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Assessing granular media filtration for the removal of chemical contaminants from wastewater

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ABSTRACT

Granular media filtration was evaluated for the removal of a suite of chemical contaminants that can be found in wastewater. Laboratory- and pilot-scale sand and granular activated carbon (GAC) filters were trialled for their ability to remove atrazine, estrone (E1), 17α-ethynylestradiol (EE2), N-nitrosodimethylamine (NDMA), N-nitrosomorpholine (NMOR) and N-nitrosodiethylamine (NDEA). In general, sand filtration was ineffective in removing the contaminants from a tertiary treated wastewater, with the exception of E1 and EE2, where efficient removals were observed after approximately 150 d. Batch degradation experiments confirmed that the removal of E1 was through biological activity, with a pseudo-first-order degradation rate constant of 7.4×10^{-3} h^{-1}. GAC filtration was initially able to effectively remove all contaminants; although removals decreased over time due to competition with other organics present in the water. The only exception was atrazine where removal remained consistently high throughout the experiment. Previously unreported differences were observed in the adsorption of the three nitrosamines, with the ease of removal following the trend, NDEA > NMOR > NDMA, consistent with their hydrophobic character. In most instances the removals from the pilot-scale filters were generally in agreement with the laboratory-scale filter, suggesting that there is potential in using laboratory-scale filters as monitoring tools to evaluate the performance of pilot- and possibly full-scale sand and GAC filters at wastewater treatment plants.

1. Introduction

Water shortages across many countries, including Australia, have meant that recycling and re-use of wastewater has become a priority. The implications of a shift toward re-use are extensive and appropriate standards are required for recycled water to ensure that public and environmental health are maintained. The incomplete removal of some chemical contaminants from wastewater using conventional treatment means that advanced treatment processes are required, which adds significantly to the cost of re-use water. The range of chemical contaminants in wastewater is much greater and potentially more damaging to human and environmental health than those present drinking water and it is

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crucial that these are removed before water is delivered for appropriate re-use. Some of the chemical contaminants detected in wastewater include herbicides, endocrine disrupting compounds (EDCs) and disinfection by-products (DBPs). Of particular concern in Australia are atrazine, estrogens and nitrosamines.

Atrazine is the most commonly detected herbicide in groundwater throughout Australia and the USA (USEPA, 2003; APVMA, 2004). It is a potent carcinogen and has also been shown to be an endocrine disruptor in frogs at environmentally relevant concentrations (Hayes et al., 2002). Both the current Australian drinking water and recycled water guidelines for atrazine are 40 μg L^{-1} (NHMRC, 2004; EPHC, 2008), while the World Health Organisation (WHO) has documented a guideline value of 2 μg L^{-1}.

EDCs are chemicals that can disrupt or interfere with the proper functioning of the endocrine system which consists primarily of glands that produce hormones that help to guide development, growth, reproduction and behavior. Normal endocrine function can be blocked by the presence of EDCs, which can interfere with synthesis of the natural hormone and/or bind to hormone receptors instead of endogenous hormones thereby blocking normal endocrine signalling. A wide range of compounds have been shown to invoke endocrine disrupting activity and a majority of these have been detected in water and wastewater, but perhaps the most documented of these are the estrogens, in particular, estrone (E1) and 17α-ethynylestradiol (EE2) (Kolpin et al., 2002; Ying et al., 2004; Racz and Goel, 2010). The current health-based Australian recycled water guidelines for E1 and EE2 are 0.03 and 0.0015 μg L^{-1}, respectively (EPHC, 2008).

