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Gray, Stephen, Tran, Thuy, Bolto, Brian, Farmer, Tony D and Collings, Tony F (2007) Ultrasound enhancement of microfiltration performance for natural organic matter removal. Organic Geochemistry, 38 (7). pp. 1091-1096.

Ultrasound enhancement of microfiltration performance for natural organic matter removal

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Abstract

Sonication of water at 1500 W power prior to microfiltration showed that short sonication times (60 s) gave a reduced flux decline. It is suggested that a less potent, smaller molecular form of the natural organic matter (NOM) was produced by sonication. Longer sonication times diminished this beneficial effect. This may be due to the formation of aggregates or compounds that are more readily adsorbed on the membrane.

Where the sonication was preceded by an alum treatment, the flux loss showed a regular decrease with longer sonication times. It is suggested that the effects of sonication on the alum flocs and on the flocs; NOM interactions may play a critical role in regulating the flux. Where sand was present on sonication at 800 and 1400 W, the cavitational energy was focussed on adsorbed organic material, resulting in more efficient destruction and the formation of compounds that counteracted the flux enhancement.

Keywords: Natural organic matter, ultrasonication, microfiltration, flux, fouling

1. Introduction

Fouling of microfiltration (MF) membranes in drinking water treatment is a significant cost in their use. Ways of extending performance have received much

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attention over the years, and include pre-treatment by coagulation or adsorption to remove foulants arising from NOM (Farahbakhsh et al., 2004). Other ways of neutralising the detrimental effect of offending NOM components may be possible, with the use of ultrasound being one example (Kobayashi et al., 2003). The application of the technique to filtration has been reviewed, including membrane processes such as microfiltration (MF), with a particular emphasis on minimisation of fouling (Pirkonen, 2001). The defouling of MF and ultrafiltration (UF) membranes is reported for cross-flow systems operating in an ultrasound field (Kobayashi et al., 2003). The flux of fouled membranes (cellulose MF treating milk and polysulphone UF treating a peptone solution) was restored after ultrasound irradiation at a frequency of 28 kHz and an output of 23 W/cm^2. In both systems decreased fouling was noted when irradiation was applied during filtration.

In other studies of organic compounds in aqueous solution, ultrasonic radiation of 33 W gave a 23% increase in the permeability coefficient of hydrocortisone through a cellulose film, and a 14% improvement for benzoic acid diffusing through a polydimethylsiloxane film (Julian and Zentner, 1986). The ultrasound influence went beyond a simple increase in temperature or agitation, with the likely focus on the membrane-solution interface. The measured activation energy for diffusion was lowered. Ultrasound improved the permeation of dextran through polyacrylonitrile UF membranes, the effect increasing with higher intensity and being dependant on the direction of the irradiation (Kobayashi et al., 1999). Better performance resulted at 28 and 45 kHz, but not at 100 kHz, which caused less cavitation. The low frequency irradiation reduced the dextran layer resistance and enhanced mass transfer through the membrane.

The permeation of simple electrolytes such as NaCl, KCl and $CaCl_2$ in aqueous solution through cellophane membranes was enhanced, depending on the intensity of the ultrasound (Lenart and Auslander, 1980; Li et al., 1995; Li et al., 1996). The main reason for the acceleration of diffusion was felt to be acoustic microcurrents in the liquid, which increased the velocity of the solute, and would result in eddy currents that clear the membrane surface. Similarly, the use of amplitude modulated ultrasound in an ion-exchange desalination process based on hollow fibre membranes gave a 40% improvement at a signal power of 61 W, increasing to 60% at 50° C (Band et al., 1997). It was thought that cavitation was the main mechanism responsible, with different steps in the overall ion-exchange process being enhanced.

