Removing oestrogenic compounds from sewage effluent

Andrew Johnson and Richard Darton

Introduction

Wherever you live, a desire for clean potable water is always likely to come near the top of your list of life's necessities. In many parts of the world though, water resources are under pressure as people move into towns and population densities increase. This problem is set to get worse if, as predicted by climatologists, global warming causes a reduction in rainfall in many areas. Humans not only need fresh water, we also generate an unending stream of aqueous waste. Thus, in many temperate parts of the world, rivers are both a drinking water source and a waste product receiver. For example the water drunk by a Londoner may have already have been through the body of a student in Oxford and an IT specialist in Reading following its transit down the River Thames! Whilst drinking water derived from surface water will have been through a water treatment plant (and Londoners can be reassured that treating is done to an extremely high standard) no such high-tech protection is available to the fish and other fauna who have to live in the river.

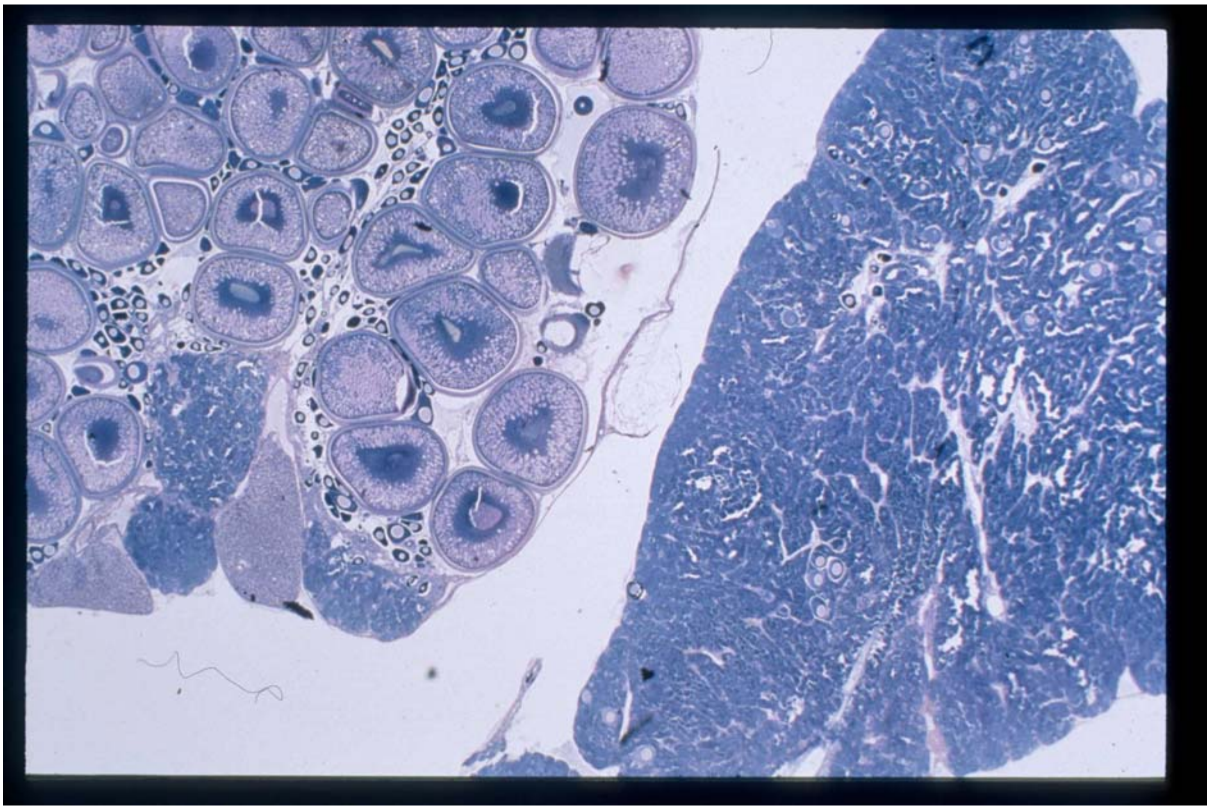
Figure 1. Rivers can be both sources of drinking water and receivers of waste

The major sewage treatment process used for large population centres throughout much of the developed world is activated sludge, first designed in Manchester in 1913. In this process, raw sewage, which is basically liquid organic waste, is converted into a solid (mainly bacteria) which is separated from the water effluent by sedimentation. This is done by feeding the sewage water into a large tank with an average hydraulic residence time of around 10 hours, together with a seed of bacteria recirculated from the final settlement tank.

