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COMMONS DEED

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COMBINED ION EXCHANGE AND MICROFILTRATION

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ABSTRACT

The purpose behind this work is to produce polystyrene-divinylbenzene cation exchange resin particles at various sizes, smaller than are conventionally available, and to use them in a microfiltration process; comparing the results with conventional column operation. As a model system, for production of droplets using membrane emulsification, sunflower oil (discontinuous phase) and 2% Tween 20 solution (continuous phase) were used. By increasing the shear at the membrane surface the droplet size decreased from 185 to 50 μm . In the seeded microfiltration process, surface microfilters with slots without internal tortuosity were used to minimize fouling. A filtration flux rate of 3432 $\text{l m}^{-2} \text{h}^{-1}$ was achieved. Rates of copper sorption on to ion exchange resin were found to be dependent on mass transport limitations due to aqueous film diffusion and internal particle diffusion. For prediction of copper sorption a model that takes into account both film and internal diffusion was used. Microfiltration combined with ion exchange has the advantage of very fast kinetics, when compared to column use, and may provide better utilization of the resin particle, depending on the internal diffusion coefficient of the transferring species within the particle.

INTRODUCTION

The research is focussed on heavy metal cations present in wastewaters from different industries including nuclear power plants, including: cesium (Cs^+), strontium (Sr^{2+}), and copper (Cu^{2+}). One of the methods for removing heavy metals from wastewaters is treatment in ion exchange columns. Columns with standard ion exchange resins have to fulfil the requirement that pressure drop within the column is low so the beads used in columns are usually large (greater than 200 μm). There is a need that fine filtration, performed before the column, to ensure that material will not deposit on the particles. The easiest way to progress metal removal is to reduce the size of particles, but smaller particles lead to high pressure drops, which is not practical in column use.

As Holdich et. al. reported (2006), decreasing the ion exchange bead diameter increased the ion exchange utilization. They investigated boron removal from water during seeded microfiltration (a hybrid process which combines microfiltration together with ion exchange) and determined that at large particle sizes the resin was poorly utilized as only the layers close to the surface took significant concentrations of boron. At the small sizes the resin was better utilized, as the diffusion gradient within the resin bead was steeper and boron was more easily transported to the bead centre. They concluded that smaller bead sizes would increase the time before breakthrough and would provide better overall performance, but that small sizes may provide handling difficulties. So the beads

should be neither too small, nor too large, and a size of 50 – 60 μm was reported as a good size.

Small beads may be produced by crushing conventional ion exchange beads, but crushing has two main problems:

- When crushed they have wide size distribution, and irregular shape,
- Because of the wide size distribution they will need to be separated into different fractions, this is time consuming and does not ensure optimal performance.

The project will make the ion exchange resin particles at the required sizes and use them in a microfiltration system. In such a system mass transfer is much faster and, once the transfer coefficients are deduced the modelling will compare the results with column use. Microfiltration combined with ion exchanger may have several potential applications, e.g. adding ion exchange resin to a system containing activity in both water and solid phases it is possible to filter the water and suspended solids through the bed of resin resulting in a significantly decontaminated stream.

EXPERIMENTAL

For production of ion exchange beads membrane emulsification will be used, and for the preliminary tests sunflower oil was used to commission the system. Conventional ion exchange resin was used (Dowex 50WX8) for removal of copper ions

as a test model in the initial seeded microfiltration work.

Emulsification used a Micropore Technologies Ltd. Dispersion Cell, see Figure 1. This device uses a 24 V DC motor to drive a paddle-blade stirrer, above the membrane surface (Figure 1). A membrane with a 10 μm pore size was used. The dispersed phase (sunflower oil) was injected through the membrane pores into the aqueous continuous phase. On Figure 1, for the membrane emulsification follow the light grey (or yellow) lines.

