Title: Low pressure drop respirator gas filters using adsorbent hollow fibres as an alternative to granular adsorbents

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Abstract

Respirator users experience a physiological burden, one aspect of which is associated with breathing resistance from the filter. The current best practice of gas filters is to provide protection using adsorbent granule filled filters which, as the particle size decreases, have better adsorption kinetics, and hence longer breakthrough times. However this comes at the price of an increasing pressure drop and hence greater breathing resistance. In this paper, adsorbent hollow fibres for use in respirator filters are presented as a potential alternative to the conventional granular cartridges. A comparison of hollow fibre and granular filter modules was carried out using scanning electron microscopy and dynamic ammonia challenge (800 ppm, 1 L/min). In addition the pressure drop was measured at flow rates between 0.5-5 L/min, and using these data, pressure drops at higher flow rates were predicted. The hollow fibres were demonstrated to compare favourably to a granular module of equal volume in terms of pressure drop, adsorption kinetics and breakthrough loading, although improvements still need to be made to hollow fibre breakthrough time, which is slightly lower than an equal volume pellet module as a result of the lower density of the hollow fibre filters. The qualities of hollow fibres will provide several options for novel filter design.

Keywords: *adsorption, hollow fibre, packed cartridge, low pressure drop, ammonia*

Introduction

Respirators are required to provide optimal protection from a wide variety of hazards, but in order to do so they can become increasingly cumbersome to wear. Part of the burden of wearing a respirator is associated with the canister, specifically in terms of its size, weight and the pressure drop of the packed filter. While using smaller adsorbent particles in the respirator filter provides a greater external surface area and shorter diffusion path, thus resulting in greater protection, there will be higher pressure drop as a consequence (Keller, 1995). This will increase

as the breathing rate of the user increases, meaning they will have to work harder to inhale. As a result of the higher pressure drop, it is widely accepted that the user will not be able to complete tasks as efficiently or for as long a duration.

Though cartridges filled with adsorbent particles have been used to provide protection from toxic chemicals for many years, alternatives are desirable in order to address several issues besides that of pressure drop. These include particle attrition, gas bypass and channelling and the need for specialised canister packing equipment. We present hollow fibre adsorbent filters in respirators as a prospective alternative to the conventional granular cartridge. Hollow fibres have the potential to enable the development of lower physiological burden respirator canisters that can be customised to protect from the greatest possible range of hazards. Currently, polysulfone hollow fibres are commonly used as membranes for gas separation (Park and Lee, 2008). To enhance separation, a quantity of adsorbent, such as zeolite, is added to produce a mixed-matrix membrane; however these are generally not specifically used for gas removal by adsorption (Aroon *et al.*, 2010). The adsorbent hollow fibres described in this paper are similar to a mixed-matrix membrane, being composed of a polymer (10-20%), typically polyethersulfone (PES), as a binder for an adsorbent powder, which makes up the remainder of the structure (80-90%). The difference is that as contaminated air passes through the fibres, specific contaminants will be removed and held by the adsorbent within the walls of the hollow fibre. This application of adsorbent hollow fibres was developed at the University of Bath, with the encapsulation of 13X zeolite particles into the walls of a polymer hollow fibre. These fibres were used for adsorption of CO_2, and were found to have a highly porous structure, allowing rapid mass transfer into and out of the encapsulated zeolite within the polymer matrix (Tai, 2007). Since then, adsorbent hollow fibres have also been used to adsorb nitrogen from air to produce enriched oxygen (Nevell and Perera, 2011). The use of adsorbent powder in fibres results in short diffusion pathways and

mass transfer resistances which are low compared to those of larger adsorbent particles (Crittenden and Thomas, 1998). As such they would be well suited for use in a respirator.

Adsorbent hollow fibres are prepared by a phase inversion process, in which the mixed adsorbent/polymer/solvent solution is extruded into water, where it solidifies into fibres as the solvent leaves the structure (Loeb and Sourirajan, 1960). This allows most powdered adsorbents and mixtures thereof to be prepared in the form of hollow fibres, and thus protection can be provided against a diverse range of possible contaminants. Furthermore, the strong thermal and chemical resistance of PES enables further treatments such as chemical impregnation and heating to enhance the adsorption capacity (Solvay, 2011). As a result of their structure, hollow fibres are less dense and hence significantly lighter than an equivalent volume of granules. Long hollow fibre modules can also be prepared in specific shapes, such as curves, potentially allowing greater flexibility in respirator design. An example of a hollow fibre module is shown in Figure 1.

