Distillation of oil field produced water for reuse on irrigation water: evaluation of pollutants removal and ecotoxicity
Barbara G. Andrade, Vivian T. Andrade, Byron R. S. Costa, Juacyara C. Campos and Márcia Dezotti

ABSTRACT

Desalination is one of the earliest forms of saline water treatment and it is still used throughout the world. In this work, a single-effect mechanical vapor compression (MVC) process was investigated to produce water for irrigation of non-edible cultures from oil-field produced water. Distillation was able to produce a condensate presenting very low amounts of 84 analyzed pollutants. Ecotoxicological assays with Pseudokirchneriella subcapitata algae, Danio rerio fish, lettuce (Lactuca sativa) and earthworm (Eisenia fetida) were performed in condensate. The condensate was non-toxic for all tested organisms, except for P. subcapitata algae that showed some level of chronic toxicity caused by ammonium nitrogen. This toxic effect was confirmed by conducting a series of ecotoxicological assays with condensate samples after ammonia removal (stripping). The condensate presented quality acceptable for irrigation of non-edible crops.

Key words | desalination, ecotoxicology, irrigation, mechanical vapor compression, oil-field produced water, reuse

INTRODUCTION

Physical, chemical and biological properties of oil-field produced waters depend on the geological formation and the geographical location of the oil reservoir. These factors determine the type and concentration of inorganic species in the formation water (silt, salts, scale salts, naturally occurring radioactive materials and metals) as well as water contaminants (hydrocarbons and gases). Sulfate reducing bacteria (due to the existence of sulfate in the formation of water or via the introduction of sulfate through seawater injection) and other anaerobic organisms can also be found in oil-field produced water. Algae and fungi can be introduced in such water, as microbial contaminants, during processing at surface facilities. Furthermore, residual chemicals used for oil production such as corrosion inhibitors, emulsion breakers, scale inhibitors and dissolvers, and biocides reach the water phase rendering the oil-field produced water matrix more complex. Thus, oil-field produced waters are very complex mixtures that present significant variation on volume generated and chemical and biological composition over the life time of producing wells (Bader 2007).

In the primary step of oil processing, water is separated from hydrocarbons, treated to remove part of the dissolved oil (flotation), discharged into the sea, re-injected into the wells (produced water re-injection, PWRI) or reused with or without further treatment. Papers dealing with the treatment of oil-field wastewater are relatively scarce in the literature. In general, several treatment steps are necessary to remove pollutants to a high degree. Ebrahimi et al. (2009) utilized microfiltration (MF), ultrafiltration (UF) (0.05 μm) and nanofiltration (NF) ceramic membranes for produced water treatment. Oil removal up to 99% and total organic carbon (TOC) removal up to 39% were achieved. Ebrahimi et al. (2010) investigated an oil field
produced water treatment that consists of a pre-treatment step utilizing microfiltration (0.1 and 0.2 μm pore size filters) and/or a simulated batch dissolved air flotation (DAF), and a multistage post-treatment step utilizing cross-flow ultra (0.05 μm pore size and 20 kDa molecular weight cut-off filters), and nanofiltration (1 and 0.75 kDa MWCO filters). Total oil removal was up to 99.5% and TOC removal reached 49%. Melo et al. (2010) assessed the quality of the produced water stream after a reverse osmosis desalination process in terms of physicochemical characteristics influencing reuse of the water for irrigation or other beneficial uses. The pilot-scale RO/NF unit effectively decreased conductivity and total dissolved solids (TDS) in the produced water under consideration and reduced the concentration of several water quality parameters considered important for beneficial reuse.

Despite the concern about energy consumption associated with distillation, this technique is finding application for the treatment of oil-field wastewater. There are currently about 14 evaporators under operation or construction, or in various stages of delivery in Alberta (Canada) and overseas. Falling film vertical tube evaporators have been utilized to recover and remove oil from water. The Alberta evaporators were very effective in removing hydrocarbons, volatile organic acids, hardness and ions like lithium, iron and copper (Heins 2006).

The quality of the condensates from the evaporation process is sufficiently high that they can be considered adequate water for reuse purposes. Scarcity of water is very common in many countries and the demand for water for agriculture is very high. For instance, in Brazil, it represents more than 70% of the total national demand of water. In such a context, water reuse for agriculture should be pursued.

