9.24)
5. Za is determined from a combination of the results in points 2 and 4.
6. Ht as a function of the flow rate is determined by use of the expression Ht = Nt / Za. Ht as function of the flow rate can now be used for any design.

9.4. Application of Ion Exchange

Mercer et al. (1970) has reported a successful application of the specific ion exchanger clinoptilolite for removal of ammonium from municipal waste water. Jørgensen (1979) reported the possibilities of recovering ammonium (ammonia) from industrial waste water. It is clear from these examinations that recovery of the regenerant by air stripping seems important, because even the neutral regenerant will cause discharge problems. An economic analysis shows, moreover, that the recovery of the regenerant will in most cases more than pay for the cost of the recovery, as the air stripping of small volumes is relatively moderate in costs as discussed in Section 7.6. As already discussed in Section 7.6 the ammonia removed by stripping should be absorbed in sulfuric acid to avoid air pollution by the released ammonia. This implies that an entire chain of processes: ion exchange, recovery of regenerant and recovery of the air stripped ammonia as ammonium sulfate, must be applied. Figure 9.17 shows a flow chart of the described process chain.

Cellulose anion exchangers have been used for removal of azo-dyes from waste water from the textile industry, as reported by Jørgensen (1978) and

Gangneux et al. (1976). The removal of azo-dyes is required due to the strong color of the waste water, rather than to remove the nitrogenous compounds in the waste water, which are unimportant for the nitrogen balance in the receiving water.

Proteins can be recovered from slaughterhouses, fish filleting plant, dairies and other food processing industries by use of a cellulose cation exchanger. The method has not found a wide application as chemical precipitations of these waste waters are sufficient to produce an effluent comparable to municipal waste water. The values of the proteins still in solution after this treatment are hardly able to pay for recovery of the proteins. It can, however, not be excluded that the process will be of increasing interest in the future due to lack of proteins and due to increasing charges imposed by the water authorities on industrial waste water effluents.

Many industries discharge waste water with high concentrations of ammonium, as referred to in Section 7.6. Ion exchange is, however, not a very attractive treatment method for removal of high ammonium concentrations, because the regeneration becomes more frequent and the operation costs are very dependent on the elution frequency. As air stripping becomes more attractive the higher the concentration of ammonium is, these types of industrial waste waters are probably better treated by biological methods or by air stripping at least from an economic's point of view. Ion exchange is an attractive method particularly for concentrations up to 100 mg/l (Haralambous et al, 1992) and for waste water and drinking water, which do not contain sufficient organics to allow a biological treatment. Ion exchange has furthermore been applied for removal of ammonium from water in recycling aquaculture plants. The advantage is here the low ammonium concentration, which makes it attractive to use ion exchange to concentrate the waste product, in this case ammonium, several thousand times. However, for all these applications of clinoptilolite, it is necessary to have sufficient contact time to allow the intracrystalline diffusion to take place; see Jørgensen (1979) and Neveu et al. (1985). Longer contact time brings about a reduced discrepancy between theoretical and practical capacity. A flow rate of 2-6 bedvolumes / h will in most cases correspond to the optimum contact time.

Ion exchange has been used for removal of nitrate from drinking water; see for instance Dore et al., 1986. They used a strong base ion exchanger, regenerated by sodium chloride and were able to remove as much as almost 1 mole of nitrate per liter of resin at a low sulfate concentration. The selectivity to nitrate is, however,

reduced by increased sulfate concentration.

The standards for nitrate in drinking water (see Section 1.4) are exceeded for many ground water bore holes. The nitrate can, however, be removed by ion exchange, but as there is no ion exchanger, that is specific for nitrate take up, nitrate removal by this method is associated with high costs. As the ion exchange process has a high efficiency, the nitrate can easily be removed to a concentration far below the standards. To reduce the costs it is therefore possible to treat a fraction of the ground water by ion exchange and then to mix the treated and untreated water afterwards and still obtain a drinking water, that can meet the standards.

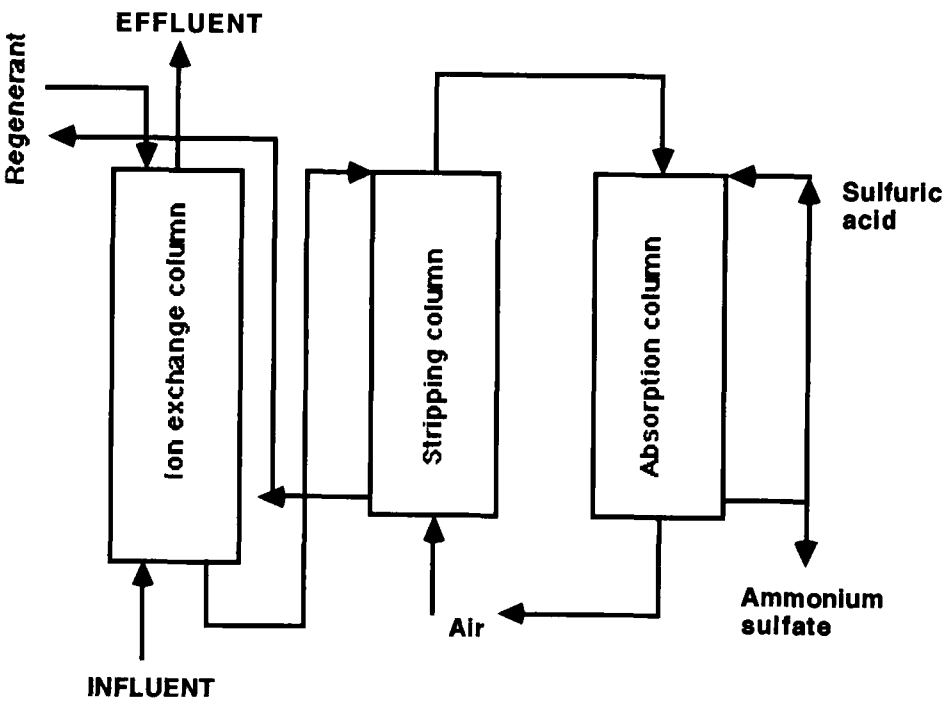


Figure 9.17. A flow chart of a combination of ion exchange, air stripping and absorption. The regenerant is recovered by air stripping, while the ammonia from the air stripping is utilized to produce a fertilizer, ammonium sulfate.