Ultrasonic forces have been used for many years for the dispersion of agglomerated powders in solution (Thoma et al., 1991). The effectiveness of ultrasonic cavitation forces on suspended particles is a complex function of the frequency, amplitude and the physical properties of the medium. Bond breaking and a reduction in the molecular weight of polymers in aqueous solution can be achieved by sonication, as has been reported for chitosan and starch (Czechowska et al., 2005). Chain scission is accompanied by side reactions that introduce carbonyl groups into the molecules. The process is slower for starch than chitosan, probably because of the different chain conformation of starch compared with the rod-like macromolecules of chitosan. The degradation of microcystins by ultrasound of frequency 150 kHz at a 40 W output has recently been reported (Zhang et al., 2005). Pentachlorophenol degradation has similarly been carried out at 500 kHz and 80 W (Gondrexon et al., 1999).

In our approach we expose a natural water containing NOM to ultrasonic irradiation before feeding it to an MF membrane. In previous work we had noted that one important finding in fouling of a polypropylene membrane was the possibility of association between NOM components, especially the strongly and weakly hydrophobic compounds (Gray et al., 2003). Such agglomerates were shown to increase the extent of fouling. The aim was to disrupt any associations of this nature by exposing the feed water to an ultrasonic field prior to membrane treatment. Ultrasound can decrease the adsorption of phenol on polymeric adsorption resins (Li et al., 2002). Other examples where ultrasound reduces the interaction of adherent particles are cell detachment (Ohl and Wolfrum, 2003) and the de-aggregation of soil and NOM (Eriksenn et al., 1995). On the other hand, ultrasonic radiation without cavitation can cause particle agglomeration (Pirkonen, 2001).

2. Experimental

2.1 Water sources

Surface water sources from two separate locations in Victoria, Australia were used. The first was from Ouyen and the second was from the Moorabool River as stored at Meredith. The water quality characteristics are summarised in Table 1. Ouyen water had a high turbidity, high total organic carbon (TOC) and low absorbance at 254 nm (UV_{254}), and thus a low specific UV absorbance ($SUVA_{254}$) compared to the Meredith water. A 5 µm pre-filter followed by reverse osmosis was used to concentrate the NOM. Although the Meredith NOM is present in greater amounts, its NOM contains more UV absorbing compounds, indicating a higher content of hydrophobic material.

2.2 Sonication

Batches of water (5 L) were exposed to high power ultrasound for various residence times up to 240 s in the reaction zone. The water was sonicated at power levels of 800, 1400 or 1500 W. In some experiments washed, pre-sonicated and screened sand (210-430 μm) was added to form 10% suspensions that were exposed to subsequent ultrasonic treatment. An ultrasonic industrial processor (UIP 2000) manufactured by D. Hielscher GmbH was used. The sonotrode (ultrasonic horn) was longer than conventionally employed; it had a diameter of 3.80 cm and a nominal operating frequency of 20 kHz. Cavitation occurs at frequencies of 20-1000 kHz (Pirkonen, 2001). There was a time interval of several days between the two events because the sonication and filtration works were carried out in different laboratories.

2.3 Membrane operation

A polypropylene (PP) hollow fibre MF membrane manufactured by Memcor was used. The membrane characteristics are as in Table 2, and the mode of operation and general procedure were as detailed earlier (Gray et al., 2005). Pre-treatment with alum at the optimum dose (322 μmol/L of Al^{3+}) was carried out in some experiments with Ouyen water using standard jar tests with the pH maintained at 6. The solution was flash mixed for 1 min at 130 rpm and the speed was then reduced to 50 rpm for 15 min, after which the treated water was left to settle for 1 h.

All results are expressed as relative flux (membrane flux at 20°C/clean water flux at 20°C) versus filtrate mass and were performed at pH 6. All water was filtered through GF-C filter paper (nominal 1.3 μm pores) before use to remove suspended material.

3. Results and Discussion

For Ouyen water, the sonication was carried out on the raw water as received, and on the water that had been pre-treated with alum, at 1500 W power for 15, 30, 60, 120 and 240 s. Results of the subsequent MF studies for the raw and alum pre-treated waters are presented in Fig. 1 and 2, respectively. Flux data for the respective waters without prior sonication are also included for purpose of comparison. In the case of the raw water without the alum pre-treatment, the shorter sonication times (15, 60 s) generally gave a reduced flux decline, compared to the longer sonication times (120, 240 s), which gave a flux profile similar to that of the raw water without sonication. The reduced flux decline for water sonicated for shorter times are in accord with NOM being presented to the membrane as a smaller species, or one that has been degraded to a less adsorbable form. It seems that sonication for longer periods is detrimental, possibly leading to species that encourage aggregation, or to material that is more readily adsorbed. This mechanism is speculative and it is noted that the flux profile for the sample sonicated for 30 s did not follow this general trend, suggesting that other mechanisms may also be active.