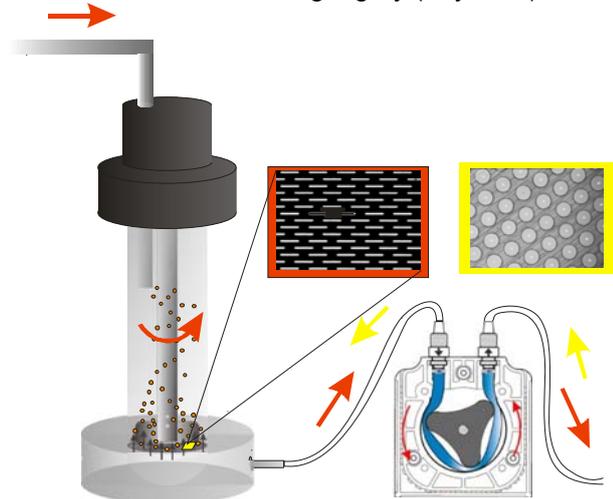


Figure 1. Equipment used for production of droplets (light grey arrows and membrane with circular pores) and also for microfiltration (dark grey arrows and slotted membrane)

For the ion exchange studies, all reagents used were analytical grade chemicals. Solutions of copper ions with concentration between 1 and 100 ppm were made by dissolving appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, UK) in distilled water. The ion exchange resin was Dowex 50WX8 (strong acid cation resin containing 8% divinylbenzene) 100-200 obtained from Sigma Aldrich. The mean size and size distribution of Dowex 50WX8 100-200 was determined by laser diffraction particle size analyzer (LA-920, HORIBA). The mean size was 240 μm (Figure 2).

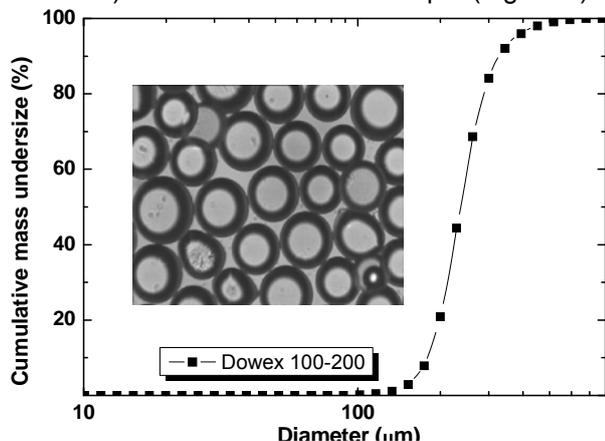


Figure 2. Cumulative distribution curve for Dowex 50WX8 100-200

Analysis of copper was performed using an Atomic Absorbance Spectrophotometer (Spectra AA-200

Varian, UK). For microfiltration copper solutions with concentrations between 1 and 100 ppm were prepared. Mass of ion exchanger used was 0.1 or 1g. All microfiltration experiments were performed in the glass cell provided by Micropore Technology Ltd. UK, Figure 1.

During all experiments a volume of 150ml was maintained in the cell. A slotted nickel membrane was fitted on the bottom of the glass cell. The membrane diameter was 3.2 cm and the working area was $8.4 \times 10^{-4} \text{ m}^2$. Fresh copper containing solution flowed into the cell (Influent) at the same rate as permeate was withdrawn from the cell (effluent). A peristaltic pump was used to induce the flow. At start-up, the cell was filled with distilled water and known mass of resin was added. A flow rate of 46 ml min^{-1} ($3432 \text{ lm}^{-2}\text{h}^{-1}$) was set. At predetermined times 10 ml of effluent sample was collected and analyzed. If no ion exchange resin was used in the cell the system acts as a CSTR (continuous stirred tank reactor) and can be modelled as such.