Preliminary experimental work showed that it is possible to produce water for reuse from oil-field produced water. However, the required treatment should be very effective because salinity and other parameters such as TDS, heavy metals and soluble organics can be associated with produced water toxicity (Allen & Robinson 1993). The environmental risk of that water should be assessed by performing bioassays with species from different trophic levels, a necessary procedure to complement physical–chemical information (Eon et al. 2007). Due to high variability in chemical composition, produced water toxicity can show a wide range of results (Patin 1999). The behavior of a single toxicant can only be fully understood if it is taken into account that physical and biochemical properties can change, mainly as a result of interactions with other substances found in the water matrix (Pokarzhevskii & Van Straalen 1996).

In many countries, there are no specific regulations about the quality required for water reuse in agriculture. Considering the risks associated with that reuse application, toxicity is a key parameter to define a given level of water quality and, in such a case, assays should be conducted with different organisms. This paper aims to describe and validate a process to treat oil-field produced water and achieve irrigation water quality standards for non-edible cultures (e.g. oleaginous sunflower and castor beans for biodiesel production and ornamental sunflower and pineapple). The oil-field produced water was treated by MVC evaporation. The condensate water is intended to be used for soil irrigation in regions close to the sites of oil exploitation.

The specific aims of this paper are: (i) investigate the performance of mechanical vapor compression to remove pollutants of oil-field produced water; (ii) characterize the condensate by chemical analyses and ecotoxicological assays; (iii) evaluate acute and chronic effects of the condensate water using organisms from different trophic levels, and (iv) correlate possible toxic effects with the presence of some pollutants.

**MATERIAL AND METHODS**

**Mechanical vapor compression**

The produced water used in the present work came from fields on shore exploited by the Brazilian company Petrobras. Produced water used in the evaporation process was collected downstream from the flotation system. Samples were transported in drums under refrigeration to Jandira city (São Paulo State, Brazil) where experiments were conducted. A pilot scale mechanical vapor compression evaporator (Destimat, LE 1400, supplied by Brasquip Ambiental S.A.) fed with a flow-rate of 0.1 m³/h was...
employed to remove excess salts, other minerals, metals and dissolved hydrocarbons from the produced water in order to obtain irrigation water to non-edible cultures. The evaporative system was used and operated with pressure and temperature ranging from 44.7 to 45.9 kPa and 84.5 to 85.1 °C, respectively. Figure 1 shows a schematic view of the MVC evaporator.

Characterization of oil-field produced water and condensate samples

Physical and chemical analyses

The oil-field produced water and the respective condensate were characterized three times corresponding to different sampling campaigns. Samples were collected over different periods of time to deal with variation in the properties of the oil-field produced water fed to the evaporation system. Eighty-four compounds, including 38 polycyclic aromatic hydrocarbons (PAHs), were determined in produced water and in condensate. Most of the compounds were determined according to established analytical procedures (APHA et al. 2005). Toxicity of the condensate was determined using four different organisms. Toxicity was assessed by monitoring effects on the germination of the seeds and root growth of Lactuca sativa; survival of the earthworm Eisenia fetida and the fish Danio rerio; avoidance assay with the earthworm E. fetida and cell growth of the algae Pseudokirchneriella subcapitata. The pH of the samples (8.4–8.7) was previously adjusted in all assays that were performed and the minerals were reconstituted for the Danio rerio and P. subcapitata bioassays according to the methods described below.

Ecotoxicological assays

Earthworm Eisenia fetida assays

Adult earthworms between 300 and 500 mg with fully developed clitella were used in the experiments. The earthworms were purchased from Arborium Vermiculture, Rio de Janeiro, and acclimatized for 2 months under laboratory conditions in the same soil in which they were created. Soil was changed every 3 weeks in order to ensure the
availability of nutrients. Sensibility assays were performed every month. A reference soil, for all the assays, was prepared by mixing 70 and 20% kaolinite clay and 10% coconut fiber. The artificial soil pH was adjusted to 6.0 ± 0.5 according to OECD protocols (OECD 2004). Earthworms were placed on the artificial soil with moisture adjusted to 35–45% of the basic substrate dry weight by adding deionized water. All containers were kept at 22 ± 2 °C under continuous illumination (400–800 lx). The pesticide 2-chloroacetamide was used as positive control and the LC(1)50 in this test was between 20 and 80 mg/kg in artificial soil, confirming earthworms sensibility.

**Acute toxicological assays**

Condensate or deionized water were added to the artificial soil to adjust moisture content to 35% w/w. Samples were maintained at rest for 24 h to achieve the necessary consistency. Earthworms were placed on wet filter paper allowing the gut content to be fully empty in 24 h. Earthworms were randomly selected, cleaned and weighed in groups of ten for each assay. Adult earthworms were placed singly on the top surface. Containers were covered with transparent perforated lids and kept in the incubation chamber at constant temperature (22 ± 2 °C) under illumination (400–800 lx). Earthworms were separated from the test soil, counted, purged for 24 h, cleaned with distilled water and weighed on the 7th and the 14th days of exposure.

