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Comparative study of NF and RO membranes in the treatment of produced water II: Toxicity removal efficiency

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HIGHLIGHTS

- The NF-treated produced water was found to be toxic at EC_{50} of 13.65%.
- The additive chemicals have potential to contribute toxicity to NF-treated water.
- The NF membrane removed 48% of TOC and shows potential to be used as a pretreatment.
- The RO-treated produced water was free of toxicity when exposed to *Vibrio fischeri*.
- The RO-treated produced water shows potential for reuse as indirect potable water.

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ABSTRACT

This study compared the filtration of produced water using two new and highly hydrophilic NF and RO membranes to assess toxicity removal efficiency in pre- and post-filtration samples for reuse as indirect potable water. The toxicity test was conducted using marine luminescent bacterium *Vibrio fischeri* to monitor changes in the level of light emission during exposure to unknown toxic substances present in the tested pre- and post-filtration samples of produced water. The results show that the quality of water obtained using the NF membrane was toxic at an effective concentration of 13.65% (EC_{50}). However, the performance of NF membrane in rejecting 48% of total organic carbon indicates that it has high potential for use as a pretreatment for the RO membrane in treating produced water because this configuration will decrease the rate of fouling by organics. Toxicity test analysis further revealed that the RO-treated produced water was free of toxicity, whereby 100% of the effective concentration (EC_{50}) caused no effects when exposed to *V. fischeri*. Therefore, converting produced water from a pollution source into a new water resource has been conclusively shown to be readily achievable, especially through the use of a combined membrane system rather than a single membrane.

1. Introduction

When it comes to reusing water from unconventional resources such as industrial wastewater, including produced water from the petroleum industry, the final decision on its suitability depends mainly on compliance with regulatory standards. With regard to available regulations [1], well-known standards for reusing treated sewerage wastewater were established long ago and their applications extended somewhat to regulate several types of light industrial wastewater [2]. In contrast, the absence of standardized regulations for reusing produced water from the petroleum industry has driven international research efforts [3–7] to apply toxicological studies to assure its safety (viz., minimization of health effects), because this water may contain unknown toxic substances. Additionally, current analytical instruments for water quality are governed by detection limits [1], which is evident from some water reuse projects in the United States and some European countries, where lowering such detection limits results in the detection of certain concentrations of target components [1].

Furthermore, currently available standards for drinking water apply only to water originating from conventional water resources for direct use [8], and to unconventional water such as treated wastewater for indirect reuse [2]. The term *indirect reuse* implies that after meeting all the listed parameters in international drinking water standards, the water can be either injected into groundwater recharge for indirect potable reuse or used in surface water augmentation for indirect potable reuse [1]. However, currently, there is only one reported project in Namibia in which direct introduction of treated wastewater is being applied.

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Most other projects on reusing treated wastewater globally practice indirect reuse after applying various types of toxicological study [1]. According to the literature, it has been concluded that one of the weaknesses of conventional toxicity tests lies in the insensitivity of organisms to some detected but unknown toxic substances [9]. Therefore, the emergence of new toxicity tests employs highly sensitive organisms, such as the Microtox toxicity test that uses *Vibrio fischeri*, which is a nonpathogenic, marine, luminescent bacterium that is sensitive to a wide range of toxicants [10]. This test is conducted on vast populations of organisms (up to 10^8 million/run) [11] and it can enable insight into the toxicity levels in particular test waters. Unlike others tests, Microtox is characterized by the requirement for only small samples (a few milliliters), rapidness, cost-effectiveness and reproducibility, all of which makes it one of the most advanced toxicity tests available in this context, and it was therefore used in the current study.

From a regulatory standpoint, in the first part of this study, a comparison of available international drinking water standards was conducted and reported as a starting point. The results showed that produced water treated by NF and RO membranes successfully met the regulatory quality standards for drinking water, except for three parameters related to ammonia, boron and molybdenum. In this second part of study, reported here, toxicity tests were carried out to ensure that (1) filtered produced water is safe and that it will not cause acute health effects from pathogens or toxic substances or (2) if samples were found to be toxic, an attempt to identify the component responsible for toxicity would be carried out. The aim was to identify the suitability of produced water treated by two new, highly hydrophilic (low fouling) NF and RO membranes for reuse as indirect potable water.

2. Materials and methods

Two new hydrophilic membranes were used in produced water filtration processes, namely the RO-BW30 and the NF1 membranes supplied by AMFOR INC®, China. All chemicals, solvents and reagents used were of analytical grade, with high purity. Microtox® diluent, reconstitution solution and freeze-dried bacterial reagent were obtained from SDIX (Newark, DE). Vials of bacterial reagent were kept frozen at −20 °C prior to reconstitution. Produced water sample (B) was obtained in Feb 2012 from the produced water treatment plant in a petroleum refinery owned by the Malaysian Oil and Gas Company. The collected samples were in the last stage of treatment prior to being discharged to the environment. The treatments of produced water processes were carried out using a dead-end stirred cell (Sterlitech, Kent, WA, Model HP4750), with a diameter of 47 mm and an effective membrane area of 14.6 cm^2. Produced water samples were filtered at a pressure of 20 bar, under stirring at 800 rpm. The stirred cell was operated by pressurizing the headspace with nitrogen from a gas cylinder. In every run, a new piece of membrane was mounted at the bottom of the stirred cell and compacted at an elevated pressure until a steady state flux was reached. The flux was then equilibrated by passage of initial permeate for 1 h, and then the desired volume of post-filtration produced water samples was collected for water quality analysis.

