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Hazardous events in membrane bioreactors – Part 2: Impacts on removal of trace organic chemical contaminants

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ABSTRACT

In complement to the initial study assessing the impact of hazardous events on membrane bioreactor (MBR) bulk performances, detailed assessment of the consequences of similar events has now been conducted on the removal of a wide range of trace organic chemical contaminants. The investigated chemicals include 12 steroidal hormones, 4 xenoestrogens, 2 pesticides, 23 pharmaceuticals and personal care products. Under salinity, DNP, ammonia and organic carbon shock conditions, overall removal of hydrophobic chemicals ($\log D_{pH7} \geq 2.5$) was not or only slightly affected. Since these chemicals are largely adsorbed to biomass, these results imply that biotransformation within the biomass structure itself was maintained. However, removal of hydrophilic chemicals ($\log D_{pH7} < 2.5$) was commonly observed to be impeded under shock load conditions, indicating loss of bioactivity. This was observed primarily for chemicals which have low or moderate biotransformability. In comparison, easily biotransformable chemicals were largely removed. The susceptibility of less readily biotransformable hydrophilic chemicals to shock loads was due to their reliance upon specific organisms or metabolic pathways for their biotransformation. The results of these experiments show that hydrophilic chemicals with low biotransformability (e.g., sulfamethoxazole, ketoprofen, gemfibrozil and naproxen) could be sensitive indicators for monitoring impacts of hazardous events on removal of trace organic chemicals by MBRs.

1. Introduction

Water recycling using membrane bioreactors (MBRs) is prevalent in many countries. This membrane application requires validation to ensure that the process is capable of providing effective treatment. The validation process is expected to capture not only normal operational conditions but also "hazardous event" conditions, where water quality is outside specification potentially posing an elevated exposure risk [1,2]. Risk assessments focused on hazardous events have been applied for a wide variety of applications, including the management of water borne diseases [3] and in the modelling of oil refinery accidents [4]. The assessment of hazardous events is a key philosophy in the approach to water quality risk assessment used by the World Health Organisation (WHO) for the development of Water Safety Plans [5] and is described in the WHO Guidelines for Drinking Water Quality [6]. Current Australian water quality management guidelines including the Australian Drinking Water Guidelines [7] and the Australian Guidelines for Water Recycling [8] are based on risk assessment and risk management considerations. As defined in these national guideline documents, a hazard is a biological, chemical, physical or radiological agent that has the potential to cause harm; and a hazardous event is an incident or situation that can lead to the presence of a hazard [7,8]. Up to now, very little attention has been paid to the assessment of hazardous events and their contribution to the risk of treatment failure or underperformance in MBRs.

Over the last decade, interest in the ability of MBRs to eliminate trace organic chemical contaminants such as steroidal hormones, xenoestrogens, pesticides, pharmaceuticals and personal care products (PPCPs) has increased [9–12]. Some of these trace organic chemical contaminants are known to have endocrine disrupting effects on

Abbreviations: MBRs, membrane bioreactors; WHO, World Health Organisation; PPCPs, pharmaceuticals and personal care products; COD, chemical oxygen demand; DOC, dissolved organic carbon; CST, capillary suction time; DNP, 2,4-dinitrophenol; WWTP, wastewater treatment plant; ATP, adenosine triphosphate; HRT, hydraulic retention time; SRT, solid retention time; PVDF, polyvinylidene-difluoride; SPE, solid phase extraction; LC–MS/MS, liquid chromatography–tandem mass spectrometry; GC–MS/MS, gas chromatography–tandem mass spectrometry; LOQs, limit of quantifications; K_{biol}, biotransformation rate constant; EPS, extracellular polymeric substance

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aquatic organisms at low concentrations and others have been linked to ecological impacts due to acute and chronic toxicity mechanisms [13–19]. The long-term effect of human exposure to most of these trace organic chemicals is still unknown but is currently the focus of much consideration. Evaluating the removal of trace organic chemical contaminants under hazardous event conditions will facilitate improved environmental and human health risk management for MBR systems. This is particularly important for assuring a desired water quality in water reuse applications.

