

Combined microfiltration and ion exchange

M.M. Dragosavac, R.G. Holdich and G.T. Vladislavljević
 Department of Chemical Engineering, Loughborough University, Loughborough
 (correspondence: r.g.holdich@lboro.ac.uk)

ABSTRACT

This research work was based on development of the technique for the determining the mass transfer properties as well as equilibrium parameters using a stirred cell. The experimental work was performed in a continuous flow stirred cell that had a slotted (8 $\mu\text{m} \times 400 \mu\text{m}$) metal microfiltration membrane fitted to the bottom of the cell. As a test system adsorption of copper ions on the polystyrene di-vinylbenzene Dowex 50W-X8 resins was studied. The equilibrium parameters for a Langmuir isotherm ($q_m=0.116 \text{ g g}^{-1}$, $b=0.003 \text{ m}^3 \text{ g}^{-1}$) were determined from both batch and the continuous flow experiments and good agreement between the two different approaches was obtained. Experiments were performed at constant pH (4.5) and ionic strength (0.2M) at feed concentrations up to 636 ppm. The filtration flux was 582 litres per square metre of membrane area per hour. Increase of the ionic strength decreased the amount of sorbed copper significantly. The limiting step for the overall process of copper sorption was internal particle diffusion. The effective diffusion coefficient of copper inside the particle was found to be $7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. Once determined, the design parameters can readily be used to model ion exchange contacting in well mixed and column operations. Further work is planned on the characterisation of the copper hydroxidacetate as a novel material for iodide removal as well as some inorganic materials for removal of strontium and caesium.

INTRODUCTION

In this work Dowex 50W-X8 resin is investigated as a sorbent material for continuous copper removal in a continuous flow stirred cell with a submerged slotted pore MF membrane¹ ("seeded MF"). This research aims at determining the equilibrium constants beside the mass transport properties

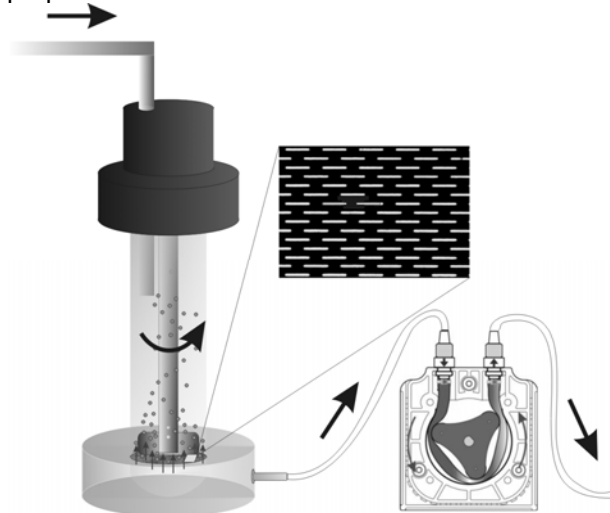


Figure 1 Diagram of seeded microfiltration system and micrograph of the slotted pore membrane used in this work

(aqueous film coefficient and internal diffusion coefficient) just by using a continuous flow stirred cell (Figure 1); introducing a new technique to determine the isotherm data without the need for separate batch tests.

Initial studies have concentrated on developing the experimental, modelling and analytical techniques. The effect of initial solute concentration and ionic strength on copper removal was also investigated. In order to predict the behaviour of the seeded MF process, a conventional mass transfer model was applied based on mass transfer resistance within the aqueous film surrounding the particles together with diffusional resistance within the particle. However, the analysis was coupled with a material balance to account for the continuous nature of the process.

By starting with a zero concentration of dissolved species within the microfilter cell, and then feeding in at the same rate as filtrate leaves the cell, it is possible to compare the rate at which the solute concentration increases within the cell with: a Continuous Stirred Tank model (CST), which is applicable when no ion exchange medium is present, and a coupled model for mass transfer using aqueous film diffusion and internal particle

diffusion – together with a Langmuir isotherm for equilibrium.