**Acute toxicological assay on the contact paper**

Acute toxicological assays on the contact paper were performed according to the method described by OECD (1984). Earthworms were placed on wet filter paper covered with wet gauze to clean the gut content and kept under such conditions for 24 h. Each earthworm (whose gut content has been purged, washed, surplus water absorbed on filter paper) was weighed and introduced into a beaker (50 mL), the surface of which was covered with filter paper moistened with 1.5 mL of test solution and closed with perforated plastic film. For each test solution ten organisms were used and the assays were made in quadruplicate. The containers were kept in a climatic chamber, in the dark, at a temperature of 20 ± 2 °C and aerated by saturated air. The lethality was assessed after 48 and 72 h of contact with the damped paper.

**Avoidance assay**

The avoidance assay was performed as described by ISO (2008). The plastic containers were divided in two equal sections by drawing a line and labeling them with the name of the corresponding treated soil. A piece of plastic was used as the container divider. The moistened soils (one soil damped with condensate and the other with distilled water), covered with a plastic film, were stored overnight and then introduced into the corresponding section. The mass of each soil was 250 g (dry wet). Four replicates were made for each sample. After introduction of soils, the container divider was removed and ten adult earthworms were added on the top of the dividing line. Assays were conducted in a climatic chamber at 22 ± 2 °C under light (from 400 to 800 lx) for 48 h. In accordance with the Draft Guideline for the Earthworm Avoidance Text (ISO 2008), the habitat function of soils is considered to be limited if, on average, more than 80% of worms are found in the control soil.

**Lactuca sativa assay**

The procedure used in this assay was recommended by ASTM (2009). Prior performing toxicity assays samples were assayed with boron acid to check test procedure reliability. Reis et al. (2007) evaluated the local availability of 29 species of lettuces over a whole year. It was verified that the species locally named ‘Baba de Verão’ is always found on the market and can be used in assays. The *L. sativa* method on filter paper requires 120 h and assesses the inhibition of seed germination and root + hypocotyl elongation. Lettuce seed germination assays were made in triplicate. Seeds were examined visually and selected manually to be used in the experiments. Seed germination assays were performed on moist filter paper (Whatman no. 1) in 9 cm diameter Petri dishes and maintained at 24 ± 2 °C in the dark. Four replicates with 50 seeds each were made for each germination test (previously moistened with 2.0 mL of sample). Seeds were considered germinated when the radicle emerged.
**Danio rerio assay**

*Danio rerio* assays were performed in accordance with the methodology proposed by the Brazilian Association of Technical Standards (ABNT 2004). Toxicity assays were supervised for 6 days and no food was provided during that period. Four replicates were made for each treatment; ten fish (aged 4–12 months) were placed in 2,000 mL glass aquaria containing the negative control (reconstituted water) or condensate (pH adjusted to 6.5 ± 0.5 at 25 ± 2 °C and aerated for at least 12 h to saturate dissolved oxygen and pH stabilization). Tests were carried out in a climatized room with a light/dark cycle of 12/12 h for all treatments. The number of dead fish was recorded after 24, 48, 72, 96, 120 and 144 h of static assay.

**Pseudokirchneriella subcapitata algae assays**

Cells were inoculated from pre-cultures in the aseptic Oligo culture environmental set-up 5 days before the experiment, according to the guideline NBR (2005). Five concentrations of each condensate sample were tested (25, 50, 75, 87.5 and 100%). The Oligo culture environment was used as control. Both control and assay flasks were first autoclaved (121 ± 1 °C) for 15 min and inoculated with 10^4 cells mL^-1, as initial concentration. All flasks were incubated (enhanced irradiation between 4,500 and 5,000 lx) on a shaking table (Quimix®, model Q225M) at 100 and 175 rpm under continuous illumination with Philips TL-D 38W aquarelle fluorescent tubes for 4 days (96 h). Triplicate measurements were made and algal biomass was measured by optical microscopy. Cell count was performed in a Neubauer’s chamber using a phase-contrast microscope (Hund Wetzlar, model H500). Growth inhibition (biomass) of the algae cells was used as the end-point of the bioassay.