In this paper, several key properties of a hollow fibre filter are compared with an equal volume filter containing pellets. We present details of how the hollow fibres and the equivalent pellets using the same adsorbent were prepared, and characterised them both by scanning electron microscopy (SEM). Both filters were challenged with ammonia, and the breakthrough curves are reported, and from these the mass transfer zone and length of unused bed at breakthrough were calculated and compared. In addition, the pressure drop of hollow fibres was measured and evaluated against that of the same volume of adsorbent pellets.

Materials and Methods

The pellets and hollow fibres were prepared using AbScents 1000 powder purchased from UoP LLC, US, polyethersulfone (PES) 3000P purchased from Solvay, Germany, 1-methyl-

pyrrolidone (NMP) from Sigma-Aldrich, UK, and Wyoming sodium bentonite, purchased from RS Minerals, UK. Ammonia gas used for testing was purchased from BOC, UK.

Preparation of pellets

20 g of Wyoming sodium bentonite powder was thoroughly mixed with 87.9 g of AbScents 1000 powder (80 g dry weight) and 105 g of tap water was added. This was formed into dough and allowed to dry for two days before extruding into 1.2 mm diameter cylinders through a hand press. The cylindrical extrusions were dried at 5 °C for two days and then fired in a kiln. They were heated to 180 °C over 18 hours and then heated to 550 °C over ten minutes and this temperature was maintained for 20 hours. The extrusions were broken into pellets and sieved, keeping what remained between 0.3 mm and 2.8 mm sieves, and then heated to 165 °C to remove water from the adsorbent.

Preparation of hollow fibres

A polymer dope was prepared by mixing 30 g of PES 3000P with 120 g of NMP. This was left to mix fully for 24 hours until a homogeneous, viscous solution was obtained. AbScents 1000 zeolite powder was gradually added until the ratio of polymer to zeolite adsorbent was 1:4, and this was stirred for 36 hours until the solution was uniform. The resultant dope was then forced through a spinneret (2 mm outer diameter) and into a water bath where the polymer/adsorbent coagulated into solid hollow fibres..

Scanning Electron Microscopy

Fibre samples were mounted on a sample tray and gold coated with an Edwards S150B Sputter Coater. Prepared samples were then examined with a JEOL JSM6480LV scanning electron microscope.

Dynamic breakthrough testing

These highly porous adsorbent fibres were closely packed in the test module, at both ends interstitial spaces were sealed with silicone rubber in order to prevent any interstitial gas flow. The test module was arranged so that the axes of the cylinders were parallel to the test gas flow direction. The dimensions of the modules tested were 5 cm long with 2 cm in diameter. These test cartridges were challenged with an 800 ppm concentration (C_0) of ammonia at 1 L/min flow rate (0.6 g/m^3) under ambient temperature and pressure. The outlet concentration (C) was measured and recorded with a Tiger PhoCheck photoionisation detector (PID), and C/C_0 was calculated and plotted against time to produce breakthrough curves. The breakthrough time was taken as the time at which the outlet concentration C reached 25 ppm. Breakthrough and equilibrium loadings were calculated from the graphs, using the adsorbent weight of the material tested (i.e., 80% of the total weight for both hollow fibres and pellets).

Length of unused bed (LUB), i.e., the quantity of the sorbent which is not used for sorption, was calculated using:

$$LUB = \frac{L\,(t_s - t_b)}{t_s} \tag{1}$$

where:

L = length of bed (cm)

t_s= stoichiometric time (hours) = breakthrough time for mass transfer zone of zero length.

t_b = breakthrough time (hours)

Mass transfer zone, i.e., the length of the adsorption front, was calculated using:

$$MTZ = u\,\Delta t \tag{2}$$

where:

$u = \frac{L}{t_s}$ (speed of mass transfer zone, cm/hour).

$\Delta t = t_{eq} - t_b$ (time required for mass transfer zone to travel its own length, hours) (Schweitzer, 1997).