In the case of the water pre-treated with alum, the effect of sonication time seems to follow a reverse trend. In particular, compared to the unsonicated water, the shorter sonication times (15 and 30 s) gave an increased flux decline, whereas the longer sonication times (240, 120 and 60 s) resulted in a reduced flux decline. In previous work (Tran et al., 2005), we have shown that the alum pre-treatment not only removes part of the NOM, but also generates unsettleable alum flocs that may readily penetrate and block the membrane pores, thus adversely affecting the membrane performance. Therefore, in addition to the degradation of the residual NOM (having less hydrophobic and charged hydrophilic fractions, White et al., 1997), the effects of sonication on the alum flocs and on the interactions between the flocs and the NOM may also play a critical role in regulating the flux. An investigation of these factors is beyond the scope of the present study. However, the results suggest that for the alum pre-treated water, longer sonication times gave better membrane performance, whereas shorter sonication times were more beneficial for the raw water.

Results for MF studies of Meredith water, which has a higher level of aromatic and hydrophobic compounds than Ouyen water, with and without prior sonication are presented in Fig. 3. The data show that on sonication at 800 and 1400 W for 180 s, the best outcome is at the higher power usage, when the cavitation intensity was greater, resulting in a lower flux decline. There is a less rapid flux decline also when there is sand present, compared to the unsonicated water, but the improvement is reduced compared to the no-sand and sonicated situation. This suggests that the beneficial effect of ultra sound is counteracted by the formation of species under the more degrading sand conditions that have some strong adsorptive properties, causing fouling behaviour. The ultrasonic intensities employed in this study are one to two orders of magnitude higher than those reported previously (Julian and Zentner, 1986; Kobayashi et al., 1999; Pirkonen, 2001).

The addition of sand to the water requires further comment. Our previous experience with high power sound applications has focussed on the removal of surface coatings from detrital minerals such as silica sand and heavy mineral sands (Farmer et al., 2000a, 2000b; Collings and Farmer, 2003) and on the destruction of organic chlorine compounds and related contaminants adhering to soil and sedimentary particles (Mason et al., 2004; Sosa Pintos et al., 1974). Localisation of the adherent or adsorbate on the solid surface is an important factor in determining the efficiency of surface cleaning.

Cavitation at the high intensities employed here is initiated at the solid-liquid interface due to the discontinuity in free energy. The collapse of bubbles at a solid interface has been shown both experimentally and theoretically to generate a high-speed jet that impinges on the solid surface (Plesset, 1974; Coleman et al., 1987). In effect, the cavitational energy is focussed on the contaminating material, whereas in conventional sonochemistry in a liquid, bubble collapse is spherical and distributed across all the dissolved material. If the addition of solid particles encourages the localisation of NOM on particle surfaces as a consequence of any inherent hydrophobicity in the NOM, efficient destruction will result. If the NOM remains in solution, this particular benefit of high power ultrasound will not apply. Under the circumstance where the NOM is localised on the sand surfaces, a long residence time in the region of maximum cavitation is probably not needed. A single pass of a few seconds rather than 180 s may suffice to break up of the NOM, and this will radically affect the power requirements. It would seem more efficient to treat the water immediately after sonication to avoid any re-aggregation. This was not possible in these preliminary experiments.