**Calculations and statistical analysis**

Analysis of variance (ANOVA) was used to analyze raw data to assess the concentration at which significant differences were found in the number of species exposed to distilled water (control). The level of significance was accepted at p ≤ 0.05. Also, a pairwise *T*-student and *F*-test were used to determine the existence of differences between the number of species exposed to the control and the condensate for each concentration. All results are presented as mean ± standard error. Calculations were performed using the statistical software package Statistica 7.0. EC(I)_{50} and values were calculated by using the Linear Interpolation Method (USEPA 1995) for *L. sativa* and *P. subcapitata* assays. LC (I)_{50} or EC(I)_{50} values for *D. rerio* were determined using the Trimmed Spearman–Karber method, version 1.5 (USEPA 1999). All the assays with *D. rerio* were considered valid if mortality in the control assay was ≤5%. The NOEC was the highest concentration tested that did not significantly differ from the control (risk α = 0.05).

**RESULTS AND DISCUSSION**

**MVC performance for pollutant removal**

In this work a pilot plant was used for the purpose of removing pollutants and toxicity. The Destimat LE 1400 evaporative system was able to remove a very high level of pollutants. However, the energy consumption by the pilot unit was 70 kWh/m^3. Process improvements to reduce energy consumption were not performed.

The literature indicates that MVC conventional systems can operate with specific power consumption between 7 and 12 kWh/m^3 (Buros 2000). A falling film type MVC evaporator with horizontal heat transfer tubes required between 16.9 and 18.5 kWh/m^3 (Hoffman 1981; Koren & Nadav 1994). Thus, in an optimized evaporative system it would be possible to decrease the energy consumption to the range of values reported in the literature. In comparison with reverse osmosis (RO), a competitive technology, MVC consumes larger amounts of energy.

Typical values such as 18 kWh/m^3 for MVC and 5 kWh/m^3 for RO are published elsewhere (Al-bahou et al. 2007). It should be mentioned that there are concerns about RO operation with very high saline wastewaters such as oil-field wastewater, since scaling and hydrocarbons can cause operation problems and reduce membrane life-time.

As already discussed, as there is no specific legislation for the application of treated industrial wastewaters in irrigation in several countries, the strictest legislation for the utilization of river waters for irrigation has been adopted.
Table 1 | Chemical and physical characteristics of oil field produced water and condensate samples obtained in the MVC process and Conama standards

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>PW 1 (mg/L)</th>
<th>PW 2 and 3 (mg/L)</th>
<th>Condensate 1 (mg/L)</th>
<th>Condensate 2 (mg/L)</th>
<th>Condensate 3 (mg/L)</th>
<th>Conama 396 (mg/L)</th>
<th>Conama 357’s class 3 (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>mg/L</td>
<td>0.11</td>
<td>0.203</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>Ammoniaca nitrogen</td>
<td>mg/L</td>
<td>119</td>
<td>99</td>
<td>20</td>
<td>45</td>
<td>52</td>
<td></td>
<td>1.0 to pH ≥ 8.5</td>
</tr>
<tr>
<td>Arsenic</td>
<td>mg/L</td>
<td>0.006</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>5</td>
<td>0.033</td>
</tr>
<tr>
<td>Barium</td>
<td>mg/L</td>
<td>7.7</td>
<td>12.6</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>Beryllium</td>
<td>mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Bicarbonate alkalinity</td>
<td>mg/L</td>
<td>150</td>
<td>1,232</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOD</td>
<td>mg/L</td>
<td>350</td>
<td>1,435</td>
<td>9.2</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boron</td>
<td>mg/L</td>
<td>11.9</td>
<td>20.8</td>
<td>0.07</td>
<td>0.081</td>
<td>0.057</td>
<td>0.5</td>
<td>0.75</td>
</tr>
<tr>
<td>Cadmium</td>
<td>mg/L</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Calcium</td>
<td>mg/L</td>
<td>199.5</td>
<td>786</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Chlorine</td>
<td>mg/L</td>
<td>3,237</td>
<td>26,473</td>
<td>0.96 ± 0.01</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>100–700</td>
<td>&lt;250</td>
</tr>
<tr>
<td>Chromium total</td>
<td>mg/L</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>0.1 (Cr&lt;sup&gt;3+&lt;/sup&gt; + Cr&lt;sup&gt;6+&lt;/sup&gt;)</td>
<td>0.05</td>
</tr>
<tr>
<td>COD</td>
<td>mg/L</td>
<td>60.94 ± 0.37</td>
<td>97.87 ± 2.53</td>
<td>8.09 ± 0.81</td>
<td>10.87 ± 0.06</td>
<td>10.87 ± 0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>mg/L</td>
<td>&lt;0.005</td>
<td>0.0264</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.2</td>
<td>0.013</td>
</tr>
<tr>
<td>Cyanide</td>
<td>mg/L</td>
<td>0.05</td>
<td>&lt;0.1</td>
<td>&lt;0.005</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>Fluoride</td>
<td>mg/L</td>
<td>&lt;5</td>
<td>1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>1</td>
<td>1.4</td>
</tr>
<tr>
<td>Hexavalent chromium</td>
<td>mg/L</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxide alkalinity</td>
<td>mg/L</td>
<td>0</td>
<td>&lt;5</td>
<td>9</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>mg/L</td>
<td>1.18</td>
<td>1.1</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.049</td>
<td>5</td>
</tr>
<tr>
<td>Lead</td>
<td>mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>5</td>
<td>0.033</td>
</tr>
<tr>
<td>Lithium</td>
<td>mg/L</td>
<td>0.67</td>
<td>0.498</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>mg/L</td>
<td>2.24</td>
<td>528</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manganese dissolved</td>
<td>mg/L</td>
<td>0.32</td>
<td>0.493</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>mg/L</td>
<td>0.0001</td>
<td>&lt;0.00006</td>
<td>&lt;0.00005</td>
<td>0.00009</td>
<td>0.00011</td>
<td>0.002</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Nickel</td>
<td>mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>2</td>
<td>0.025</td>
</tr>
<tr>
<td>Nitrate</td>
<td>mg/L</td>
<td>&lt;5</td>
<td>&lt;50</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Nitrite</td>
<td>mg/L</td>
<td>19.6</td>
<td>10</td>
<td>0.06</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>7.1 ± 0.1</td>
<td>6.9 ± 0.1</td>
<td>8.7 ± 0.1</td>
<td>8.4 ± 0.1</td>
<td>8.4 ± 0.1</td>
<td>6–9</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/L</td>
<td>0.3612</td>
<td>0.257</td>
<td>0.00045</td>
<td>0.0928</td>
<td>0.075</td>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>mg/L</td>
<td>3.51</td>
<td>8.2</td>
<td>0.02</td>
<td>0.032</td>
<td>0.032</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td>mg/L</td>
<td>242.2</td>
<td>243</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sedimented solids</td>
<td>mL/L h</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selenium</td>
<td>mg/L</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>0.02</td>
<td>0.05</td>
</tr>
</tbody>
</table>