Pressure drop

The pressure drop was measured by subjecting 5 cm long x 2 cm diameter (15.71 cm^3) cylindrical modules that were 1) empty 2) contained a hollow fibre bundle and 3) packed with pellets to flow rates of air from 0.5 – 5 L/min, in 0.5 L/min increments. The pellets were packed by hand with a module density of 0.50 g/cm^3 and the hollow fibre module density was 0.44 g/cm^3. The resulting pressure drop was measured using a u-tube manometer filled with water. The values were compared to pressure drop modelled by the Hagen-Poiseuille equation for laminar flow and the Ergun equation (Ergun, 1952) for inertial flow for the modules tested.

Results and discussion

For comparison, scanning electron micrographs were recorded for an AbScents 1000 pellet and a hollow fibre. It is apparent in Figure 2 that the pellet had a relatively closed macrostructure. By contrast, the hollow fibre had a very open macrostructure, shown in Figure 3, with smaller zeolite crystals held within. These macrovoids and channels were present throughout the hollow fibre structure and on the inner and outer walls, as can be seen in Figure 4. These macrovoids were formed as the fibres coagulated; the inner skin layers are highly porous due to the use of a mixture of NMP/water in the bore fluid, while the less porous outer skin is due to spinning into a water bath with no solvent. The macrovoidal structure of the hollow fibres, seen in the low magnification image in Figure 3, suggests that they should exhibit rapid adsorption kinetics.

Experimental breakthrough curves for a hollow fibre and an equivalent volume pellet module can be seen in Figure 5, with data presented in Table 1. These readings were taken every 10 seconds, and the many data points in these experimental results formed a line for each set of data. Though the pellet module had a longer breakthrough time than the hollow fibres (2.21 hours compared to 1.72), the breakthrough loading (i.e. the weight of ammonia sorbed onto the module at the breakthrough time) was higher in the hollow fibres (1.21%wt in the fibres to 0.93%wt in the pellets). At equilibrium, with the same adsorbent material present in both modules, the equilibrium loadings should be the same. This was seen to be the case, suggesting that the adsorbent is accessible by contaminant to the same extent in pellet and fibre modules, despite the different adsorption profiles of the two.

Figure 5 shows that the fibre module had a far sharper breakthrough curve than the pellet module, translating to a shorter mass transfer zone and length of unused bed of the hollow fibres, shown in Table 1. This indicates more efficient use was made of the hollow fibre module, with a short adsorption front traveling through the fibre. Meanwhile the AbScents 1000 pellets took longer to reach equilibrium, displaying a longer mass transfer zone and greater proportion of the adsorbent left unused (Table 1). For the pellet module, the 1.63 cm length of unused bed constitutes over a quarter of the length of the module, compared to 0.65 cm for the fibre module. To standardise by weight, C/C_0 was plotted against time/weight (in hours/gram), and this is shown in Figure 6. In this case, the hollow fibres are shown to have greater breakthrough time/weight than the equivalent volume of pellets. Due to their low density, it was observed that hollow fibres are a favourable alternative to pellets in terms of breakthrough loading when weight is a limiting factor, but less so when volume is more limited.

The calculated pressure drops per length for the hollow fibre module and the pellet module are shown in Figure 7. The hollow fibre module had lower pressure drop than the pellet module at

all flow rates. This was due to the direct passage of air through the lumen of the hollow fibres, rather than the tortuous path that gas must take through the packed module of pellets. As breathing rates are significantly higher than 5 L/min, models were required to predict pressure drop at higher gas flow rates. Pressure drop in hollow fibres has been found to follow the Hagen-Poiseuille equation for laminar flow (Feng *et al.*, 1998). Therefore this equation was used to model pressure drop in the hollow fibres. Flow through packed beds is inertial dominant, meaning the Ergun equation is a more fitting model (Ergun, 1952). As the Ergun equation is not suitable for extrapolation, the Hagen-Poiseuille equation was plotted in Figure 8 to determine pressure drop in the hollow fibre module as flow rate increases. As the rate of increase is linear and the predicted pressure drop at 150 L/min is 354 Pa/cm, it can be concluded that hollow fibres present a good alternative in terms of pressure drop to an equivalent volume packed bed, particularly as flow rate becomes high.

