Herbicide Extraction using Polymer Inclusion Membranes for Environmental Applications.

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The removal of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) and its derivative 2,4-dichlorophenol from environmental water samples by Polymer Inclusion Membranes incorporating Aliquat 336 (mixture of quaternary ammonium chlorides) as both plasticiser and ion carrier was investigated.

Membranes were prepared using various polymers including; polyvinyl chloride (PVC), cellulose acetate and cellulose triacetate with polymer content ranging from 70 – 30 wt.% and Aliquat 336 content ranging from 30 – 70 wt.%. PVC membranes were also prepared with reduced amounts of Aliquat 336 and incorporating dibutyl phthalate, nitrophenyl octyl ether or dioctyl sebacate at 20 wt.% as an alternative plasticiser. The favoured composition for 2,4-D extraction and membrane stability was 60 wt.% PVC and 40 wt.% Aliquat 336. This formulation was used to determine the equilibrium extraction constant, in extraction and stripping experiments and in microsphere production (yield 68%) for comparison with TEVA resin, a commercially available product.

Above pH 5, 2,4-D is de-protonated and extracted via an ion exchange mechanism with the chloride ion of Aliquat 336 shown in figure 1.

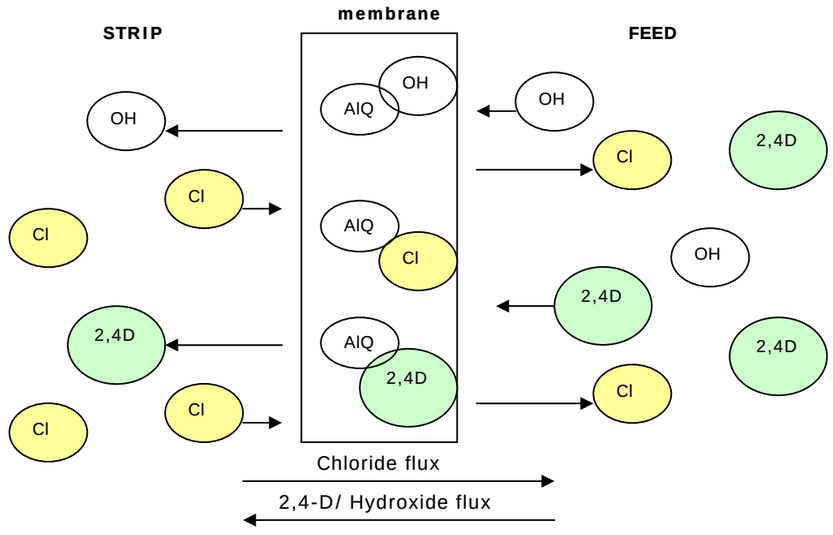

Figure 1. Schematic of 2,4-D, chloride and hydroxide counter coupled transport. OH = hydroxide, 2,4D =2,4-Dichlorophenoxyacetic acid anion, Cl = chloride, AlQ = Aliquat cation.

Under alkaline conditions, hydroxide ions are co-extracted with the 2,4-D anion, and at high alkalinity (0.1 M NaOH) a Hoffmann rearrangement caused decomposition of the quaternary amines of Aliquat 336 as shown in figure 2.

The co-extraction and subsequent decomposition of Aliquat affected the performance of the membranes, microspheres and TEVA resin. The performance of polymer microspheres prepared from PVC and Aliquat 336 was severely limited by the aqueous production technique, as Aliquat was found to leach into solution. Production of the polymer microspheres used large volumes of water, and caused a decrease in expected microsphere extraction efficiency by 30%.

Polymer Inclusion Membrane performance can be enhanced when extraction occurs at a low to neutral pH, thereby limiting the co-extraction of hydroxide ions and subsequent Hoffmann rearrangement. However, the pH must also take into account the pKa or dissociation constant of the analyte.

Thus, the optimal pH to ensure complete de-protonation of 2,4-D and ensure the stability of the membrane is to utilize a pH between 5 - 5.5.

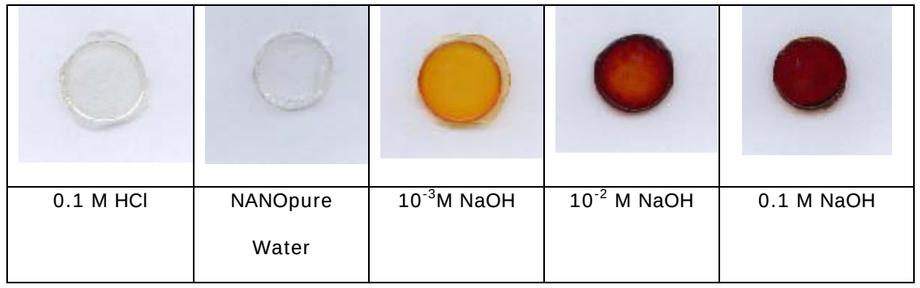

Figure 2. PVC:Aliquat membrane discolouration due to a likely Hoffmann rearrangement of Aliquat 336 under alkaline conditions.