(continued)
as the benchmark. In this sense two local regulations were taken as references: Resolution 357 class 3 and Resolution 396 (article 16) for metals, bicarbonate alkalinity, chlorine, fluorite, nitrate, nitrite, pH, phenols, sulfate, total dissolved solids, benzene, ethylbenzene, \( m/p \)-xylene and \( o \)-xylene. The two resolutions were established by the National Environmental Council (CONAMA, Brazil).

The regulation standards cited above are also shown in Table 1, where available. In condensates only ammonium nitrogen and volatiles (benzene and toluene) presented concentrations above the standards (Table 1). Condensate 1 presented toluene and ammonium nitrogen concentration of 49.5 \( \mu \)g/L and 20 mg/L, respectively, Condensate 2 presented benzene and ammonium nitrogen of 7.8 \( \mu \)g/L and 45 mg/L, respectively, and Condensate 3 presented benzene, toluene and ammonium nitrogen of 7.9 \( \mu \)g/L, 12.8 \( \pm \) 0.05 \( \mu \)g/L and 52 mg/L, respectively. Most of the analyzed substances and parameters were removed at a very high level by the MVC process. In terms of physical and chemical parameters, as shown in Table 1, the condensate presented was high quality, allowing its possible reuse for irrigation.

Among organic toxic substances, BTEX (benzene, toluene, ethylbenzene and xylene) and PAHs are considered to be those of most concern. PAHs (16), shown in Table 1, represent the total concentration of 16 polycyclic aromatic hydrocarbons listed as priority pollutants by the US Environmental Protection Agency (US-EPA). In Figure 2, PAHs concentrations (expressed as ng/L) of the three condensate samples (1, 2 and 3) are shown. The ratios between priority PAHs and total PAHs (PAH(16)/PAH total) in condensate samples 1, 2 and 3 were 19, 17 and 22\%, respectively.

The results presented in Figure 2 reveal that priority polycyclic aromatic hydrocarbons, found in low concentrations in the produced water (\( \mu \)g/L), were removed to a high extent by the MVC process. Furthermore, removal
efficiencies were closed in the three replicated experiments, indicating process performance uniformity.

**Toxicity removal by MVC process**

Regarding toxicity, the main contributors to acute toxicity (short-term effects) of produced water are aromatic and phenolic fractions of the dissolved hydrocarbons, as observed by Frost et al. (1998). In addition, particularly with deep offshore operations, the existing separation equipment cannot remove enough oil and grease to meet regulatory limits. In such cases chemicals are used, but some of these chemicals can be toxic. The impact of produced water and its constituents in the short term depend largely on the concentration of the pollutants at the discharge point. Actual impact will depend on the biological effect (e.g. toxicity, bioaccumulation, oxygen depletion) of produced water at the concentrations and exposure times typical of the real environment conditions (Cline 1998).