4. Conclusion

Sonication of Ouyen water at the high power level of 1500 W showed that there was a reduced flux decline at shorter sonication times and that this beneficial effect was diminished at longer sonication times. It is suggested that a less potent, smaller molecular form of the NOM was produced by the shorter sonication, whereas the longer sonication may lead to species that encourage aggregation, or to material that is more readily adsorbed. Where there had been prior coagulation with alum for removal of some of the NOM, the flux loss showed a regular decrease with sonication time. It is suggested that, in addition to the degradation of the residual NOM, the effects of sonication on the alum flocs and on the flocs; NOM interactions may also play a critical role in regulating the flux. For Meredith water, with sand present on sonication at 800 and 1400 W there was a more rapid flux decline, with the best outcome at the higher power usage. Sand causes the cavitational energy to be focussed on adsorbed material, resulting in more efficient NOM destruction and the formation of compounds that counteract the beneficial effect of ultra sound.

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FIGURE CAPTIONS

Fig. 1. Relative flux profile for raw Ouyen water after sonication at 1500 W for varying times, compared with the unsonicated raw water

Fig. 2. Relative flux profile for raw Ouyen water with alum pretreatment after sonication for varying times at 1500 W, compared with the unsonicated alum pretreated water

Fig. 3. Relative flux profile for Meredith water, with and without sand present on sonication at 800 or 1400 W, compared with the unsonicated raw water

TABLE CAPTIONS

Table 1. Characteristics of the two waters

Table 2. Polypropylene Membrane properties

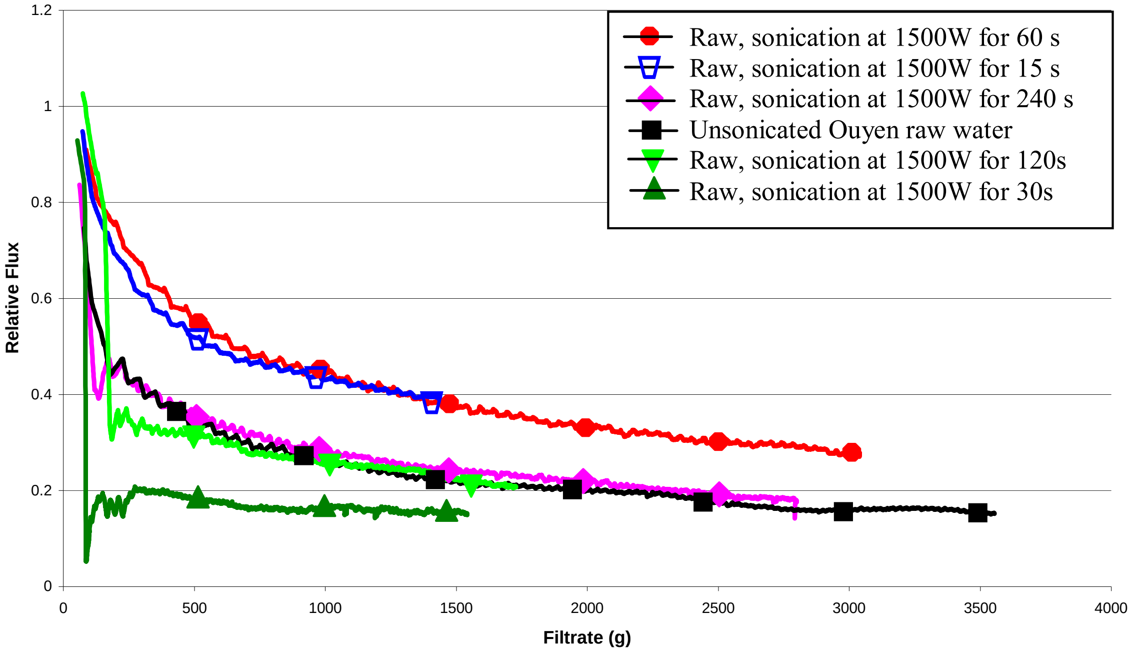
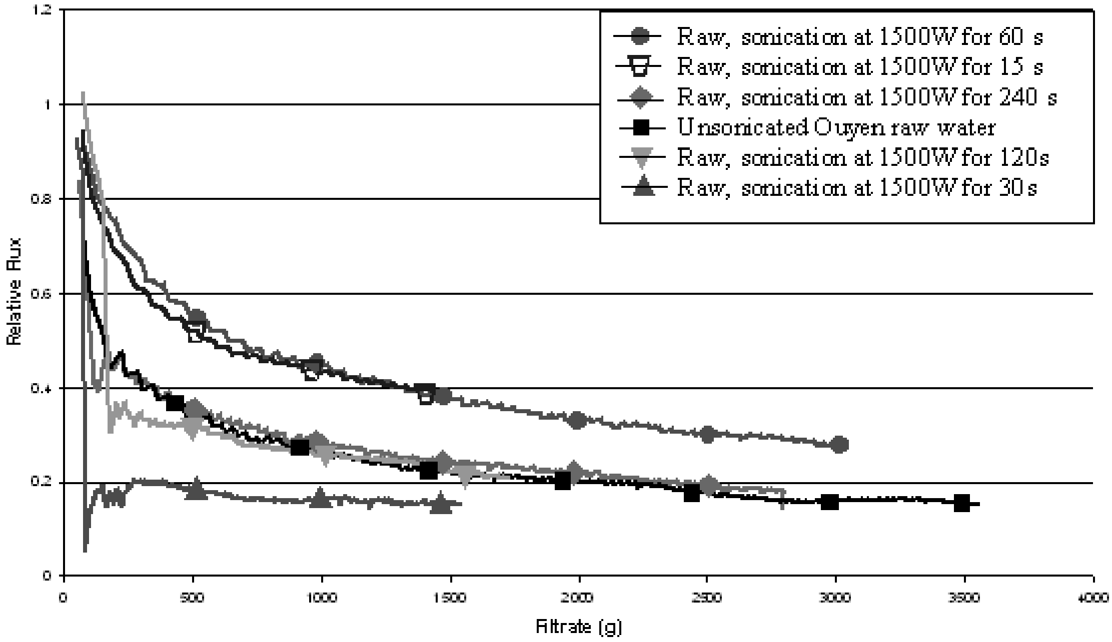


