Removing steroid oestrogens from wastewater

Andrew Johnson, **Monika Jürgens**, **Richard Darton** and **Tony Amato** report on recent research aimed at controlling a growing problem

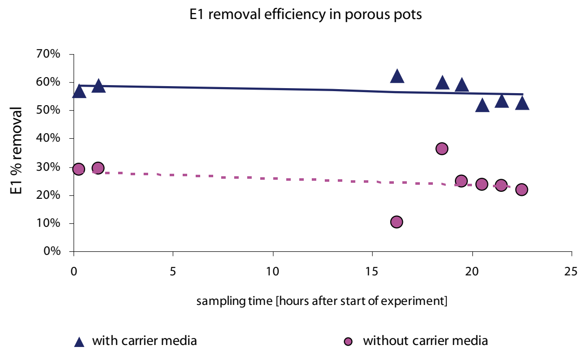
THE most important method of treating wastewater from our major towns and cities is the activated sludge (AS) process. This removes organic contaminants by natural bio-degradation in a large aerated basin in which active bacteria are suspended. In a subsequent settling tank most of the bacterial sludge is removed and recycled to the AS tank, while a small surplus is taken off for disposal. Such sewage treatment plants (STPs) do a remarkably efficient job of removing dissolved organics from municipal wastewater, but a very small amount of contaminant, mainly molecules that are somewhat resistant to biodegradation, escapes into the effluent and hence into our rivers. A problem can arise when some of these escaping molecules are biologically active. For example small amounts of natural and synthetic steroid oestrogen hormones, such as ethinyloestradiol (EE2, active ingredient of the contraceptive pill) and the naturally-occurring female hormones oestradiol (E2) and oestrone (E1) can slip through the STP, and disrupt the physiology of wild fish, even at parts per trillion concentrations. As an island with a relatively high population density (much of it living inland) and small rivers this is an important issue for the UK, and particularly for central and southern England. Predictions of population growth and drier summers, with less water in our rivers to provide dilution indicate that this issue is likely to grow in importance.

Figure 1: Example of an aeration lane within an activated sludge sewage treatment plant. Can we improve oestrogen removal here?

This issue is taken very seriously in the UK, as research funded by the Environment Agency has shown that oestrogenic disruption of wild fish is very widespread. These findings have caused serious consideration on how oestrogens might be removed from sewage effluent.

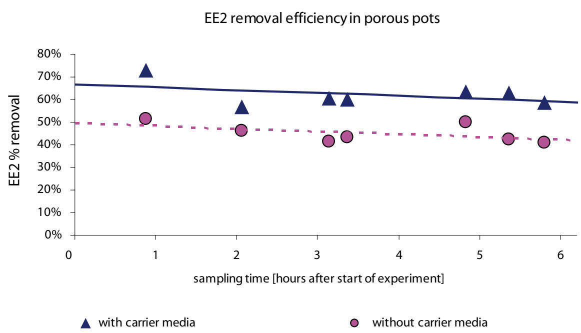
In the periodic review of price limits for the 2005–2010 period (PR04) which Ofwat sets out for the water industry, around £24m ($48m) will be spent on a research project entitled "Endocrine Disruption Demonstration Project". This is now well underway and is designed to examine various sewage treatment technologies to see how effective they might be at removing these hormones. However, the technologies being tested, such as granulated activated carbon, ozone, and chlorine dioxide treatment are usually associated with drinking water production, and are expensive to operate in the dirty matrix of sewage effluent. The presence of many non-target organic molecules can reduce the expected effectiveness of oxidation processes and reduce the bed life of filters such as activated carbon. The main problem is one of scale. A city such as Northampton, UK, with a population of 200,000, produces wastewater at a rate of around 40 t/min. It is easy to imagine that applying energy intensive drinking water purification technology in such a case would be an expensive undertaking. Moreover, a large increase in energy requirement would also increase CO_2 emissions – hardly a sustainable solution. What are the alternatives?

One approach would be to boost the efficiency of the existing



	Total biomass present (g/l)	Average E1 removal	Estimated half-life with 1.3 h residence time
With carrier media	12	57%	1.0 h
Without carrier media	3.6	25%	3.0 h

Figure 2: Removal of spiked E1 by porous pot fed with synthetic sewage with and without the presence of biofilm on carrier media (linear trendline drawn through points)



	Total biomass present (g/l)	Average E1 removal	Estimated half-life with 2.5 h residence time
With carrier media	13	64%	1.8 h
Without carrier media	5.6	44%	2.9 h

Figure 3: Removal of spiked EE2 by porous pot fed with settled sewage with and without the presence of carrier media with biofilm (linear trendline drawn through points). E1 showed a similar behaviour (data not shown)

Above: Figure 4: Oestrogen removal trials in 1 m³ flow through tanks at Northampton. Two tanks are used, one with a media filling, and the other as a control

Below: Figure 5: Example of carrier media with attached biomass

biological treatment. Oestrogens are inherently biodegradable and so in theory should not present an intractable problem. However, in practice there are significant difficulties in adapting the activated sludge plant to remove them at high efficiency. One approach could be to increase significantly the amount of activated sludge bacteria present in the tank. Alternatively, the aeration tank could be made several times as big to hold onto the water for longer and permit more complete biodegradation. This would mean dramatically enlarging the STP at the cost of much extra land, and capital.

the bioscreen concept

Another way forward is to improve the performance of the existing aeration tank through the introduction of biofilms supported on appropriate media within the tank. This approach has been previously used in the water industry to improve both overall organic carbon removal and nitrification. Treatment tanks can be partially filled with media to maximise bacterial growth (and minimise sludge production) to treat high loadings of organic waste, and this is often used in industrial applications.