**Earthworm *Eisenia fetida* assays**

After confirming earthworms' sensibility in soil using 2-chloroacetamide in the range of 20 and 80 mg/kg (ISO 11268-1/2006), acute toxicity assays were performed. In all assays, no worm died or escaped during the exposure period. Figure 3(a) shows the mean earthworms weight fluctuation (%) determined after 14 days of exposure to soils irrigated with deionized water (control) and irrigated with condensate. The following mean values and standard deviations were obtained: 97.5 ± 0.8 (control 1), 97.2 ± 0.6 (condensate 1), 87.7 ± 2.2 (control 2 and 3), 87.8 ± 2.4 (condensate 2) and 90.0 ± 1.9 (condensate 3). The weight of the earthworms kept in soils irrigated with condensate did not present significant differences in relation to the control data (*p* < 0.05). Therefore, statistical analysis (ANOVA) showed that the three condensate samples did not promote change on the weight of the tested organisms.

Results of the behavioral experiments of earthworms in soils irrigated with condensate 1, 2 and 3 after 48 h of exposure to condensate are shown in Figure 3(b). The percentage of earthworms in the container section irrigated with condensate was fairly higher at 20%, a limit value established by ISO guideline (ISO 2008). Since there was no need for adjustments in water characteristics to ensure the survival of organisms during the assays (only the moisture was adjusted to approximately 35%, as required for testing), the results showed no impact of contaminants remaining in the condensate samples to an important soil organism, such as the earthworm.

The experiments with condensate 2 and 3 were conducted for a long time (120 h), far beyond the value

---

**Figure 2** Concentrations of PAHs (ng/L) in the three condensate samples (1, 2 and 3). N: Naphthalene; 2MN: 2-Methylnaphthalene; 1MN: 1-Methylnaphthalene; C2N: C2-Naphthalene; C3N: C3-Naphthalene; C4N: C4-Naphthalene; A: Acenaphthene; Ace: Acenaphthyene; Flu: Fluorene; CFu: C1-Fluorene; C2Fu: C2-Fluorene; C3Fl: C3-Fluorene; DBT: Dibenzo thiophene; C1DBT: C1-Dibenzothiophene; C2DBT: C2-Dibenzothiophene; C3DBT: C3-Dibenzothiophene; Phen: Phenanthrene; C1Phen: C1-Phenanthrene; C2 Phen: C2-Phenanthrene; C3Phen: C3-Phenanthrene; C4Phen: C4-Phenanthrene; Anth: Anthracene; Ft: Fluoranthene; Py: Pyrene; C1Py: C1-Pyrene; C2Py: C2-Pyrene; BaA: Benz(a) anthracene; Chry: Chrysene; C1Chry: C1-Chrysene; C2Chry: C2-Chrysene; Bnf: Benzol[b]fluoranthene; Bnf: Benzol[k]fluoranthene; BaPy: Benzo[a]pyrene; Per: Perylene; Fpy: Indeno[1,2,3-cd]pyrene; DbahA: Dibenzo[a]anthracene; BghiP: Benzo[g,h,i]perylenec. Detection limit (DL) = 0.6 ng L⁻¹, Quantification Limit (QL) = 2.0 ng L⁻¹.
established by the guideline (ISO 2008). The average percentages of earthworms in soils irrigated with condensate 2 and 3 (12 assays) were 72.50 ± 4.63 and 80.83 ± 3.98%, respectively. In all tests the largest number of earthworms was found between 48 and 120 h in soil irrigated with condensate.

Table 2 shows lethality results obtained on filter paper damped with condensate and control assay results using ten organisms for test solution. Earthworms had 100% survival after 72 h of exposure to condensate, indicating that condensate samples were not toxic to E. fetida. Ten percent lethality observed in assays is in accordance to the limit value accepted by the adopted method.

The results of lethality assays give an important response of organisms exposed to toxic substances because in those assays organisms are forced to live on the paper filter during the whole test period. Organisms cannot escape from the test environment. The same does not occur in the avoidance test.

**Lactuca sativa assay**

There is no inhibition of seed germination during the exposure of the condensate samples (1, 2 and 3) without dilution. Results of *L. sativa* root elongation are shown in Figure 4. No significant reduction of growth during the exposure to condensate in different concentrations (50.0, 66.7, 83.3 and 100% w/w) was observed in comparison with the control sample a (p < 0.05).