With the combination of lower pressure drop and improved mass transfer resulting in higher breakthrough loading, we have shown that adsorbent hollow fibre modules present a viable alternative to an equivalent volume packed bed, although despite their greater breakthrough loading, they are hindered by a slightly lower breakthrough time in the tested conditions. This may be in part due to the presence of the polymer support hindering access to adsorption sites. Research is currently being carried out using porous polymers instead of polyethersulfone to enhance adsorbent accessibility (Jeffs *et al.*, 2013)

Conclusion

Hollow fibres offer potential as a method of lowering the physiological burden in respirators whilst providing new opportunities to enhance respirator design to take advantage of the intrinsic benefits of the hollow fibres. Hollow fibres were shown to be macrovoidal with a more open

structure than a pellet, and as a result a sharper breakthrough curve indicating a more rapid mass transfer rate was observed, as well as enhanced breakthrough loading, with greater breakthrough time/gram of hollow fibre. In addition, the pressure drop was significantly lower in hollow fibres than in the equivalent volume pellet module, and by modelling pressure drop at higher flow rates, a major improvement in pressure drops was seen from 30 L/min upwards. Hollow fibres were found to compare favourably to pellets in cases where pressure drop and weight are limited. However, the breakthrough time was slightly lower for a hollow fibre module compared to an equivalent volume pellet module, in part due to the low comparative weight of fibre in the module compared to pellets, and ways to address this will be explored in future research.

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Tables

Table 1 Adsorption data for 5 x 2 cm hollow fibre and pellet modules challenged with 800 ppm 1 L/min NH_3

	Hollow fibre module	*Pellet module*
Adsorbent weight (g)	4.79	7.72
Breakthrough time (h)	1.72	2.21
Breakthrough loading (% wt.)	1.21	0.97
Equilibrium time (h)	2.88	4.69
Equilibrium loading (% wt.)	1.37	1.41
Mass transfer zone (cm)	2.91	3.78
Length of unused bed (cm)	0.65	1.63

Figure caption list

Figure 1. An example of a hollow fibre module, showing the bores of the fibre, through which gas will flow.

Figure 2. Scanning electron microscope (SEM) images of the surface of a AbScents 1000 adsorbent pellet, x30 (top) and x350 (middle).

Figure 3. SEM images of hollow fibre containing AbScents 1000, x45 cross section (top) and x250 cross section (bottom).

Figure 4. x350 SEM images of hollow fibres containing AbScents 1000, inner surface of fibre (top) and outer wall of fibre (bottom).

Figure 5. Experimental breakthrough curves for 5 long x 2 cm diameter hollow fibre (solid line) and packed bed (dotted line) modules challenged with 800 ppm 1 L/min NH_3.

Figure 6. Experimental breakthrough curves per weight (hours/gram) for 5 long x 2 cm diameter hollow fibre (solid line) and packed bed (dotted line) modules challenged with 800 ppm 1 L/min NH_3.

Figure 7. Pressure drop values measured from 5 cm long modules, calculated per cm bed depth for an empty module, a hollow fibre module and a 0.16 cm average particle diameter pellet module.

Figure 8. Extrapolated pressure drop/cm for 5 cm long x 2 cm wide hollow fibre modules using the Hagen-Poiseuille equation.

Figures

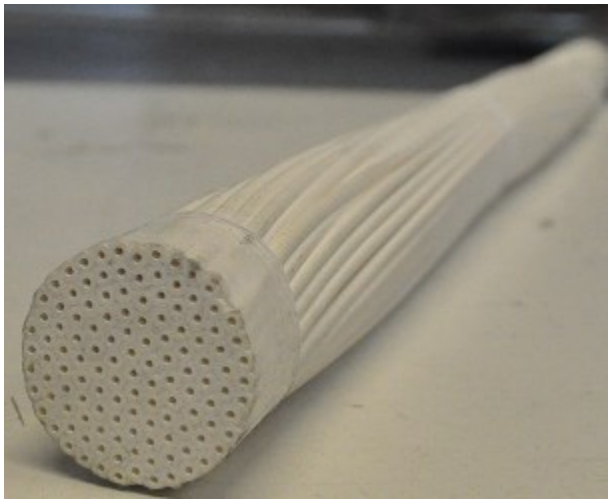

Figure 1.