Activated sludge tanks typically run at a biomass content of between 2.5–5 g/l. Higher biomass concentrations cause problems in getting all the bacteria to sediment out in the final settlement tank. However, a biofilm attached to carrier material in a bioscreen does not cause the same difficulty because the bacteria remain fixed in the aeration tank. Given the typical nutrient range of the raw sewage water, a biomass of 12–35 g/l could be sustained within discrete parts of the activated sludge tank. The extra quantity of biomass would present many times more biodegradation capacity to the passing water than currently available per litre of activated sludge tank. The appropriate combination of high biomass concentration at strategic locations within the tank could improve the ability to sorb and degrade organic contaminants from the aqueous phase.

Research on the current performance of activated sludge plants has suggested that good oestrogen removal is associated with long sludge ages, in other words the slower growing bacterial communities seem to contain more oestrogen degraders. This might favour bioscreens as they permit bacterial communities to establish as biofilms and remain *in situ* for long periods.

experimental

Following successful laboratory tests at the small 50 ml "test tube" scale we have been testing the approach at larger scales of 4 l to 1 m³ in more realistic environments using different types of media.

Samples of different types of media were placed in an aeration lane at a Northampton STP and biofilms were allowed to grow on them naturally. Following establishment of a biofilm, the media were brought back wet to the laboratory. Experiments were carried out using porous pots which are 4 l vessels with a fine porous liner which retain the bacteria but allow liquid to flow through. Two of these pots were filled with activated sludge from the aeration lane, with one also containing the media and attached biofilm. The media used on this occasion were cylindrical and fixed in place within the porous pot. Synthetic sewage, consisting of very diluted skimmed UHT milk with additional inorganic nutrients and 100 µg/l E1, was pumped through each pot at a rate which gave a 1.3 h residence time. The E1 concentration we used is at least 1000 times greater than the natural level, and was necessary for us to be able to perform the analysis of the samples. Both pots were aerated (0.4 l/min) and the experiment was run continuously over a 24 h period. Samples were taken regularly from the inflow and outflow of each pot and analysed for the presence of E1 using liquid chromatography mass spectrometry (LC-MS).

A second experiment was carried out, this time using free mobile media and real, rather than artificial, primary settled sewage as the feed. This work was done on site at the same STP. Two porous pots were filled with fresh activated sludge with one containing carrier media with attached biofilm. A diffuser in each pot supplied air (1–2 l/min) to maintain dissolved oxygen concentrations and keep the biomass and media well mixed. The primary settled sewage (the influent of the activated sludge tank) was pumped directly from the activated sludge tank influent channel to the porous pots and spiked in line with E1 and EE2 to a nominal concentration of 100 µg/l. The residence time was about 2–3 hours and the water temperature was only about 4 °C in the porous pots (compared to 12.5 °C in the AS tank at that time). The experiment was run continuously for about 6 h and the influent and effluent of each pot was regularly sampled and analysed as above.

In both experiments the average oestrogen removal in the presence of media with biofilm was around 60% whereas without the media it was only 25% in the first case and 44% for the second, so the biofilm provided a useful improvement. These tests suggested to us that a careful re-engineering of the AS process may well be able to reduce oestrogens to the level that might be required by the more stringent specifications that may eventually be adopted by regulatory bodies. However this remains still to be proven.

We are now doing further testing at the Northampton STP using two large (1.2 m^3) insulated stainless steel tanks. These are provided with their own air supply through diffusers at the bottom of the tanks, and are constantly fed activated sludge from the adjacent aeration lane. Unlike the previous porous pot experiments, the spiked oestrogen concentrations are now much closer to the realistic tens of nanogrammes per litre levels. The key to this improvement in our test protocol has been the development of a new analytical procedure, using a series of concentration and cleaning steps, with an internal deuterated standard used to check on method efficiency. These tanks are dosed with 100 ng/l E1 during experimental periods. This is slightly above ambient concentrations to give a greater chance for successful analysis of the remaining E1. Apart from demonstrating removal under realistic conditions, this trial is examining ways to deal with the practical problems of fouling, finding the appropriate aeration delivery rate and method, appropriate media, and location for the bioscreen within a real aeration lane. Preliminary results continue to suggest that if an AS plant is not already removing substantially all these chemicals (and some do), then re-engineering may be possible using media with biofilms to produce a satisfactory performance. **tce**

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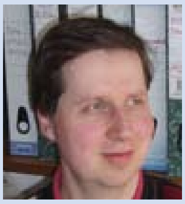

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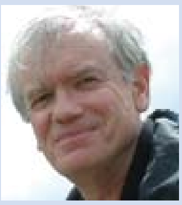

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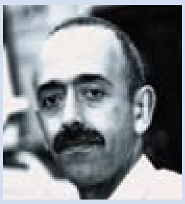

Tony Amato has been involved in the development of a number of water treatment processes since 1975; he is currently employed at Enpure as technology manager; looking at both existing and emerging technologies which can be applied to water treatment and other industries.