Condensate 2 and 3 results were similar to those obtained for condensate 1. Root elongation of *L. sativa* exposed to condensate (100% w/w) results ranged from 4.3 to 4.6 cm (condensate 2); 4.2 to 4.4 cm (condensate 3) and 4.2 to 4.8 cm (control). No significant differences on root elongation were observed for these two condensate samples.

<table>
<thead>
<tr>
<th>Control 1</th>
<th>Control 2</th>
<th>Control 2</th>
<th>Condensate 2</th>
<th>Condensate 3</th>
<th>Control 3</th>
<th>Condensate 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>48 h</td>
<td>72 h</td>
<td>48 h</td>
<td>72 h</td>
<td>48 h</td>
<td>72 h</td>
<td>48 h</td>
</tr>
<tr>
<td>Lethality</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total lethality</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table 2** | Lethality in experiments with condensate (1, 2 and 3) and in control experiments. Ten organisms were used in each assay.
Danio rerio assay

To perform assays the condensate was mineralized after the desalting process promoted by the evaporative process, according to the adopted experimental procedure (ABNT 2004). The reconstituted water presented 32.4 mg/L alkalinity and 42.0 mg/L CaCO₃ hardness and dissolved oxygen (DO) concentration higher than 6.0 mg/L.

No lethality was observed in the control (reconstituted water) and condensate (1, 2 and 3) samples (not diluted) in four assays performed (48 and 144 h of exposure). The NOEC (non observed effect concentration) values, NOEC-48h and NOEC-144h were 100%, and consequently the toxic unit (TU) was 1. These results allow us to conclude that D. rerio was not sensitive to condensate samples (the condensate samples were remineralized before testing).

Pseudokirchneriella subcapitata assays

The response of the tested organism exposed during 96 h to different concentrations of condensate is shown in Figure 5. Up to a condensate concentration of 87.5%, no significant effect was observed on the cell count for all tested samples condensate 1, 2 and 3 in relation to control. However, when the condensate concentration was 100%, a significant decrease on cell count was observed ($p < 0.05$). P. subcapitata was the most sensitive among the assayed organisms.

It is always difficult to establish relationships among contaminants and ecotoxicity. This is particularly true for industrial wastewaters that, even treated to a greater extent, still present a large number of pollutants at different concentrations. In addition, interactions among these pollutants render the interpretation of toxicity results difficult. Despite these difficulties, we made an attempt to clarify the possible role of condensate pollutants on ecotoxicity. As shown, toxic effects of condensate wasters was only observed for one of the tested organisms (P. subcapitata).

Ammonium nitrogen and volatile compounds (benzene and toluene) were the only compounds found in concentrations above CONAMA standards in the three condensate samples. Since a step of sample sterilization is required in the assay of algae growth, volatile compounds could be removed in that step and the toxic response observed for 100% condensate could not be caused by these substances. Thus, ammonium nitrogen remains a suspect substance for causing ecotoxicological effects on P. subcapitata.

Although total PAHs were removed to a greater extent by the evaporative process, residual levels (2.1–7.5 μg/L) were observed in the condensate samples. Pérez et al. (2001) determined the occurrence of 16 US EPA PAH in the sewage sludge and their contribution to acute toxicity in the luminescence of Vibrio fischeri (ToxAlert bioassay). The level of each PAH found in the sewage sludge samples varied from 17 to 2,030 μg/kg and the total 16 PAH varied from 1,019 to 5,520 μg/kg in the sewage sludge sample. In all samples examined phenanthrene was the most prominent compound, with EC₅₀ of 3.56 μg/mL. The EC₅₀ varied from 159 to 720 μg/mL for extracts of sludge. For Aquacheck (reference sewage sludge sample) containing 2,859 μg/mL of total PAH the EC₅₀ was 750 μg/mL. Therefore, the PAH concentration found in the condensate samples in this work (0.4–1.3 μg/L) is probably not toxic for V. fischeri.