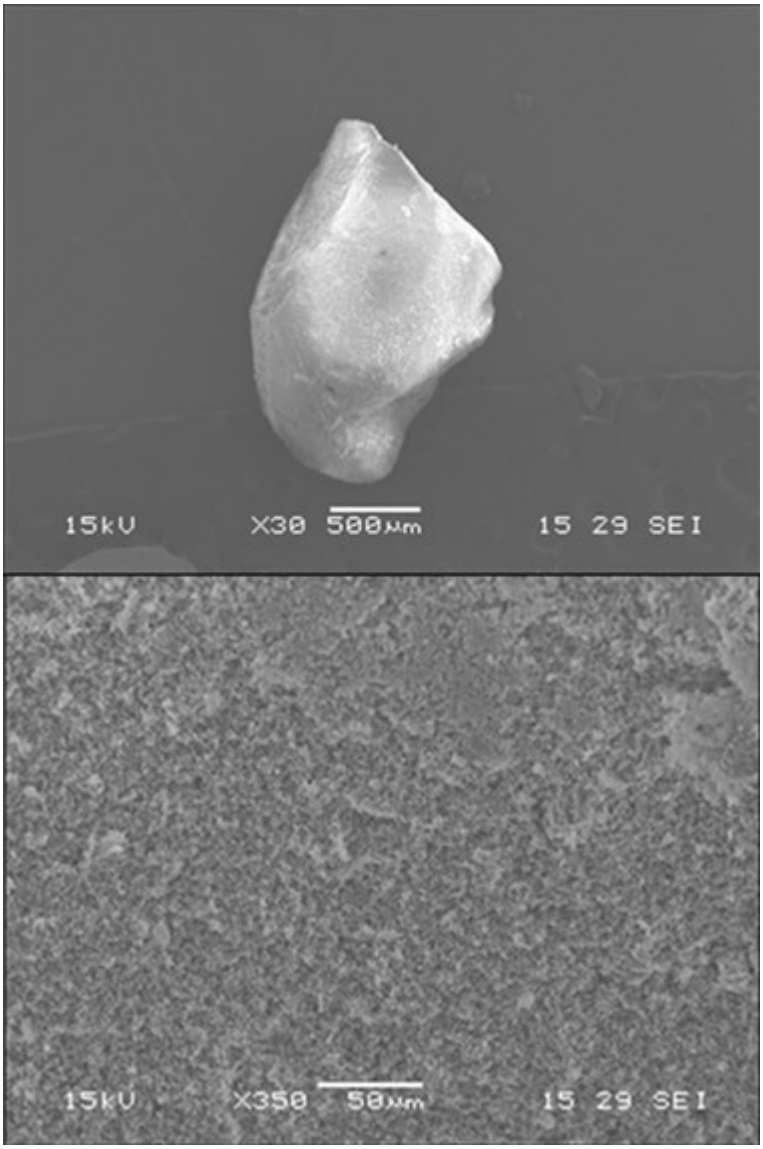

Figure 2.