This paper is the second part of a large study focussing on the impact of hazardous events on MBR performance. In the initial section of this work, the potential impacts of a series of operational hazardous events were characterised based on the removal of key bulk water quality and operational parameters including pH, turbidity, chemical oxygen demand (COD), dissolved organic carbon (DOC), biomass concentrations, capillary suction time (CST) and membrane fouling rate by MBRs [20]. The present article reports the impacts of similar hazardous events on the removal of a wide range of trace organic chemical contaminants by MBR technology. The investigated hazardous events in this study include salinity shock, 2,4-dinitrophenol (DNP) shock, ammonia shock, organic carbon shock, feed starvation, loss of power supply and physical membrane damage. Salinity, organic carbon and ammonia shocks are commonly reported to exhibit short peak loads in full-scale wastewater treatment plants (WWTPs) [21–23] so they were selected in this study. DNP shock was selected as a representative peak load caused by discharge of industrial wastewater containing electron inhibitors as it is a well-known inhibitor of efficient energy production in cells with mitochondria [24,25]. DNP uncouples oxidative phosphorylation by carrying protons across the mitochondrial membrane, leading to a rapid consumption of energy without generation of adenosine triphosphate (ATP) and, at high concentrations, can disrupt a variety of important bacterial metabolic processes [26–30]. The other hazardous events selected for this investigation were identified through an expert workshop at the beginning of the study. More background about the choice of those hazardous events is provided in the initial part of this large study [20]. The trace chemicals of interest in this study include 7 steroidal estrogens, 5 androgens, 4 xeno-estrogens, 2 pesticides and 23 PPCPs. These trace chemicals were selected due to their potential adverse impacts to human health and the environment, their high annual consumption in Australia [31], their diversity in terms of physio-chemical characteristics (e.g., neutral, acidic, ionic, hydrophobic and hydrophilic), and their potential to serve as an appropriate indicator chemical to assess MBR performance.

2. Materials and methods

2.1. Laboratory-scale MBRs and hazardous event simulation experiments

A laboratory-scale MBR test system was comprised of four identical experimental MBRs (30 L each), fed from a single continuously-mixed influent tank (200 L). Each MBR was designed to operate with a hydraulic retention time (HRT) of 1 day, a solids retention time (SRT) of 30 days and a flux of 10 L m^{-2} h^{-1}. The membranes used in this study were polyvinylidene-difluoride (PVDF) membranes with a nominal pore size of 0.04 μm. The test systems were located at a local municipal WWTP to facilitate testing with the use of primary treated effluent filling a common influent tank daily. The aerobic chamber (20 L) of each MBR was intermittently aerated with 15 min on/off cycles to stimulate nitrification (aerobic) and denitrification (anaerobic) microbial processes. The membrane chambers (10 L each) were aerated continuously to assist biofouling control. To facilitate membrane relaxation, the permeate pump was turned off manually for 10 min every day.

The investigated hazardous events include salinity shock, DNP shock, ammonia shock, organic carbon shock, feed starvation, loss of power supply and physical membrane damage. These hazardous event simulations are described in Table 1. The MBR system and the hazardous event simulation experiments were reported in more details in the initial part of this large study [20].

For the shock load experiments, besides the samples described in the initial paper [20], permeate and mixed liquor samples at 3 h after introducing the shocks were taken for trace organic chemical analysis. Similarly, for the loss of power experiment, additional permeate and mixed liquor samples were taken at 3 h after the power supply was reinitiated. For physical membrane damage experiment, permeate samples were collected at 0.3 h, 2 h, 3 h, 24 h, and 48 h, and mixed liquor samples were collected at 3 h, 24 h and 48 h after cutting the fibres for trace organic chemical analysis.

2.2. Control experiments

Before starting the hazardous event simulation experiments, the four experimental MBRs were operated under the same conditions for one week to assess the reproducibility of performance between the four parallel systems. In addition, during the hazardous event simulation experiments, one of the four MBRs was operated under steady-state conditions as an experimental control while the other MBRs were subjected to various hazardous events.

2.3. Sample preparation and analysis

After collection, all samples were stored on ice and immediately transported to the laboratory for further processing. Upon arrival at the laboratory, the mixed liquor samples (0.5 L each) were immediately filtered through 0.7 μm Millipore glass fibre prefilters and the solid biomass was stored in 60 mL plastic containers. These samples were then frozen and further processed following the procedure reported in previous publications [11,32]. The influent samples (0.25 L each) were also immediately filtered through 0.7 μm Millipore glass fibre prefilters. All aqueous samples including filtered influent and permeate (1 L each) were then spiked with isotopically labelled standards of trace chemicals of interest for accurate isotope dilution quantification. These samples were extracted using solid phase extraction (SPE). The SPE

Table 1
Description of hazardous event simulations.

Hazardous event	Simulation description
Salinity shock	NaCl was added as a single dose to the bioreactor to achieve 20 g L^{-1}
DNP shock	DNP was added as a single dose to the bioreactor to achieve 0.2 g L^{-1}
Ammonia shock	NH_4HCO_3 was added as a single dose to the bioreactor to achieve 0.7 g L^{-1} ammonia
Organic carbon shock	A mixture of glucose and glutamic acid (1:1) was added as a single dose to the bioreactor to achieve 5 g L^{-1} COD
Starvation	The feed to the MBR was stopped for 6 days
Loss of power supply	The power supply to the MBR was terminated for 2 h
Physical membrane damage	2 out of 120 fibres were cut (resulting in damage ratio of 1.66 %) by a sharp knife at a depth of 10 cm