This experimental approach is very sensitive to elucidating the mass transfer parameters: a small error in any of them results in a significant divergence between measured and predicted, solute transfer with respect to time. Furthermore, only small masses of ion exchange medium are required, typically less than 1 gram. The initial studies used copper, extracted using Dowex 50W-X8 resin with Sauter mean radii of 87 and 42 μm in separate studies, Figure 2.

Experiments were performed at pH 4.5 and ionic strength 0.2M while the inlet copper concentration varied from 19 to 636 ppm. Increasing the ionic strength from 0 to 0.2M decreased the amount of adsorbed copper. The limiting step for the copper adsorption was internal particle diffusion. The effective diffusion coefficient of copper inside the particle was found to be $7 \times 10^{-11} \text{m}^2 \text{s}^{-1}$, and the influence of ionic strength was found to be very significant on both the kinetics and equilibrium data. This paper provides data and details from the initial studies.

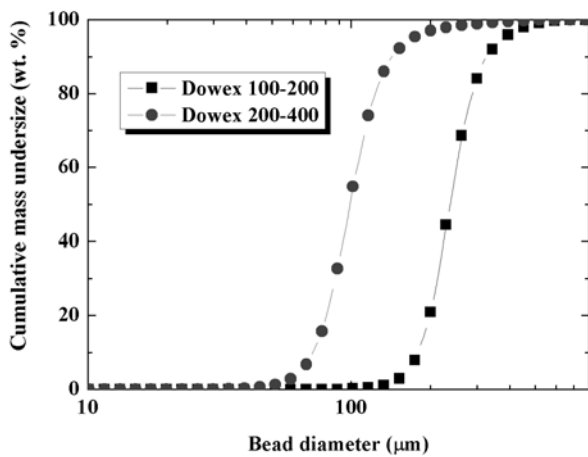


Figure 2 Particle size distribution of Dowex 50W-X8 resin used in this work

KINETIC MODELLING OF ION TRANSFER

Mass transfer in seeded microfiltration is much faster compared with that obtained in fixed bed ion exchange columns², which makes it useful in laboratory experiments for estimating the mass transfer coefficient and intraparticle diffusivity. The following assumptions are made in modelling: isothermal operation, rapid chemical reaction of binding the copper to ion exchanger, adsorption equilibrium described by the Langmuir isotherm, ideal mixing in the system with continuous flow, mass transfer of copper through external aqueous phase film by film diffusion and through pores represented by a single internal diffusion coefficient.

The mass balance of copper for adsorption in a well-mixed continuous flow stirred cell can be expressed as follows:

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

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

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

where R is the Sauter mean radius of the resin particles and r is the radial distance from the centre of particle. Fick's second law for diffusion of copper inside a spherical particle is given by:

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

where D_{eff} is the effective diffusion coefficient of copper inside the particle. The total mass of copper entering the solid phase per unit time is

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

where A is the total surface area of the resin particles, C_e is the equilibrium concentration of copper in the liquid phase at the interface and k is the mass transfer coefficient in the liquid phase. According to the film theory³

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

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

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

$$Sh = \frac{k2R}{D_{liq}} \quad Sc = \frac{\mu}{D_{liq}\rho} \quad Re_{slip} = \frac{v_{slip} 2R\rho}{\mu} \quad (7)$$

where μ is the liquid dynamic viscosity, ρ is the liquid density and v_{slip} is the relative particle-liquid velocity (slip velocity). We have assumed in our modelling that v_{slip} was equal to the terminal particle velocity, due to relatively low agitation speed in the cell. The concentration of copper in the liquid phase at the interface can be found from Langmuir isotherm by assuming that at the interface the liquid phase is in equilibrium with the surface layer of the solid phase:

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

The total surface area of the resin particles, A can be expressed in the terms of the Sauter mean radius:

$$A = \frac{3m}{\rho_s R} \quad (9)$$

Therefore, the mass rate of copper entering the particle is given by:

$$m \frac{d\bar{q}}{dt} = A \rho_s D_{eff} \left. \frac{\partial q}{\partial r} \right|_{r=R} = \frac{3}{R} m D_{eff} \left. \frac{\partial q}{\partial r} \right|_{r=R}$$

and hence, Eq. (1) can be rewritten as:

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

For solving the differential equation (10) the boundary conditions have to be specified. At the beginning of the process, there is no copper in the liquid phase inside the cell:

$$q(t=0, 0 \leq r \leq R) = 0 \quad C(t=0) = 0 \quad (11)$$

The concentration gradient is zero in the centre of the bead ($r=0$):

$$\left. \frac{\partial q(t \geq 0)}{\partial r} \right|_{r=0} = 0 \quad (12)$$

and for the full radius of the beads ($r=R$) the boundary condition is

$$\left. \frac{\partial q(t \geq 0)}{\partial r} \right|_{r=R} = \frac{k}{D_{eff} \rho_s} (C - C_e) \quad (13)$$

The system of equations (3) and (10) subject to boundary conditions (11), (12), and (13) must be solved simultaneously in an equation solver capable of solving partial differential equations.

For this purpose, PDESOL (Numerica, Dallas, USA) was used in this work. Constants used in modelling are: $q_m=0.116 \text{ kg kg}^{-1}$, $b=3 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}$, $m=10^{-3} \text{ kg}$, $F=1.3 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$, $V=0.14 \times 10^{-3} \text{ m}^3$, $\mu=0.001 \text{ Pa s}$, $\rho_s=1443 \text{ kg m}^{-3}$, $\rho=1000 \text{ kg m}^{-3}$ and $D_{iq}=1.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

DISCUSSION AND CONCLUSIONS

Figure 3 illustrates the Langmuir isotherm on the Dowex material. The data was acquired in the conventional way: shaking flasks for several weeks. The equilibrium parameters obtained for the Langmuir isotherm are $q_m=0.116 \text{ g g}^{-1}$ and $b=0.003 \text{ m}^3 \text{ g}^{-1}$. In Figure 4 data is shown that is used to obtain the isotherm by some simple experiments, performed over 3 hours, as an alternative to the conventional isotherm technique. The copper concentration in the effluent from the microfiltration cell, Figure 1, was monitored with time and the shaded region between the CST curve and the CST+resin curve represents the

amount of copper adsorbing onto the resin. Hence, the mass of copper on the resin at its point of saturation is determined. This is termed the 'Stirred cell experiments and is compared in Figure 5 with the conventionally determined isotherm.

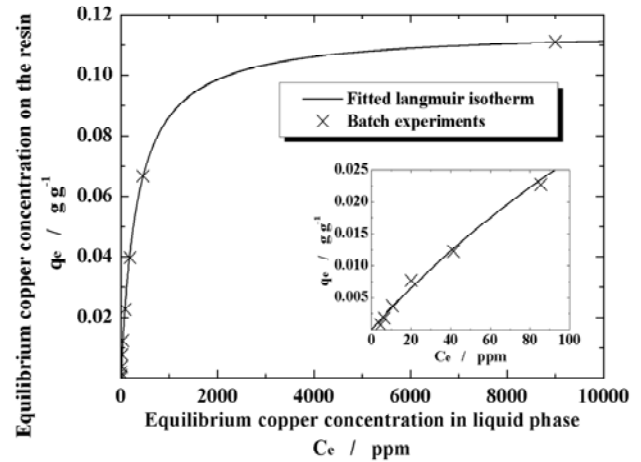


Figure 3 Langmuir isotherm for copper adsorption on Dowex 50W-X8 determined by batch experiments. The inset represents the Langmuir isotherm at copper concentrations in the liquid phase below 100 ppm.

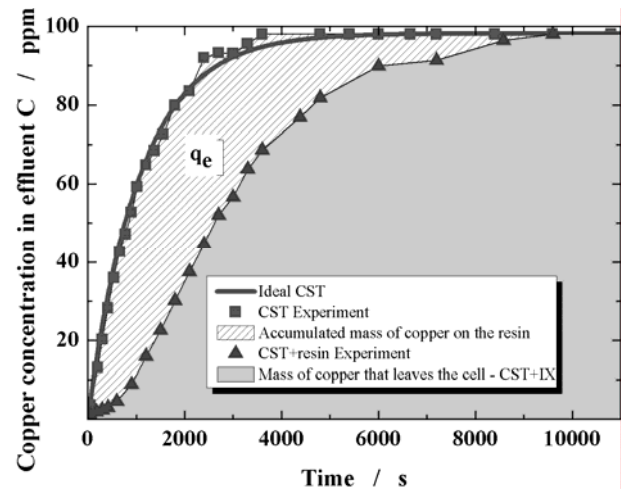


Figure 4 Graphical explanation for calculating the amount of adsorbed copper q_e on the resin