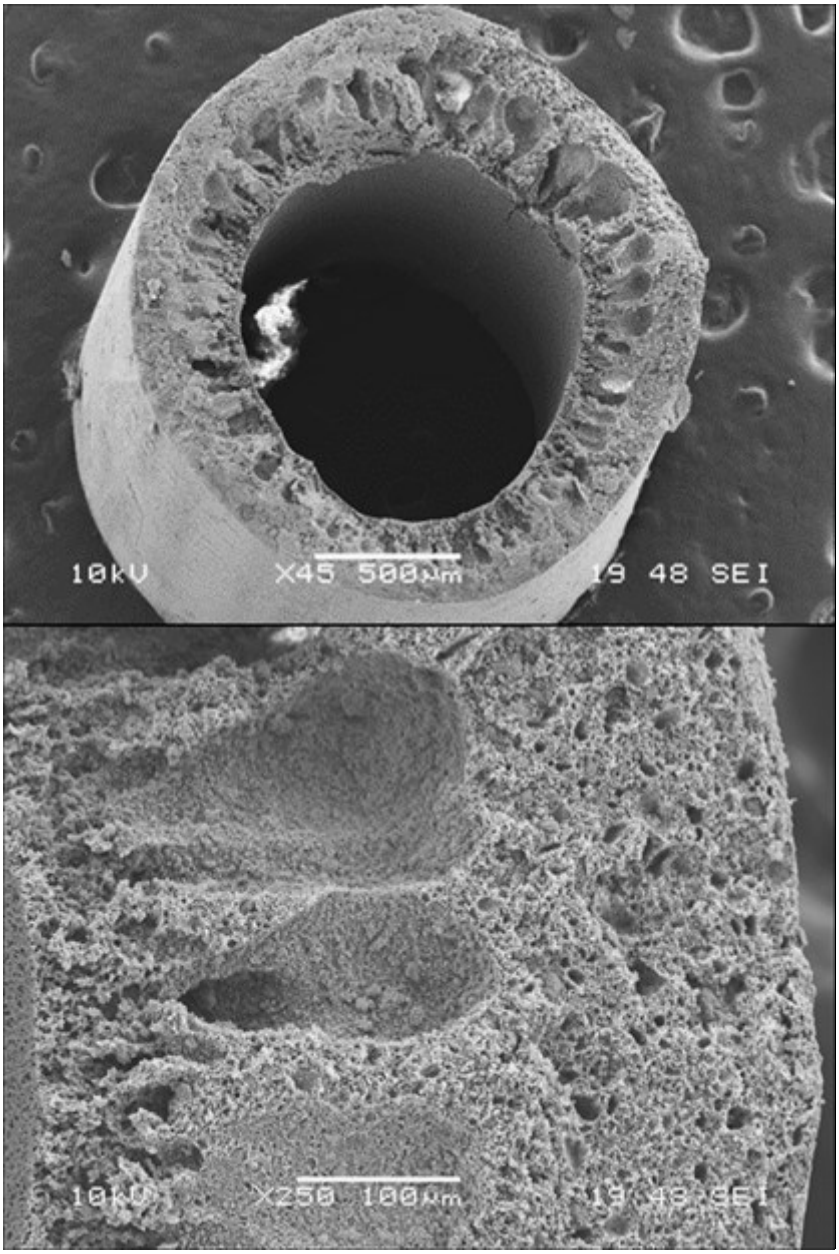

Figure 3.

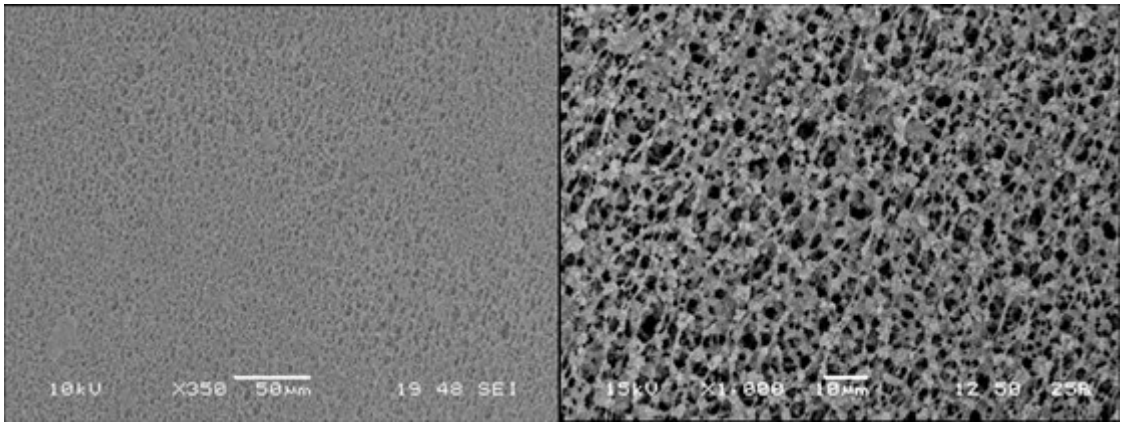

Figure 4.