Nitrosamines are potent carcinogens whose appearance in the environment can be attributed to chlorine-based disinfection of water and wastewater. In addition, recent studies have indicated that high levels of nitrosamines in the environment can be attributed to waste from various industries including the rubber industry (de Vocht et al., 2007; Krauss et al., 2009). Most studies have focussed on N-nitrosodimethylamine (NDMA) which is highly water soluble and does not appear to be readily absorbed by soils; however, other nitrosamines are also detected in wastewater, including N-nitrosomorpholine (NMOR) and N-nitrosodiethylamine (NDEA) (Kaplan and Kaplan, 1985; Gunnison et al., 2000; Sharp et al., 2005). The Australian drinking water guideline for NDMA is set at 100 ng L^{-1}, while the guideline for water recycling is 10 ng L^{-1} (NHMRC, 2004; EPHC, 2008).

Ozonation, advanced oxidation processes and membrane filtration (in particular nanofiltration and reverse osmosis) have been documented to be effective for the removal of atrazine, estrogens and NDMA from wastewaters (Maldonado et al., 2006; Liu et al., 2008, 2009; Frierdich et al., 2009; Shaalan, 2009; Wert et al., 2009; Racz and Goel, 2010; Yangali-Quintanilla et al., 2010; Hatzinger et al., 2011). Effective oxidation of these contaminants appears to be through the generation of hydroxyl radicals, while tight membranes can reject these compounds through size exclusion, charge repulsion and adsorption mechanisms. However, these methods are costly and require significant resources and infrastructure. Biological filtration (biofiltration) using granular media may offer a low cost solution for the treatment of these contaminants of concern in wastewater. This treatment option is often employed as one of the final barriers in the production of drinking water but has not been used extensively in the treatment of wastewater destined for re-use. The most suitable application of biofiltration in wastewater treatment would be as a final polishing step, prior to final disinfection. One of the major advantages of biofiltration systems is that they are able to remove contaminants, through biodegradation mechanisms, without the addition of other chemicals that may have the potential to produce undesirable by-products. However, due to reasons such as site specificity and lack of optimisation, effective removal of these contaminants cannot always be guaranteed through these systems. Studies have shown that atrazine, E1, EE2 and NDMA are biodegradable in water and soils (Kaplan and Kaplan, 1985; Gunnison et al., 2000; Wackett et al., 2002; USEPA, 2003; Shi et al., 2004; Sharp et al., 2005; Yang et al., 2005; Racz and Goel, 2010); consequently, there is potential in using biofiltration as a treatment option for these contaminants in wastewater.

The aim of this study was to assess the effectiveness of biological granular media filtration to remove atrazine, E1, EE2, NDMA, NMOR and NDEA from a tertiary treated wastewater destined for re-use. Sand and granular activated carbon (GAC) media were evaluated for the biofiltration of these contaminants. Sand filters are generally existing infrastructure at most wastewater treatment plants (WWTPs), while GAC filters have been identified as an alternative, viable option as a polishing step in wastewater treatment (Chaudhary et al., 2003; Rowsell et al., 2009).

2. Experimental procedures

2.1. Materials and reagents

Tertiary treated effluent (TTE) water was obtained from the Bolivar WWTP in Adelaide, South Australia. This water was sampled prior to the sand filters at the tertiary dissolved air flotation filtration (DAFF) plant and used for laboratory-scale sand and GAC column experiments and batch degradation experiments. The treatment processes upstream of TTE water include preliminary grit removal, primary sedimentation, secondary activated sludge treatment and detention in waste stabilization lagoons (for ~20 d) prior to the tertiary DAFF plant. In addition, activated sludge treated effluent (ASTE) water was used for laboratory-scale sand column experiments for short periods of time. Characteristics of these waters are presented in Table 1.

Atrazine (≥99% purity; Sigma, Australia) was dissolved in ultrapure water (Millipore Pty Ltd, USA) to create a stock solution, which was spiked into sample waters at the desired concentrations. E1 and EE2 (≥99% purity and ≥98% purity, respectively; Sigma, Australia) were reconstituted in methanol to create stock solutions which were subsequently spiked into sample waters at the required concentrations. NDMA, NMOR and NDEA (all 99.9% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), as were their deuterated forms; NDMA-d6, NMOR-d8 and NDEA-d10; these were used as internal standards. Each nitrosamine was