Air is fed in as fine bubbles to encourage aerobic biodegradation of the waste. In these few hours this remarkably efficient and cost-effective process removes between 90-95% of all the organic material in the feed. Widespread use of activated sludge plants has enabled fish to return to many previously grossly polluted rivers. However, such treatment plants were never tasked with removing *all* the organic molecules entering the works and a small proportion do indeed escape in the effluent. A potential problem arises when some of these escaping molecules are biologically active. For example, some micro-organic contaminants (ie those present in very small concentrations) are now recognised as having a subtle but potentially significant impact on the physiology of sensitive fish species.

Micro-organic contaminants

The problem of micro-organic contaminants in sewage effluent has been brought to light by the issue of endocrine (hormonal) disruption. An oestrogenic response in caged male fish exposed to sewage effluent was first reported in 1994, when it was found that such fish had very high plasma vitellogenin concentrations. Vitellogenin is an oestrogen-responsive egg yolk protein usually found only in female fish. Its presence in males suggested exposure to oestrogenic chemicals. Subsequent studies reported the presence of intersex roach, with oocytes in the testes, downstream of many domestic sewage effluents in the UK (figure 2).



Figures 2(a) Roach fish. 2(b) Testis of intersex roach showing presence of ova within the testicular tissue on the left. These photos are reproduced by kind permission of Dr Susan Jobling, Brunel University.

The occurrence of testicular oocytes can be induced in the laboratory by exposure to oestrogenic chemicals, suggesting that these roach had been exposed to similar chemicals in the wild. Initially suspicion fell on industrially derived oestrogen mimics, such as nonylphenol, a breakdown product of a range of commonly used non-ionic surfactants, but more recently concern has focused on natural steroid oestrogens such as 17β-oestradiol (E2) and oestrone (E1), which are excreted by all humans, together with the contraceptive pill active ingredient 17α-ethinyloestradiol (EE2). In general activated sludge plants seem to remove around 70-88% of E2, 50-75% of E1 and 50-85% of EE2 from the waste stream. This performance still leaves 1-10 ng/L (parts per trillion) of these natural and synthetic hormones in the effluent. Even this astonishingly small quantity can have a drastic impact on the endocrine system of sensitive fish species if the waste water is not sufficiently and quickly diluted. Studies have shown that the birth control chemical, EE2, is the most important endocrine disrupter for the aquatic environment. Because of its societal benefits, no one is arguing that this pharmaceutical product be banned, but these observations have raised concerns with environmental regulators all over Europe. The UK is particularly vulnerable with its high population densities and small rivers, and the UK Environment Agency is contemplating measures to regulate the release of these steroid hormones.

Many of the endocrine disrupting compounds identified have hydrophobic characteristics. This means that in a mixture of water and organic liquid such as octanol, partitioning will favour the organic phase. The particles of live and dead bacteria which make up activated sludge possess the qualities of an organic matrix and consequently can absorb and concentrate these hydrophobic compounds. We know that the industrially derived nonylphenol will concentrate in sludge and survive anaerobic digestion, and this may also be true of EE2. So whilst it may have no ecotoxicological significance, the disposal of sewage sludge to land is another potential route for endocrine disrupters to enter the environment.

Now that the risk of EE2 to the aquatic environment has been identified, researchers are becoming aware that a proportion of the many pharmaceuticals and personal health care products we all use in our daily lives is also escaping into the aquatic environment. A recent survey of streams across America detected a bewildering range of small quantities of such compounds, like antiobiotics, anti-inflammatory medicines, and heart drugs. It is unclear whether any of these compounds will have a deleterious effect on the health of the environment, but the issue needs to be considered. All the more reason to improve the efficiency with which activated sludge plants remove micro-organic contaminants.

State of the art

All the endocrine disrupters mentioned, such as E2 and nonylphenol, 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 double, treble or even quadruple the amount of activated sludge bacteria present in the tank. However, this would cause problems in getting all the bacteria to sediment out in the final settlement 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 sewage treatment works at the cost of much extra land, and capital.