Fig. 1. Colour Version for Web



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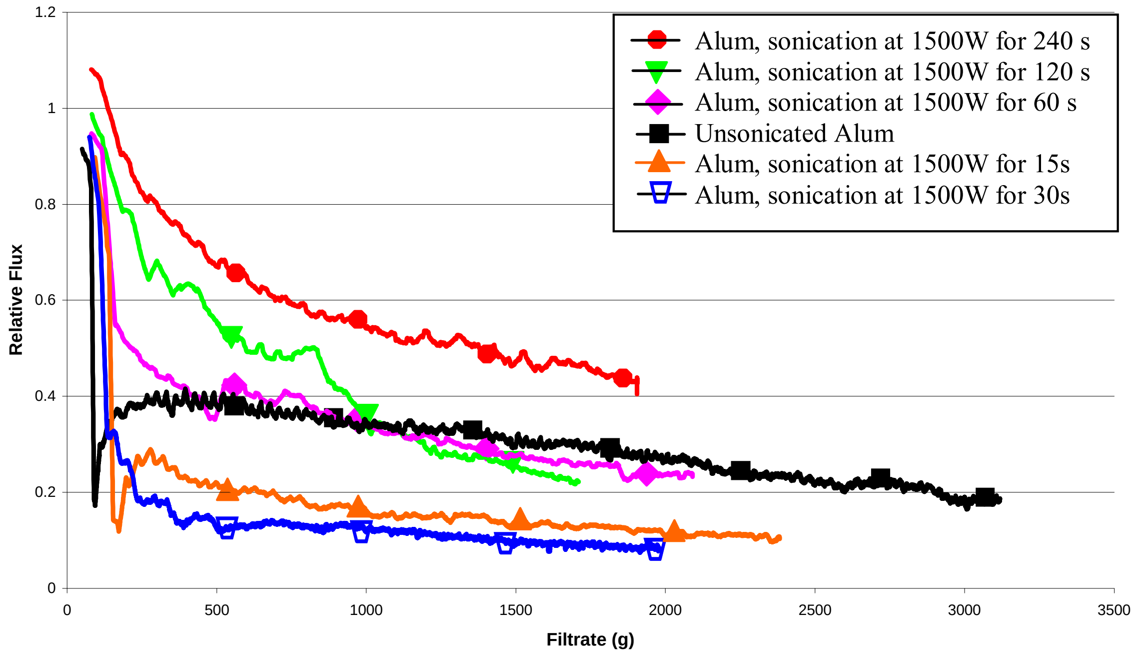
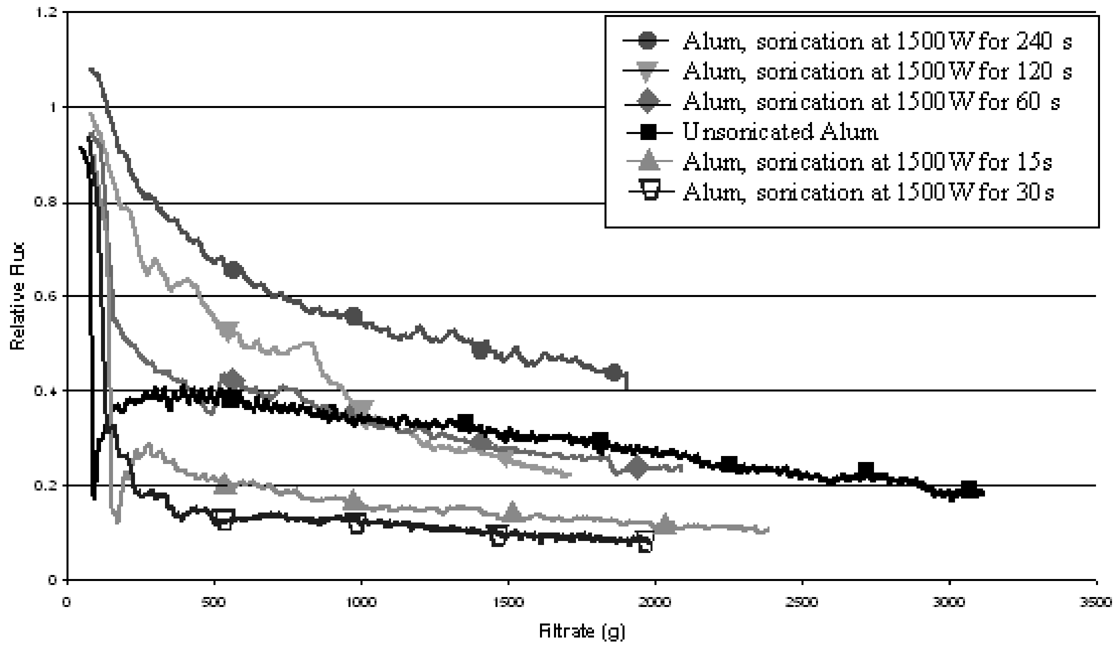