For the tests at a controlled ionic strength, the fit is excellent. The only data point adrift from the conventional isotherm curve is one in which the ionic strength was not controlled: labelled no NaNO_3 in the cell. The same experiments used to determine the isotherm data are also used to determine the mass transfer modelling parameters. An example of the copper concentration in the effluent, for four different inlet feed concentrations, is shown in Figure 6. The markers show the measured points, obtained by atomic absorption analysis, and the continuous curves are the model, obtained by solving equations 3 and 10, using a single and constant empirically derived diffusion coefficient within the resin particle. The model that was used had only the effective diffusivity for describing the adsorption although it can be split into diffusion through macro pores and diffusion through micropores^{4,5}. The effective diffusion

coefficient of copper inside the particle, D_{eff} that gave the best fit of experimental results was $7 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. This is a constant value irrespective of resin size, feed concentration and liquid throughput. Hence, the technique appears to be a robust method for determining the transport properties during ion exchange.

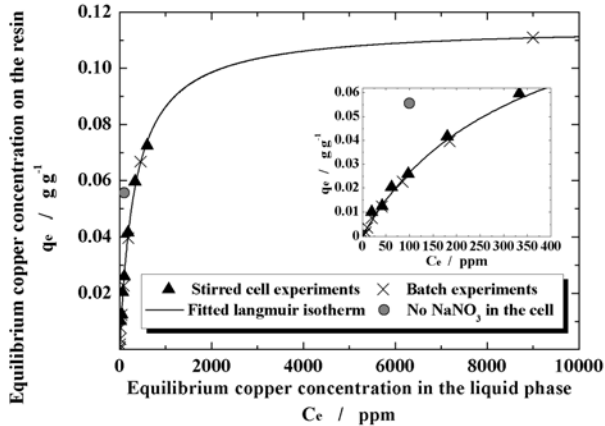


Figure 5 Comparison of the Langmuir isotherm obtained from the batch and the continuous experiments

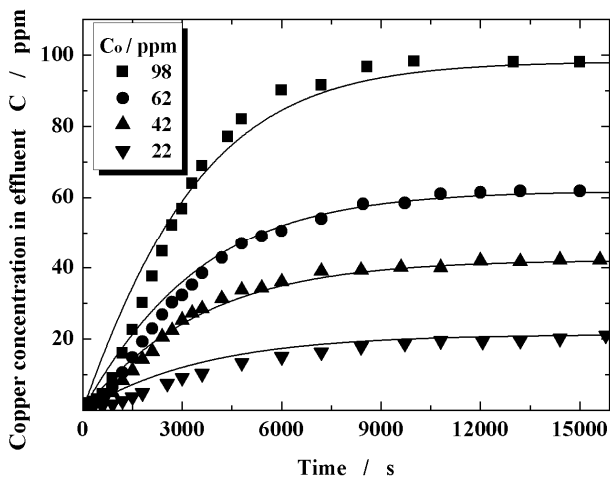


Figure 6 Influence of inlet copper concentration (22–98) on the effluent, small beads (84 µm)

The modelling can also be used for process scale-up; for both conventional column use and possible process scale seeded IX microfiltration, where the resin may be contacted in a crossflow microfiltration system using a similar slotted filter to that shown in Figure 1. This would allow finely divide particulate matter to pass through the filter, whilst retaining the active ion exchange material. Ionic strength was found to have a major influence on the ion exchange, see Figure 7, where copper concentration is plotted as a function of time during identical tests at different ionic strength. Sodium sorption on the resin was tested, and found to be negligible, hence it is concluded that the results are due to changes in the activity coefficient of the copper caused by alterations in ionic strength, which influences the isotherm considerably and, hence, the extraction kinetics.