The removal technologies being given consideration at the moment largely originate from the water purification industry. These include: treatment with ultraviolet light after addition of a TiO_2 catalyst, contacting with ozone, microfiltration and reverse osmosis, and activated carbon adsorption. It is widely thought by industry insiders in the UK and regulators in Germany and Japan that these technologies, whilst offering promising technical possibilities, would be too costly to apply. The main problem is one of scale. Even a modestly sized town, the size of say Northampton, can produce waste water at a rate of around one tonne per second, and end-of-pipe treating of all this waste water by such methods would require a huge plant. Further, none of these technologies would prevent oestrogens accumulating in secondary sludge, and several of them require the use of costly chemicals or adsorbents. Tertiary biological treatment such as sequenced batch reactors, or membrane bioreactors have not so far been tested against oestrogens, but they would need high biological activity maintained over long periods to be effective. Nutrients are limited downstream of the main activated sludge tanks and long residence times would be needed in large vessels, so the prospects for tertiary bio-treatment are not good.

An alternative approach is therefore needed to improve the performance of existing plants, and to offer more cost effective treatment in new plants. Simply constructing larger activated sludge tanks in order to give more residence time does not seem like intelligent engineering!

Principle of removing steroid oestrogens and similar micro-organic contaminants

The proportion of an organic contaminant that can be removed from the sewage influent depends on the attractive power of the sorbent and the quantity of sorbent present per unit of volume. Since the ability to increase the 'attractiveness' of the biological sorbent is limited, we can instead increase the amount of sorbent present locally. Activated sludge tanks run at a biomass content of between 2.5 to 4 g/L, since a higher concentration would give rise to settling problems. However, a biofilm attached to carrier material does not cause the same difficulty in removing sludge from the effluent. Given the typical strength range of the raw sewage water, a biomass of 12-35 g/L could be sustained within a discrete part of the activated sludge tank. This would present many times more sorbent binding surface and biodegradation capacity to the passing water than currently available per litre in an unmodified activated sludge tank. The appropriate combination of high biomass with high-presented surface area will provide the greatest improvement in the ability to sorb and remove organic contaminants from the aqueous phase.

The removal of a micro-organic contaminant such as oestradiol can be seen as a two-stage process:

- initial binding to the bacterial surfaces
- biodegradation on the bacterial surfaces

This basic approach allows a wide range of mild to strongly hydrophobic organic contaminants to be intercepted and biodegraded in situ. The binding/sorption process alone would be insufficient to remove permanently the contaminant from the water phase, since the binding surfaces would soon become exhausted and fail to adsorb more contaminant.

We have conducted a series of experiments over the last three years to develop an alternative treatment technology along these lines. The idea is to improve the performance of existing activated sludge treatment plants by placing supported biofilms in the aeration tanks, with staged flow of liquid through these packed zones. Small-scale laboratory tests show that such an arrangement can remove substantially all the steroid oestrogens, at a modest extra cost. The method is principally designed for employment within the aeration tank of an activitated sludge tank where some degree of plug flow is occurring.

Laboratory tests

To show how biofilms can be supported and grow under actual plant conditions we have acquired and placed a wide variety of different media in stainless steel cages, and submerged them in the aeration tank of a typical activated sludge plant. Later, we took the media out of the tank for analysis and further testing in the laboratory. In these follow-up tests we used the naturally occurring biofilm to seed bacterial growth in a bench-scale unit (figure 3). In the laboratory, for practical reasons, we treated a synthetic sewage made from UHT skimmed milk (with added nitrogen and phosphorus), having the same BOD range as normal raw sewage. This feedstuff was spiked with steroid oestrogen. The media with biofilm attached was placed in an upflow glass bioreactor. The feed liquor moved through the biofilter, was aerated and then overflowed to the next reactor. The typical hydraulic residence time in the bioreactors was around 20 minutes. Both the feed and effluent were constantly monitored for oestrogen using Liquid Chromatography Mass Spectroscopy.