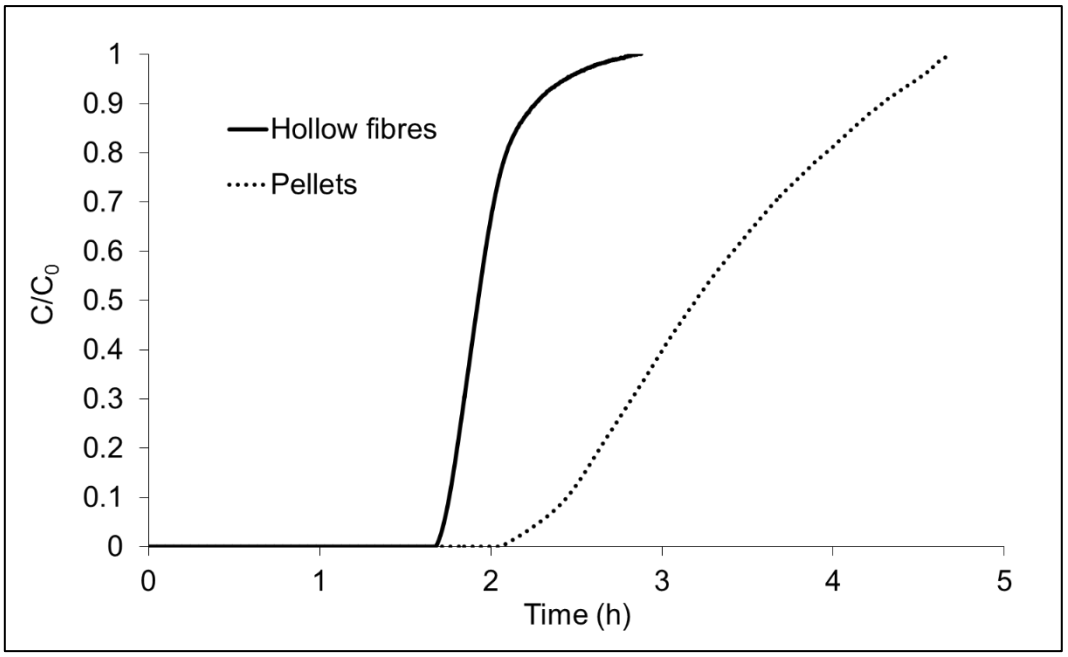
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C/C0
Hollow fibres
Pellets
0
1
2
3
4
5
Time (h)

Figure 5.

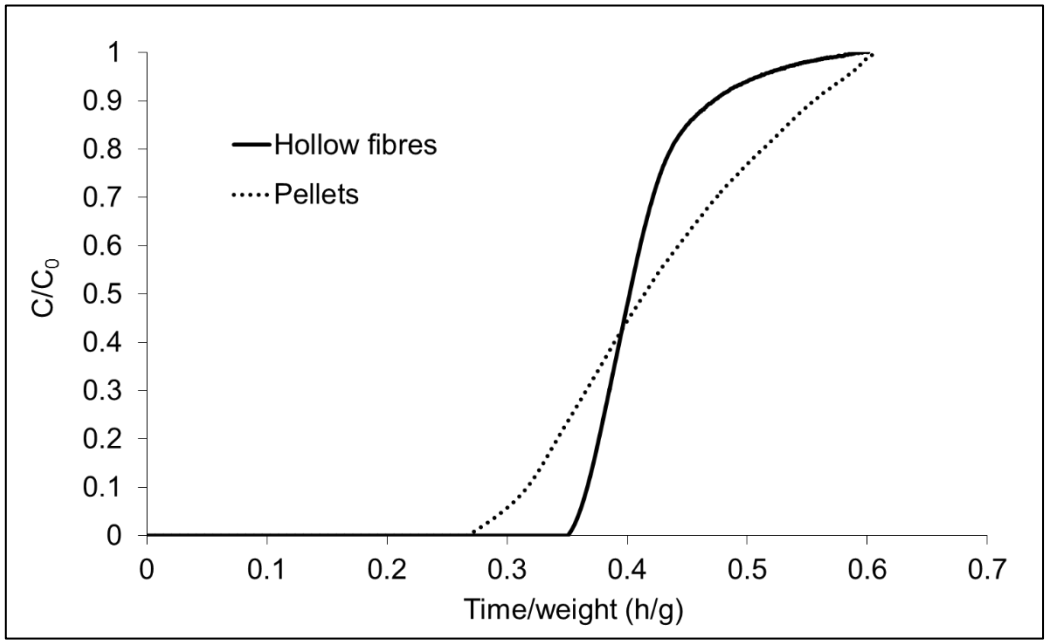

Figure 6.

