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Activity Based Adsorption Isotherms for Adsorption From Mixed Solvents

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Activity based adsorption isotherms for adsorption from mixed solvents

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Adsorption is a very efficient technology for the removal of dissolved organic components from aqueous streams. High loadings on the sorbent can be achieved even at low concentrations in the feed and the residual concentrations in the water are low. For the removal of dissolved acrylonitrile from an industrial process water stream “Solvent Swing Adsorption” will be applied. Solvent Swing Adsorption is a hybrid technology which combines adsorption with extraction and overcomes one of the biggest drawbacks of adsorption which is the recovery of the adsorbed compound. Acrylonitrile is a very toxic component and a valuable raw material. It must be removed from the aqueous stream and be reused in the production process for ecological and economical reasons.

Solvent Swing Adsorption consists of two steps: In the first step the water stream containing dissolved acrylonitrile is fed to an adsorption column where the acrylonitrile is adsorbed. Just before the acrylonitrile concentration in the water outflow starts to increase, the desorption step starts. In this second step a solvent with a high affinity for acrylonitrile is fed to the column. Where the solvent meets sorbent particles loaded with acrylonitrile, the acrylonitrile desorbs and very high concentrations in the solvent result. As soon as the acrylonitrile is removed from the column, the next adsorption step starts. It is crucial to minimize the amount of solvent which is used per cycle and maximize the acrylonitrile concentration in the solvent since the desorbed acrylonitrile will be separated from the solvent by distillation. The acrylonitrile will go back to the industrial production process and the solvent will be reused in the next desorption step.

Fast kinetics and favorable isotherms are prerequisites for the application of Solvent Swing Adsorption. Dowex Optipore L-493 was selected as adsorbent material for the Solvent Swing Adsorption process because the absence of functional groups on its internal surface ensures complete reversibility of the adsorption. The intraparticle diffusion coefficient of acrylonitrile in the Dowex Optipore particles (diameter: 0.8 mm) was experimentally determined and it was found to be larger than 4.6×10⁻¹⁰ m²/s at 20°C which is very high compared to other adsorbent materials (e.g. activated carbon). This allows running adsorption columns at a high superficial velocity of the feed which is desirable for industrial processes.

Solvents with a high affinity for acrylonitrile were found by combining computer aided molecular design with lab experiments. Acetone was eventually selected as desorption solvent for the adsorption-desorption process because of its high affinity for acrylonitrile, its miscibility with water, its low boiling point, and its good environment, health and safety properties.

In order to determine the adsorption equilibrium of acrylonitrile onto Dowex Optipore, solutions of 100-50,000 ppm acrylonitrile in water/acetone mixtures where mixed with the adsorbent and shaken in flasks during 8 hours at 25°C. It was shown in preliminary experiments that the adsorption equilibrium was reached after less than 1 hour. The acrylonitrile concentration in the liquid was measured and the adsorbed amount was calculated using a mass balance. Fig.1 (dots) shows the results of these batch experiments. It is clear that the adsorbed amount is strongly dependent on the acetone fraction in the solvent which is desirable for the process.

Figure 1: Concentration based adsorption isotherms of acrylonitrile onto Dowex Optipore L-493 for solvents with different acetone volume fractions. Experimental (dots) and calculated by use of activity based isotherms as explained below (lines).

A correct description of the adsorption isotherms is required for the design and the dimensioning of the Solvent Swing Adsorption column. The description of the equilibrium with only one equation which is applicable for all solvent compositions is preferable. Since the adsorbed amount of acrylonitrile onto Dowex Optipore depends on the water/acetone ratio of the solvent, the equilibrium cannot be described with a conventional isotherm based on the acrylonitrile concentration in the solution. Therefore, instead of describing the adsorbed amount as a function of the equilibrium concentration, the loading was described as a function of the acrylonitrile activity in the solution. For this purpose the activity of acrylonitrile in the solution was calculated by use of UNIFAC. The calculation is based on the functional groups of which the three molecules present in the liquid mixture consist. The UNIFAC model uses group specifications and group-group interaction parameters which can be found in literature\(^1,2\). For the range of solution compositions which can appear in the bulk solution of the adsorber, the activity of acrylonitrile was described as a function of the mol fractions of acetone and acrylonitrile. Fig. 2 shows the activity of acrylonitrile estimated by use of UNIFAC. The low activity at high acetone concentrations leads to small adsorbed amounts for acetone rich solvents.

For each experimentally determined data point of the isotherms shown in Fig. 1, the activity of acrylonitrile in the solution was found by use of Fig. 2. The activity based isotherms are shown in Fig. 3. It can be seen that for water/acetone solvents with 10-100v% acetone the adsorbed amount of acrylonitrile at a certain activity is always the same no matter which is the water/acetone ratio of the solution. The acrylonitrile adsorption for all solution compositions can therefore be described by use of one common activity based Freundlich isotherm which is given by Eq. (1) and shown in Fig. 3. The equation was fitted to the data points given in Fig. 3 by adjusting the parameters \(k_F\) and \(n\).

Figure 2: Acrylonitrile activity as a function of acetone and acrylonitrile mol fractions

Figure 3: Activity based adsorption isotherms of acrylonitrile onto Dowex Optipore L-493 for solvents with different acetone volume fractions

\[ q = k_F \cdot a^n \]  

\( q \)  
equilibrium adsorbed amount of acrylonitrile, mg/g

\( k_F \)  
Freundlich parameter, mg/g (\( k_F = 725.4 \text{ mg/g} \))

\( n \)  
Freundlich parameter, 1 (\( n = 0.783 \))

\( a \)  
acrylonitrile activity in the solution, mol/mol_{tot}

The Freundlich isotherm in Fig. 3 can be converted into ten different concentration based isotherms which are shown in Fig. 1 (lines). In order to convert the single activity based isotherm into ten conventional concentration based isotherms, for each acetone fraction the activity of AN is converted into a concentration by use of Fig. 2. It can be seen that the model describes with good accuracy the whole range between 10v% and 100v% acetone.

These findings indicate that at solvent compositions of 10-100v% acetone in water the acrylonitrile loading is mainly controlled by its non-ideal behavior in the solution and not by competition with adsorption of acetone and water molecules in the adsorbed phase.

A fast intraparticle mass transfer of acrylonitrile in the sorbent particle and a high affinity of the solvent for acrylonitrile are requirements for an efficient Solvent Swing Adsorption process. By selecting Dowex Optipore L-493 as an adsorbent and acetone as a solvent these requirements are fulfilled. The activity based acrylonitrile isotherm together with the UNIFAC-based calculation of the acrylonitrile activity in the solution enables us to describe the acrylonitrile concentration in the adsorber as a function of time and position in the column. By use of these relations the dimensions of the Solvent Swing Adsorption column and the operating parameter can be optimized in order to minimize the acetone stream and therefore the energy consumption of the separation of acrylonitrile from water.

References:


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