Soil samples from a former cookery site polluted with PAHs were assessed for their toxicity. The total concentration of the 16 PAHs listed as priority pollutants by the

Figure 5 | P. subcapitata cell count results. Cells were exposed to different condensate concentrations (% w/w) for 96 h. (a) condensate 1, (b) condensate 2, (c) condensate 3.
US Environmental Protection Agency (US-EPA) was 2,634 ± 241 mg/kg dw in contaminated soil sample. EC values were expressed as percentage water extract in the test media (v/v). *P. subcapitata* algal growth (EC$_{50}$-3d = 2.4 ± 0.2% of the water extracts) was severely affected. The toxicity of the soil samples was assessed on the survival and reproduction of earthworms (*E. fetida*) and on the germination and growth of higher of *L. sativa* plants. The EC$_{50}$ values were expressed as percentage contaminated soil (w/w%) and indicated severe effects on reproduction of the earthworm *E. fetida* (EC$_{50}$-28d = 18% and EC$_{50}$-56d = 8%, based on cocoon and juvenile production, respectively). Only *L. sativa* plant growth was inhibited (EC$_{50}$-17d = 26%) while germination was not (*Eon et al.* 2007). The *P. subcapitata* alga was the organism most severely affected between the organisms exposure to soil polluted with PAHs. According to *Eon et al.* (2007), the PAHs caused chronic toxicity to the *P. subcapitata* with a concentration of 63.2 mg/kg (EC$_{50}$-3d), which is higher than the concentrations found in condensate samples (from 0.40×10$^{-3}$ to 1.34×10$^{-3}$ mg/kg) in this work. Therefore, the condensate toxicity for the *P. subcapitata* alga is probably not due to the presence of PAHs.

Considering that benzene, toluene and PAHs were not responsible for the toxic effects to *P. subcapitata*, additional experiments were performed to confirm ammonium nitrogen toxicity. In the first one, condensate sample was submitted to air stripping (pH > 11) for 20 h, in order to remove ammonia before the ecotoxicity assay. In the second experiment, different levels of ammonium nitrogen were incorporated in the water used in the control experiment to verify if concentrations below 20 mg/L (the minimum value observed in distillates, Table 1) were harmful to *P. subcapitata*. The results shown in Figure 6(a) reveal that there is no statistical difference between the inhibition of *P. subcapitata* growth in condensate (after stripping, ammonium nitrogen concentration was <1 mg/L) and in the control medium (Oligo culture environmental). Figure 6(b) shows the inhibition of *P. subcapitata* growth when algal cells were exposed to different ammonium nitrogen concentrations (ratio 2). Concentrations over 5 mg/L of ammonium nitrogen caused severe inhibition of algal growth.

It is interesting to note that no inhibition of algal growth was observed in assays using 87.5% of condensate (Figure 5). In those assays the ammonium nitrogen concentrations, based on data shown in Table 1, were 17.5, 39.4 and 45.5 mg/L for condensate 1, 2 and 3, respectively. These values are higher than the growth inhibition limit of 5 mg/L observed in the control experiment water. The large number of substances found in low concentrations in condensate constituted a complex matrix, which was able to attenuate the toxic effects of ammonium nitrogen to *P. subcapitata*.

**CONCLUSIONS**

Desalination of oil-field produced water presenting high total dissolved solids contents (>40,000 mg/L) was very effective for the removal of pollutants. The pilot MVC evaporative system used in the present work required 70 kW/m$^3$ of condensate. However, by improving energy utilization it would be possible to reduce energy consumption to 18 kW/m$^3$. This value was already attained in MVC systems and was reported in the literature. If a low cost energy
source is available, turbine exhaustion gas is recovered or renewable energy (solar, wind, etc.) is used, the implementation of MVC systems to desalinize very salty waters could be an interesting technical alternative.

The condensate obtained by evaporative process from oil-field produced water presented a quality acceptable for reuse, in particular for irrigation of non-edible crops. Ecotoxicological results showed no toxicity for *D. rerio*, *L. sativa* and *E. fetida* and signs of chronic toxicity to *P. subcapitata*.

Ammonium nitrogen and volatiles (benzene and toluene) in condensate samples presented concentrations above local standards for utilization of river water for irrigation purposes. Assays performed with the water used in the control experiments and with condensate samples previously submitted to air stripping revealed that toxicity to *P. subcapitata* can be attributed to ammonium nitrogen.

**ACKNOWLEDGEMENTS**

This work was supported by the Petrobras, Brazilian Agency (CAPES) and Brazilian Research Council (CNPq).

**REFERENCES**

ABNT (Brazilian Association of Technical Standards) 2004

Aquatic Ecotoxicology – Acute toxicity – Method of Assays with Fishes. NBR 15088, Rio de Janeiro, Brazil.

ABNT (Brazilian Association of Technical Standards) 2005

Aquatic Ecotoxicology – Chronic Toxicity – Test with Green Algae (Chlorophyceae). NBR 12468, Rio de Janeiro, Brazil.


ASTM (American Society for Testing and Materials) 2009


sludge and their contribution to its toxicity in the ToxAlert® 100 bioassay. Chemosphere 45, 705–712.


First received 9 May 2011; accepted in revised form 10 October 2011