MODELLING

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A mass balance for a well mixed system for copper can be expressed as below:

$$V \frac{dC}{dt} = F(C_o - C) - m \frac{d\bar{q}}{dt} \quad (1)$$

where V is the liquid volume in the cell, C is the concentration in the solution (both in the cell and the exit), C_o is the concentration in the feed to the cell, F is the feed flow rate, m is the mass of the resin in the cell and \bar{q} is the average mass of copper per mass of resin. The average mass of copper per mass of resin can be obtained by integrating the local mass throughout the resin form $r=0$ to $r=R$

$$\bar{q}(t) = \frac{3}{R^3} \int_0^R q(r,t) r^2 dr \quad (2)$$

where R is bead radius and the diffusion equation for mass transfer inside the particle is

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (D_{\text{eff}} r^2 \frac{\partial q}{\partial r}) \quad (3)$$

where r is radial position inside the particle and D_{eff} is effective diffusion coefficient of cation inside the particle. The mass rate of cation entering the particle is

$$m \frac{d\bar{q}}{dt} = kA(C - C^*) \quad (4)$$

where A is the surface area of the resin bead, C^* is the equilibrium concentration of cation at the surface of the resin and k is the mass transfer

coefficient in the liquid phase. According to film theory

$$k = \frac{D_{liq}}{\delta} \quad (5)$$

where D_{liq} is the diffusion coefficient of cation in liquid phase and δ is the film thickness (distance over which the liquid phase diffusion takes place). Frossling equation is used to evaluate k , using Sherwood, Particle Reynolds and Schmidt dimensionless numbers

$$Sh = 2 + 0.6 Re_{slip}^{0.5} Sc^{0.33} \quad (6)$$

$$Sh = \frac{k \cdot 2R}{D_{liq}} \quad Sc = \frac{\mu}{D_{liq} \rho} \quad Re_{slip} = \frac{v_{slip} 2R \rho}{\mu}$$

where μ is the dynamic liquid viscosity and ρ is liquid density. Terminal velocity is depending on particle size and for small particles when Particle Reynolds number is smaller than 0.2, terminal velocity may be calculated by Stokes law:

$$v_{slip} = \frac{g(2R)^2(\rho_s - \rho)}{18\mu} \quad (7)$$

If Particle Reynolds number is larger than 0.2 various correlations can be used (Holdich 2002). For mass transfer coefficient combination of Frossling equation together with Sherwood dimensionless number can be used. Rearranging the isotherm equilibrium concentration of cation at the surface of the particle can be expressed:

$$C^* = \frac{q|_{r=R}}{b(q_m - q|_{r=R})} \quad (8)$$

The cation exchange resin has a spherical shape, and using specific surface area of a sphere, surface area can be expressed as following:

$$\rho_s = \frac{m}{V_{resin}} = \frac{6m}{Ax} \Rightarrow A = \frac{6m}{\rho_s x} \quad (8)$$

V_{resin} is resin particle volume, ρ_s is density of the particle, A is surface area and x is diameter of the resin bead. Flux of the cation inside of the resin can be expressed as follows:

$$kA(C - C^*) = m \frac{dq}{dt} = A \rho_s D_{eff} \frac{\partial q}{\partial r} \Big|_{r=R} \Rightarrow m \frac{dq}{dt} = \frac{3}{R} m D_{eff} \frac{\partial q}{\partial r} \Big|_{r=R}$$

So the mass balance of the cation is:

$$V \frac{dC}{dt} = F(C_o - C) - \frac{3}{R} m D_{eff} \frac{\partial q}{\partial r} \Big|_{r=R} \quad (10)$$

For solving of differential equations boundary conditions have to be determined. At the start cell has fresh liquid:

$$q(t=0, 0 \leq r \leq R) = 0 \quad C(t=0) = 0$$

In the centre of the bead there is no cation at the centre ($r=0$).

$$\frac{\partial q(t \geq 0)}{\partial r} \Big|_{r=0} = 0 \quad (11)$$

And for the full radius of the bead ($r=R$) boundary condition is

$$\frac{\partial q(t \geq 0)}{\partial r} \Big|_{r=R} = \frac{k}{D_{eff} \rho_s} (C - C^*) \quad (12)$$

The system of equations must be solved simultaneously in an equation solver capable of solving partial differential equations, PDESOL (Numerica, Dallas, USA) was used. As a start, for model data the following were taken from Awang (2001).