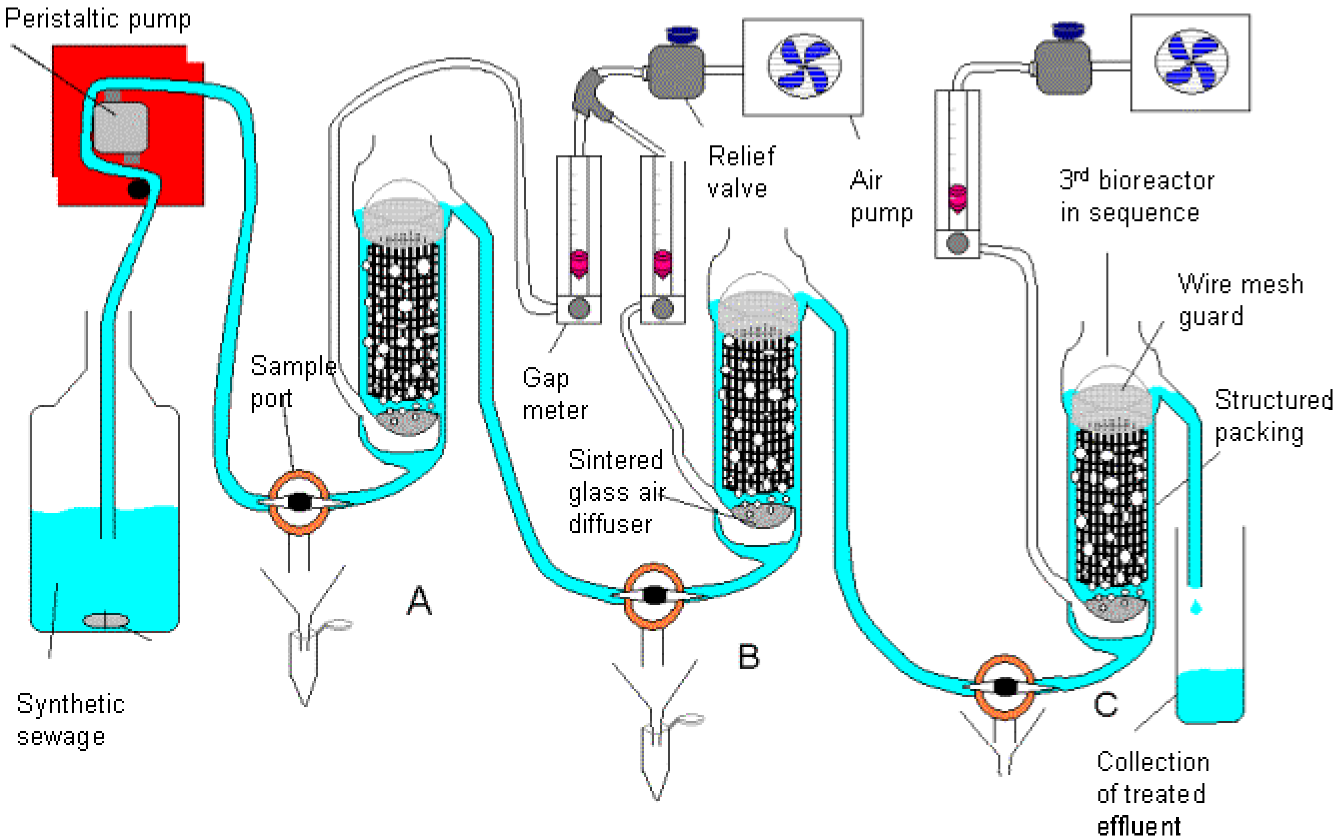


Figure 3 Laboratory multi-staged treating unit

To demonstrate that the biofilm could sustainably remove steroid oestrogens we added 100 µg/L ethinyloestradiol to our synthetic sewage and pumped this through the bioreactor continuously for 20 days. Throughout the test period 90-95% of the EE2 was removed (Figure 4). Although it is more difficult to manage, similarly good results have been obtained with genuine filtered activated sludge as the feed material.