Fig. 2.: Colour version for web



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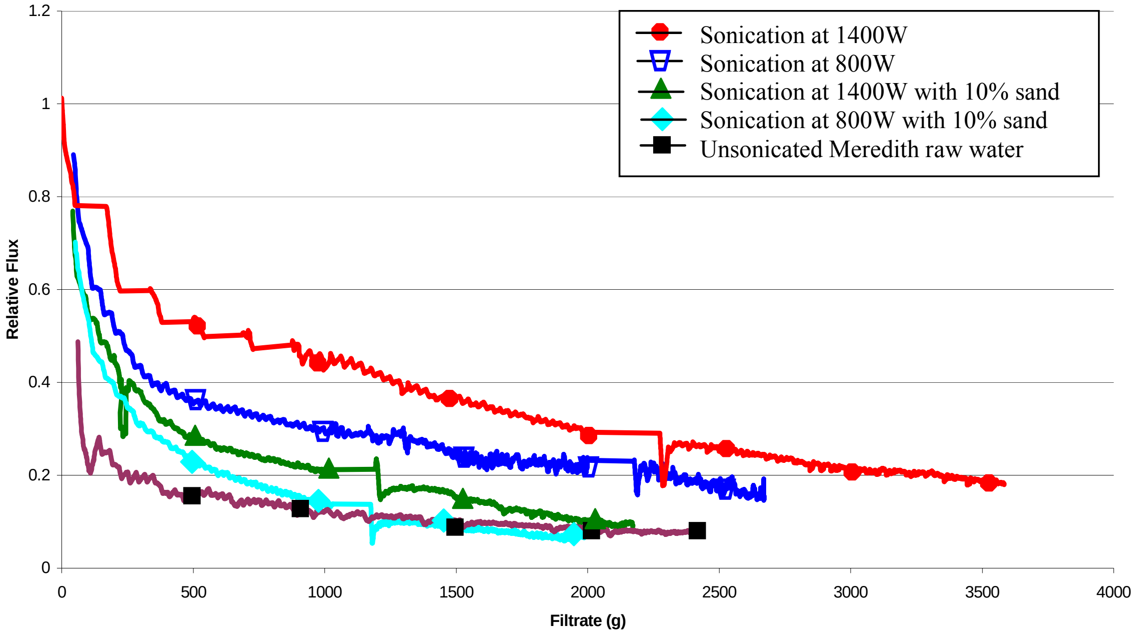