Table 1 Data necessary for modelling of mass transfer during microfiltration with Dowex 50W8X 100 ion exchanger

q_m (mg mg ⁻¹)	b (m ³ g ⁻¹)	D_{liq} (m ² s ⁻¹)	D_{eff} (m ² s ⁻¹)
120.48	13.365	$7 \cdot 10^{-10}$	$7.2 \cdot 10^{-13}$

RESULTS AND DISCUSION

membrane emulsification

As a model system for production of droplets sunflower oil and 2% Tween 20 solution was used. Figure 3 shows the influence of paddle stirrer rotation speed (i.e. shear) on droplet size. From the figure it can be seen that increasing the rotation speed decreases the droplet size from 185 μ m down to 50 μ m. Also shown on Figure 3 are a few microscopic photographs of emulsions at different rotation speeds.

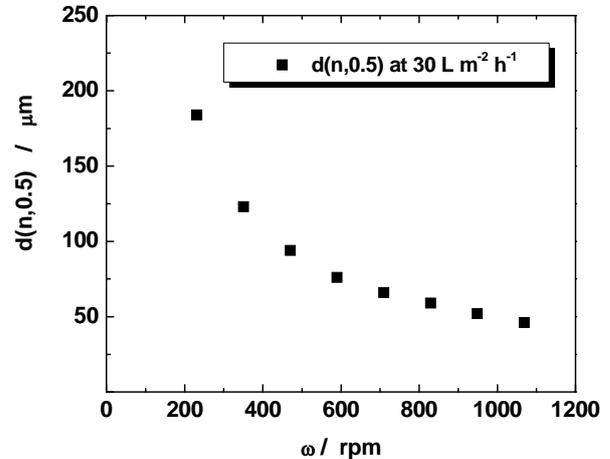
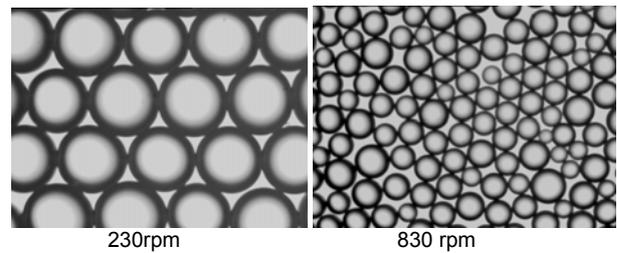


Figure 3. Influence of rotation speed on droplet size.

combined ix and microfiltration

Starting copper concentration in the feed solution was 1.2ppm when 0.1g of ion exchange resin was used and 1.5ppm when 1g of ion exchange resin was used. Experiments lasted for 5000 s. For both masses of resin the experiment was repeated and results are presented in Figure 4. As can be seen even after 5000 s, for both masses (0.1 and 1g), the resin was not saturated: an approximately constant effluent concentration was reached which did not correspond to the inlet concentration (C_0). Using the previously described model it was determined that it would take 2.5 days to reach the inlet concentration and a few characteristic parts on the modelled curves were deduced (Figure 4 **A**, **B** **C** and **D**).

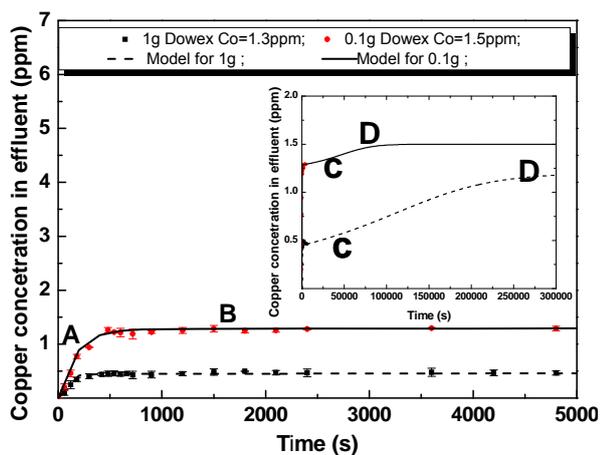


Figure 4. Different mass of ion exchanger.