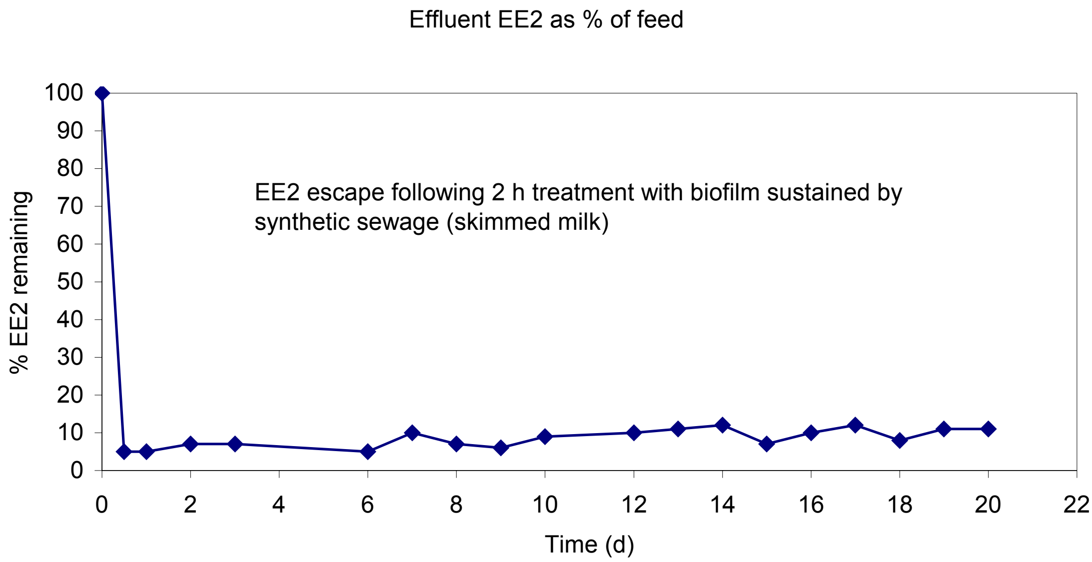


Figure 4. Twenty day trial of ethinyloestradiol removal

A number of different factors which might affect biofilter performance have been tested, such as flow rate, nutrient source, steroid mixtures and, as demonstrated here with oestrone (E1), the aeration rate (Figure 5).

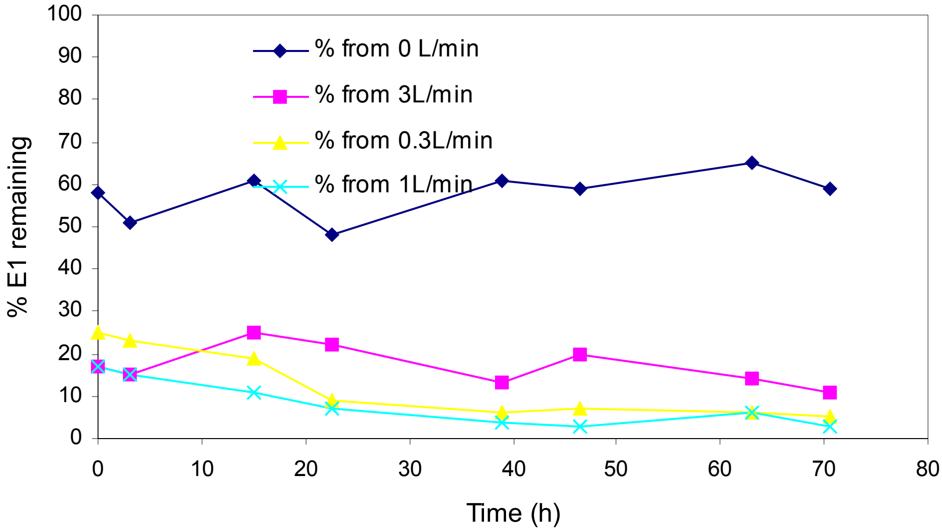


Figure 5. Investigation of effect of aeration on removal of oestrone

The best E1 removal performance was observed at between 0.3-1 L/min of air supply. Anaerobic digestion (with no aeration) was not particularly effective. Note again the high removal performance, better than 95% at optimum conditions, which compares very favourably with the ~70% value observed in a typical activated sludge plant for this compound.

How the water purity could be improved in practice

Based on our plant and laboratory tests, and kinetic/equilibrium modelling of bio-reactor performance, the approach we suggest is to use biofilters located in the front part of the aeration tank. The job of the carrier media is to encourage biofilm growth, yet at the same time not restrict through-flow. As far as possible, the design must guarantee contact with passing micro-organic contaminants. It would be attractive to use mobile carrier particles at a packing density that would permit their movement in the water and air-flow (fluidised bed approach), and so minimise the clogging danger. However, a low packing density may lead to more contaminants by-passing the biofilms altogether. A fixed matrix is more likely to give us a certain contact with contaminants. Excess biofilm growth leading to clogging will need to be managed by recirculating the biofilters within the tank. At the high removal efficiencies required, any by-passing would be very undesirable.

The best layout involves several packed zones, as shown in figure 6. A pulse of organic contaminant not only reacts with the activated sludge floc particles but then meets additional fresh sorbent/biodegrading surface on the filters in its passage through the tank. This provides a stepwise reduction in the organic contaminant concentration. The biofilters themselves may not need to have a depth greater than a couple of metres, so the aeration tank with its remaining activated sludge flocs should still function as normal (such tanks can be around 50 to 100 metres long). Since more of the biomass within the aeration tank is now fixed, operators have the additional advantage of reduced sludge production.

