The Use of Reed bed Technology for Treating Oil Production Waters in the Sultanate of Oman

Abdullah Al Mahruki (SQU, College of Agricultural and Marine Sciences, SWAE, Oman); Brian Alloway (Arnolds Close, Kingston, Kingsbridge, Devon); and Heiko Patzelt (Sultan Qaboos University, College of Science, Oman).

Introduction

The environmental challenges facing oil production in Oman are not exceptional compared with other countries in the world. In particular they include: waste from drilling activities, oil transport, spillage and leakage and proper handling and disposal of the associated leftovers or by-products from oil. This is especially true when these activities have to be synchronized in an environmentally sound approach and in compliance with legislation. Oil production in Oman is associated with large volumes of water (oil production water, OPW), where the ratio of water to oil can be as high as 1:6 after preliminary separation. The volume of water currently produced by PDO is 600,000 m$^3$ d$^{-1}$ and is predicted to rise to 900,000 m$^3$ d$^{-1}$ by 2013. Only 40% of the production water is utilised for the maintenance of the reservoir pressure by injection while the remainder is disposed of into shallow aquifers (SWD) and into deep aquifers (DWD).

Over the last three decades, both methods of disposal progressively became unacceptable for various environmental reasons. One of the major concerns was the possibility of contaminating the precious exploitable ground water resources with toxic organic and inorganic contaminants. This stipulated the prime need to re-assess disposal practices and evaluate potential methods of treatment and utilisation. PDO has therefore set up a water management team, which endorsed a strict water management strategy based on the following principles: minimise production water during oil extraction, maximise its reuse, gradually phase-out shallow disposal, return waters to their producing reservoirs, and dispose only to aquifer formations that have a salinity over 35 g L$^{-1}$.

Ultimately, PDO’s care for the environment was thus reflected by its policy to invest in various research projects aimed at better utilization of the production water. Water treatment and reuse plans were therefore developed, driven by the concept of “Greening the Desert” using reed beds to treat the production water. The objective of this paper is to evaluate the potential of reed bed technology for the treatment of oil production waters in Oman.

Overview of reed beds biotechnology

In recent years, there has been increasing interest in the application of environmental biotechnologies due to their potential in the removal of organic and inorganic contaminants from soil, water and wastewater. For instance, reed beds have been successfully implemented to treat water, wastewater and effluent from different sources including household,

Abstract

The safe and environmentally benign disposal of oil production water is of major concern in the Sultanate of Oman. Petroleum Development Oman (PDO) is currently producing 600,000 m$^3$ d$^{-1}$, and the volume is predicted to rise to 900,000 m$^3$ d$^{-1}$ by the year 2013. This water is contaminated with petroleum hydrocarbons (10-800 mg L$^{-1}$), traces of phenols, emulsifiers and a wide range of metals at variable concentrations; it also shows a relatively high (12 dS m$^{-1}$) electrical conductivity. The currently adopted methods of disposal into shallow and deep aquifers are no longer meeting the environmental legislation.

In this study, the use of reed bed technology for the treatment of oil production water was evaluated and insights into its associated chemical and biological processes in contaminant removal are presented. This reed bed system is constructed in Nimr concession site of PDO to treat 3000 m$^3$ of production water per day.

The results obtained demonstrated that inorganic and organic contaminant concentration was significantly reduced in the effluents. Metal concentration decreased by 78% for Al, Ba, Cr, Cu and Zn, up to 40% for Fe, Li, Mn, Pb, As, Cd, Co, Mo, Ni, Se, Ti and V. The total hydrocarbon concentration was reduced by an average of 96%. The removal mechanisms were attributed to the complex interactions between substrate, macrophytes and the associated microorganisms. Aerobic processes seem to dominate the system over the anaerobic ones in the removal of both groups of contaminants.

In model pot experiments, a sandy loam soil matrix and a surface flow regime proved superior to a pure loam matrix with subsurface flow of Nimr. The latter modification may render existing reed bed decontamination sites even more effective.
agricultural, industrial and mining effluents contaminated with toxic organic contaminants and heavy metals. Environmental biotechnology, as such, has therefore been described as environmentally sound, cheaper than conventional systems and sustainable. The most recently reviewed literature on phytoremediation by Henry, revealed that the interaction between the soil matrix, plants and microbial population brings about many processes responsible for the clean up of contaminants. These include: phytoretrieval, phytostabilization, rhizofiltration, phytovolatilisation. Henry therefore described this innovative technology as a “green revolution”.

Currently, treating wastewaters at their source is known as point source treatment. It has been widely implemented and its use has grown very rapidly. The technology is more in line with the philosophy of environmentally sound approaches to sustainable development. It has become a topic of increasing interest around the world; governmental regulators and scientists in different countries have come to appreciate the multiple benefits of this technology. The hundreds of operating systems treating a wide range of liquid wastes throughout the world implies that the advances in adapting this technology are likely to proceed ever more swiftly.