From the Figure 4, it can be seen that the increase of copper concentration in the effluent is very quick at the start, and after that it reaches a constant value (**A-B**). In order to test the full capabilities of the resin the concentration of influent was increased to 100 ppm (Figure 5). It can be seen that the curve has the expected regions (**A**, **B** **C** and **D**). These are explained as follows. Region **A** indicates a quick increase in effluent concentration and is the period when the aqueous film concentration gradient develops, hence all the mass transfer resistance is in the aqueous film.

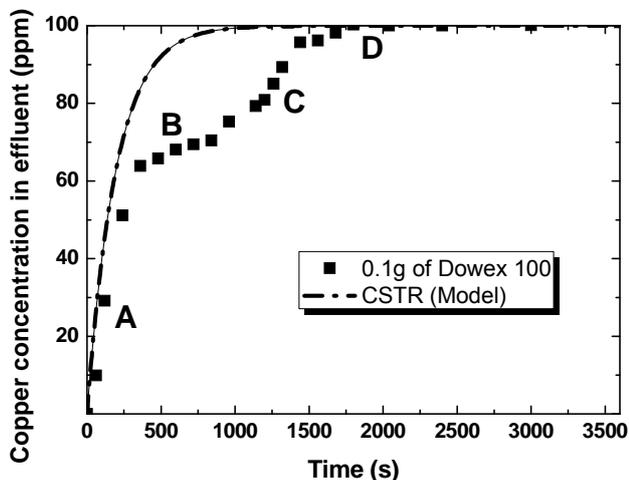


Figure 5. Different mass of ion exchanger.

When a suitable concentration gradient is achieved and the resin has good internal diffusivity copper is easily transferred internally (region **B**). Internal transfer of copper will continue until resin resistance to mass transfer increases when copper concentration in the resin becomes high (region **C**), but at some point the resin will become saturated (region **D**).

CONCLUSIONS

As a model system for production of droplets sunflower oil was injected in to 2% Tween 20 solution and droplets in the size range between 184 and 50 μm were produced. Malik, et al. (2009) reported recently that it is possible to produce crosslinked polystyrene co-divinylbenzene adsorbent microspheres with median diameter between 40 and 300 μm in a similar device, and this will be used for future production of the ion exchange resin beads.

In the seeded microfiltration process, surface microfilters with slots without tortuosity were used to minimize internal fouling. By using seeded microfiltration a high filtrate flux rate 3432 $\text{l m}^{-2} \text{h}^{-1}$ was achieved. Rates of copper sorption on to ion exchange resin were found to be dependent on mass transport limitations, due to aqueous film diffusion and internal diffusion and a model suitable for its analysis (and column prediction) was tested. Seeded microfiltration (microfiltration combined with ion exchange) may have several potential engineering applications, and may become a useful laboratory technique for transport property evaluation of resin particles and systems.

REFERENCES

- AWANG, A.R.B., 2001. Seeded microfiltration of copper with modified activated carbon, PhD Thesis, Loughborough University.
- HOLDICH, R.G., 2002. Fundamentals of particle technology. MidlandIT, Shephed, UK.
- HOLDICH R.G., CUMMING I.W., PERNI S., 2006. Boron mass transfer during seeded microfiltration. *Chemical Engineering Research and Design*, **84**(1), pp. 60-68.
- MALIK, D., WEBB, C., HOLDICH, R., RAMSDEN, J., WARWICK, G., ROCHE, I., WILLIAMS, D., TROCHIMCZUK, A., DALE, J. and HOENICH, N., 2009. Synthesis and characterization of size-selective nanoporous polymeric adsorbents for blood purification. *Separation and Purification Technology*, **66**, pp. 558-585.