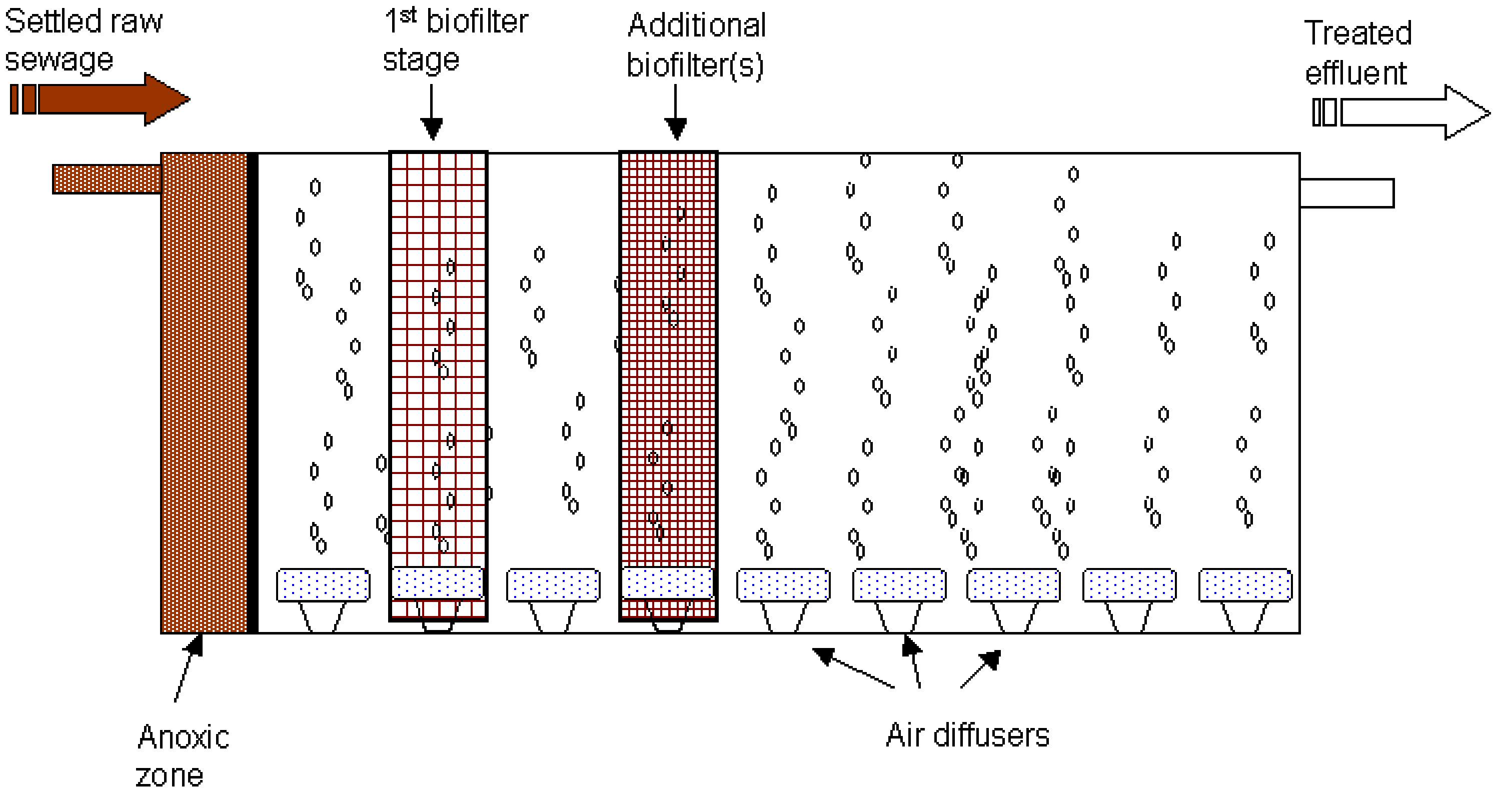


Figure 6. Two biofilter stages inserted near the influent in the aeration tank to form hybrid biofilter/activated sludge treatment tank with plug flow

In this arrangement, the oestrogens are removed and degraded within the aeration tank, and so do not escape either in the water phase, and also do not accumulate in the secondary sludge. This advantage is not offered by any of the competing end-of-pipe technologies. We plan to demonstrate this performance in larger-scale trials.

Acknowledgements
The authors wish to thank the NERC innovation fund and the Department of Engineering Science at Oxford University for helping to fund this work. Thanks are also offered for the analytical expertise of Neville Llewellyn and the key contributions of Tamir Abo-El-Nour, Andrew Thompson, Tim Hurford and Matthew Sullivan.

About the authors
Andrew Johnson is a principal scientist with the Natural Environment Research Council's Centre for Ecology and Hydrology at Wallingford, and Richard Darton is Professor of Engineering Science at the University of Oxford.