### Materials and Methods

A large-scale reedbed system was set up in Nimr, in the south of Oman, consisting of eight beds, where each of the reed beds is 75m x 48m in size with an area of 3,600 m² (Fig.1). Each line of four reed beds is called a train and is expected to treat 1,500 m³/d after the reed beds have matured. Initially, two trains were constructed (train A and B) to treat 3000 m³/d with gradual expansion to 170,000 m³/d.

The beds of each train were set at different elevations, where the primary reed beds A1 and B1 were highest to promote sequential water flow by gravity through the four beds in each train. Each of the beds was also lined with either HDPE or bentonite and was projected for specific function (Fig.1). The last three evaporation beds in train B were originally intended to enhance evapotranspiration as an alternative method of disposal. However, their function was reoriented to further polish the effluents leaving the primary reed bed (B1) allowing good quality effluents to be utilized for saline agriculture.

The beds were filled with a mixture of desert topsoil, bentonite, chopped hay and sewage sludge at a ratio of 8240, 140, 320 and 100 m³, respectively. The first two constituent were expected to play a major role in metal uptake especially the desert soil that was rich in various oxides and CaCO₃ and other clay minerals like palygorskite and illite. The latter two were added to enhance microbial activity. The beds were planted with common reed Phragmites australis known to be tolerant to a very wide range of water conditions, having been widely used for wastewater treatment. Campbell and Ogden define the common reed as a tall annual grass with extensive perennial rhizomatous roots that typically penetrate to a depth of 45cm. Their height ranges from 1.8-3.6m, with flower spikelets in July and October. They are attractive plants, lush in appearance, and provide a good background when height is needed, and are very effective in transferring oxygen to significant soil depths. They are also characterized by having high organic matter productivity of up to 100 t dw ha⁻¹ year⁻¹.

The water flow regime is subsurface, where the beds are kept saturated with the water level just below the soil surface through an adjustable arm (level pipe). Frequently the level may have to be raised in order to counteract any salinity effects on the plants within the system. Rates of application to the system were intended to be typically 0.05 m³/m² d at the beginning and are expected to rise slowly over the period of the trial by 4-5 times this value.

Within each reed bed, the inlet water is introduced above the gravel ditches located at 12m spacing and then seeps down to the bottom of the bed. When the ditches are saturated, water starts to seep laterally for a distance of 6m towards two parallel drainage pipes (outlets) to the inlet ditches at the bottom of the bed. Accordingly, the cleaned water flows by gravity from the primary treatment reed bed (B1) to B2, B3 & B4, respectively. As water passes through each bed, the water evaporates and the salinity level increases. The residual effluent is then pumped to a sprinkler system and flows to an open pan evaporation ponds that has been set up to process 400 m³/d water for salt production.

### Sampling and Analyses

Eight liquid and four solid samples were collected at different time intervals over the monitoring period of three years (2000 to 2003).

- **Influent and Effluent.** Two 1L influent and effluent samples were collected for each bed in polyethylene and glass bottles for inorganic and organic analyses. Samples were transported in a cool box to the laboratory, where the pH and EC were analysed prior elemental analyses as prescribed by Eaton for wastewater samples. A standard liquid-liquid extraction technique was adopted for the extraction of hydrocarbons where 1L of water sample was extracted three times with 30 ml di-chloromethane (DCM) using a separation funnel. Samples for the determination of BOD₅ were collected...
in airtight glass bottles completely filled to expel any air bubbles, processed and run in a WTW OxiTop® respirometer set at 20°C for five days.  

**Soil and plant material.** Samples were *aqua-regia* digested using a laboratory microwave digestion system (Milestone ETHOS SEL Lab-station), programmed at two temperature stages according to the manufacturer’s instructions. A Perkin Elmer (PE) Optima 3300 Dual View ICP-OES was used for all elemental analysis. The microwave extraction technique has recently become more widely acceptable method for the extraction of organic contaminants. It was therefore used to extract hydrocarbons from soil and plant samples. The petroleum hydrocarbons were analysed using GC-MS (Shimadzu 17A), equipped with an AOC-20i/20s auto-sampler.

**Results and Discussion**

The discussion is limited to the performance of train B reed beds, as each train was projected to meet different objectives.