Laboratory analysis for produced water assessment and organic compounds extraction were conducted according to the USEPA and APAH methods [12]. Biological oxygen demand (BOD) was measured using a dissolved oxygen meter (YSI 5000, APHA 5210B); total organic carbon (TOC) was analyzed by a TOC analyzer (Aurora model 1030, Aurora Model 1030, OI Analytical, APHA 5310D); and a UV–vis spectrophotometer (Cary50, Varian) was used to analyze chemical oxygen demand (COD) following the APHA 5220D method. The extraction of hydrocarbon compounds were conducted according to USEPA 5030B/USEPA 8260B methods for total petroleum hydrocarbon (C_6–C_9) and volatile organic compounds (VOC) using a GC–MS/purge and trap (model 5973MSD, Agilent Technologies), while total petroleum hydrocarbon (C_{10}–C_{36}) compounds were extracted by gas chromatography with flame ionization detector (GC-FID, model 6890N, Agilent Technologies) based on the methods of USEPA 3510C/USEPA 8015B. The semi-volatile organic compounds were extracted through USEPA 3510C/USEPA 8270C methods using a gas chromatography–mass spectroscopy system (GC–MS, 7890A/5975C Inert, Agilent Technologies). For quality control (QC) in sample analysis, laboratory control samples (LCS), method blanks (MB), matrix spikes (MS), laboratory duplicates (Dups) and surrogates (for all extractions and analyzed organic compounds) were applied in accordance with the National Environment Protection Measures (NEPMs). Results of selected parameters analyzed for QC purposes are presented in Appendix 1.

The toxicity test was conducted using marine luminescent bacterium (*V. fischeri*) to monitor changes in the level of light emission during exposure to unknown toxic substances present in the tested samples of produced water in pre- and post-filtration processes. Acute toxicity assay tests were conducted using a Microtox analyzer (Model 500, SDIX), following the standard procedure described by the Western Canada Microtox Users Committee (WCMUC, 1994) [11]. The toxicity test was performed by rehydrating freeze dried cultures of the (lyophilized) luminescent bacterium *V. fischeri*, supplied by SDIX as the Microtox reagent, containing a population of 1 million organisms, with each organism being less than 1 mm in diameter/vial. According to the WCMUC, the principle of the test is to determine the initial light output of homogenized bacterial suspensions due to disruption of the respiratory process after exposure to a toxicant (in this case potentially present in the produced water sample), which affects the metabolic pathway that converts chemical energy via the electron transfer system of the bacteria to visible light. The effective concentration (EC) of a produced water sample causing a 50% decrease in light production (EC_{50}) at 15 °C after 15 min exposure was calculated by log-linear plotting of concentration (C) versus % light decrease (%Δ), or more precisely by plotting Gamma (Γ) (which is the corrected ratio of the amount of light lost to the amount of light remaining) versus concentration on a log–log graph. Following completion of the plot (manual and computerized), the EC_{50} value is determined by drawing a best-fit line through the points or by connecting points with several line segments when significant deviation from linearity of the log–log plot is observed. Reports of the Microtox assay results in this study are given in "percentage of the original sample of produced water". The final data was generated by the software package provided with the Microtox analyzer, with a 95% confidence limit as an indicator for sensitivity and statistical significance.

3. Results and discussion

3.1. Removal efficiency for toxicity

Three samples of produced water were analyzed using the basic test of the Microtox analyzer to investigate the potential toxicity of raw and treated produced water, using NF and RO membranes. As can be seen in Fig. 1, the findings of this study reveal that the raw produced water was found to be toxic after the *V. fischeri* was exposed to 14.27% (EC_{50}) of raw produced water within 15 min. This was expected because the raw produced water was treated by primary and secondary conventional technologies to meet the environmental standards. This finding agrees with previous studies that exposed produced water (meeting discharge standards) to *V. fischeri* and other organisms, and found various levels of toxicity [3–7].

Regarding produced water treated by NF and RO membranes, a surprising finding was obtained for produced water nanofiltered by NF1, in that it was found to be toxic at an effective concentration of 13.65% (EC_{50}). When this NF water sample was exposed to *V. fischeri*, it led to the death of half a million of the bacterial population. In contrast, RO membrane-treated produced water was found to be free of toxicity, wherein 100% effective concentration (EC_{50}) caused no effects when exposed to *V. fischeri*. The findings of these toxicity tests show that for