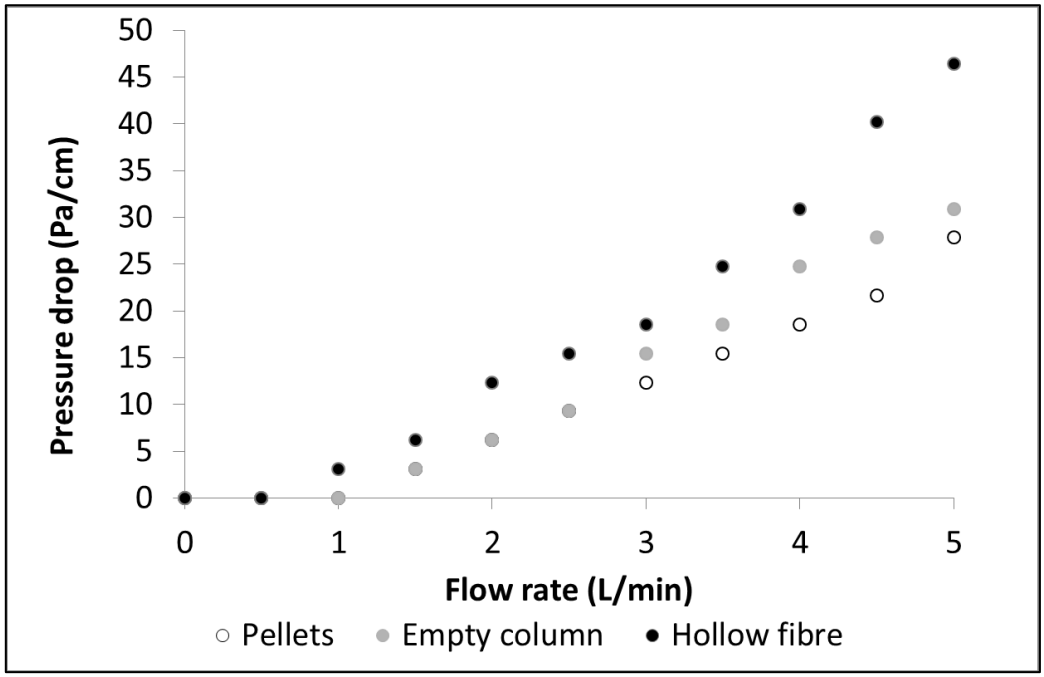

Figure 7.

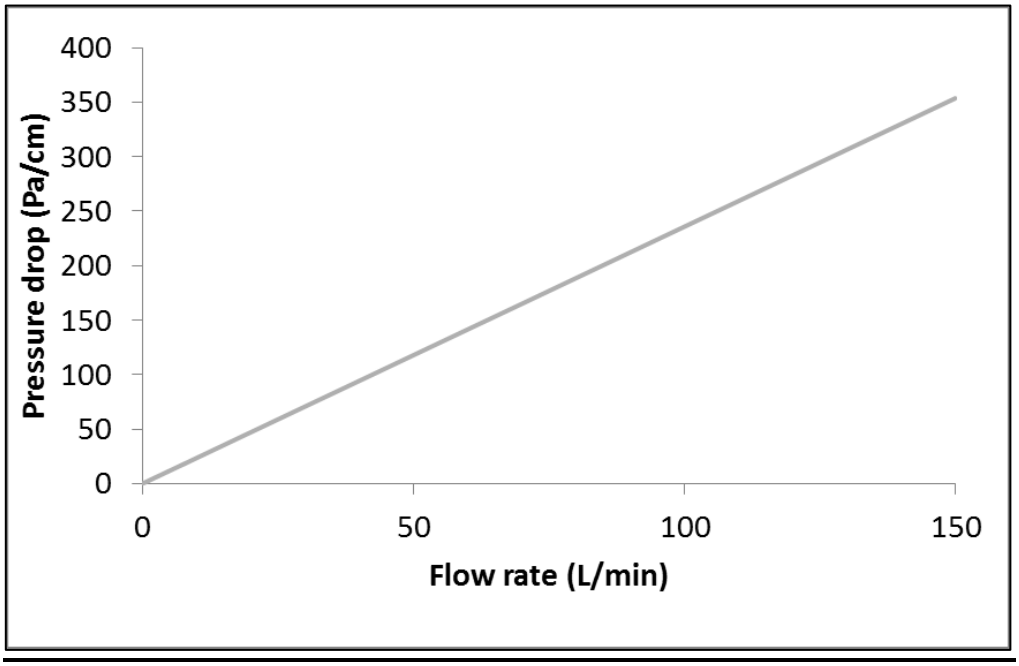
Pressure drop (Pa/cm)
400
350
300
250
200
150
100
50
0
0
50
100
150
Flow rate (L/min)

Figure 8.