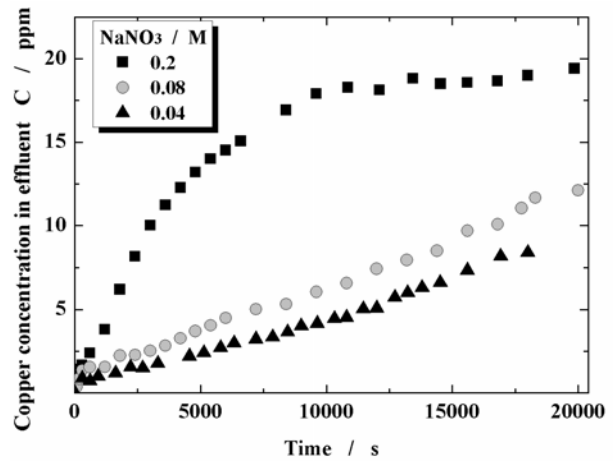


Figure 7 Influence of ionic strength on copper adsorption on to Dowex 50W-X8. Inlet copper concentration in all experiments was 20 ppm

This is reflected in both the modelling and the experimental data. Hence, robust modelling requires constant ionic strength.

Equilibrium and mass transfer parameters obtained with the stirred cell were used to model the work of the column. Column was divided into 11 sections and each section was modelled (Equ. 1-10) as the stirred cell. Figure 8 presents experimental results as well as model. The model gave a very good fit of the breakthrough curve.

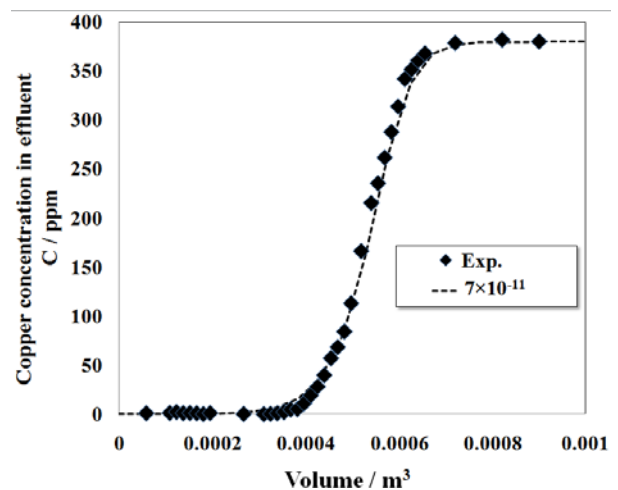


Figure 8 Cu(II) removal and corresponding effluent. Model – dashed curve. Conditions: pH of influent solution 4.5; inlet copper concentration $C_0=380$ ppm; flow rate $4.3 \times 10^{-5} \text{ m}^3 \text{ h}^{-1}$. Column IDxL=1x10cm.

Continuous stirred cell represents an effective laboratory technique for determining both equilibrium and mass transfer parameters. After having achieved the mass transfer and equilibrium data, it is possible to use the same mathematical model to predict the performance of a seeded microfiltration process using larger volumes of liquid, filter area, etc. to enable the design of a combined ion exchange and microfiltration process, or other types of contactors.

Further work is planned on the characterisation of the copper hydroxidacetate as a novel material for

iodide removal as well as some inorganic materials for removal of strontium and caesium.

REFERENCES

- 1 Holdich, R. G.; Cumming, I. W.; Kosvintsev, S.; Bromley, A. J.; Stefanini, G., Clarification by slotted surface microfilters, *Minerals Eng.*, **2003**, 16, 121-128.
- 2 Holdich R.G., Cumming I.W., Perni S., Boron mass transfer during seeded microfiltration, *Chem. Eng. Res. Design*, **2006**, 84, 60-68.
- 3 Helfferich, F. G., Ion exchange, Courier Dover Publications, **1995**.
- 4 Al Duri, B.; McKay, G.; El Geundi, M. S.; Wahab, M. Z. A., Three-Resistance Transport Model for Dye Adsorption onto Bagasse Pith, *J. Environ. Eng.*, **1990**, 116, 487-502.
- 5 Hall, K.; Eagleton, L.; Acrivos, A.; Vermeulen, T., Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions, *Ind. & Eng. Chem. Fundamentals*, **1966**, 5, 212-223.