Fig. 3. Colour for web version

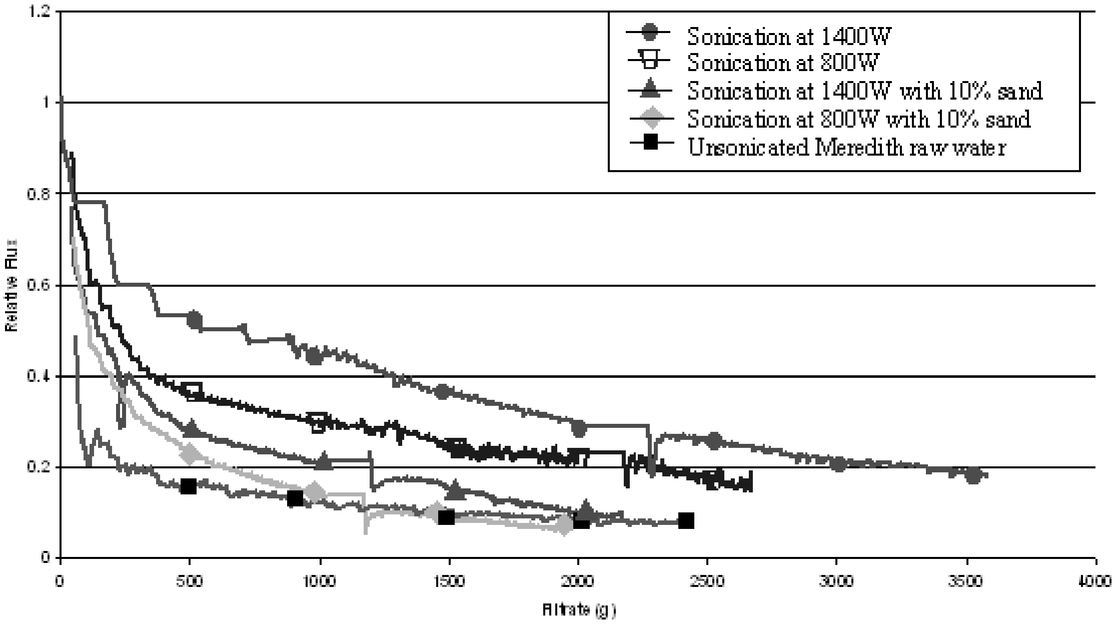

Fig. 3. Black and white version for hardcopy

Table 1

Water	TOC (mg/L)	UV_{254} (cm^{-1})	$SUVA_{254}$ (L/mg.m)	Turbidity (NTU*)
Ouyen water	20.5	0.059	0.28	2.01
Meredith water	9.1	0.154	1.69	1.62

* Nephelometric turbidity units

Table 2

Fibre Dimensions		Nominal Pore Size	Porosimetry Results			Clean Water Flux	Contact Angle (degrees)
Outer diameter. (mm)	Inner diameter. (mm)	(μm)	BET area, (m^2/g)	Pore vol. (cm^3/g)	Av. Pore diam. (μm)	(L/h/bar/m^2)	
0.50	0.25	0.2	21.1	0.149	0.028	1200 ± 200	160