**Wastewater Quality.** The characterization of production water confirmed the presence of a wide range of contaminants. These can be broadly categorized into three major groups: organic, inorganic contaminants and diverse suspended mineral and organic particulates. The contaminants were found to vary from one location to another and from the same location with time. The variation in the concentration of organics was attributed to the performance efficiency of the preliminary separation technique. Typical variations in the amount of oil in water monitored for some production areas in Oman revealed it to fluctuate in the range of 20 to 800 mg L⁻¹. The long term monitoring of production water provides a pragmatic understanding of the elemental constituents and their concentration ranges. Basically, a wide range of elements were present including: Na, B, Sr, Cd, Al, Ba, Cl, Cd, Cr, Cu, Co, Fe, Li, Mn, Si, Zn, Pb, Ag, Se, Hg, As and Ni at concentrations that ranged from 10 to 10⁶ µg L⁻¹. The quality of such production water does not meet Omani standards for agricultural reuse and thus proper treatment is necessary.

**Change of physicochemical parameters.** The removal of BOD and turbidity was essentially achieved within the primary treatment reed bed (B1) (Table 1). Thereafter levels remained within a narrow range in the effluents percolating through the other three beds. The BOD removal was inconsistent with either time or along the train of reed beds throughout the monitored period of time.

Generally, the effluent values were lowered by ~50%, which seems to be within the achieved removal range for most systems depending on the inlet concentrations, depth of the root system and temperature. Other parameters like pH of the inlet and outlet water remained almost unchanged, but the values of TDS, EC and Cl were considerably elevated as water percolated through the sequence of the four reed beds due to high evapotranspiration rates under the high temperatures of the desert climate.

### Table 1: Mean concentrations of the main physicochemical and biological parameters in the inlet and outlet samples. Note: All calculations were based on the average sample number (n=8) except for turbidity (n=4)

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>BOD (mg L⁻¹)</th>
<th>Turbidity (NTU)</th>
<th>EC (dS/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>92 ± 4</td>
<td>198.6 ± 133</td>
<td>10.9 ± 0.7</td>
</tr>
<tr>
<td>B1 Outlet</td>
<td>52 ± 5</td>
<td>0.4 ± 0.2</td>
<td>17.7 ± 3.1</td>
</tr>
<tr>
<td>B2 Outlet</td>
<td>49 ± 10</td>
<td>0.3 ± 0.1</td>
<td>16.9 ± 3.3</td>
</tr>
<tr>
<td>B3 Outlet</td>
<td>45 ± 6</td>
<td>0.4 ± 0.1</td>
<td>20.5 ± 3.3</td>
</tr>
<tr>
<td>B4 Outlet</td>
<td>46 ± 5</td>
<td>0.3 ± 0.1</td>
<td>28.0 ± 11.2</td>
</tr>
</tbody>
</table>

**Removal of inorganic contaminants.** The highest removal rates were achieved for Al, Ba, Cr, Cu, and Zn at percentages ranging between 40-78%, upto 40% for Fe, Li, Mn, Pb, As, Cd, Co, Mo, Ni, Se, Tl and V (Table 2). Their removal was mainly achieved by the substrate and the growing macrophytes, which effectively acted as an efficient sink in the retention of metals.

Metals were efficiently retained by the soil substrate, reaching a concentration range of 1 to 1000 mg kg⁻¹, depending on the metal, within the first year with no further increase in the following two years of operation due to the increased role of macrophytes in metal uptake. The reduction in the Eh values of the primary reed bed (B1) soil matrix from 260 mV at 10cm to -88 mV at 55cm deep suggests that metals were immobilized by either or both commonly known aerobic and anaerobic associated processes. Generally, in calcareous wetlands such as this one, carbonate minerals and calcite in particular are the dominant components of the soil and they act as the major controller of metal mobility. This is accomplished through the continuous dissolution of calcium carbonates which increase alkalinity and creates suitable conditions for metal removal and precipitation.

The metal uptake by the macrophytes was unselective and substantial despite then being present at low concentrations and at high pH values. For instance a one year old stand accumulated a total of 4291 mg kg⁻¹ of Al, As, Ba, Cr, Cu, Fe, Ni, Pb, Ti, V & Zn. *Phragmites* has shown ability to uptake and accumulate various salts at higher levels than the soil matrix itself e.g. Na (>4000 mg kg⁻¹), B (=1000 mg kg⁻¹) and Sr but at lower levels than the soil matrix. These elements are the least or non-sorbed by the soil matrix and therefore tend to be concentrated in the effluent by the evapotranspiration process leading to levels that exceed discharge limits. Their uptake is also advantageous, otherwise they would also have deleterious effects on the crops irrigated with treated effluents. These findings were found to conform with similar studies demonstrating the ability of *Phragmites* to tolerate high metal concentrations and salts and thus sustaining system’s efficiency.
Table 2: Average metal removal efficiencies by the primary reed bed (B1). *Negative values indicate the concentration was greater in the effluent than influent. The SD denotes the standard deviation of eight samples.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Ba</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Removal (%)</td>
<td>77.7</td>
<td>63.7</td>
<td>59.8</td>
<td>40.5</td>
<td>26.3</td>
<td>138*</td>
</tr>
<tr>
<td>SD</td>
<td>17.1</td>
<td>4.9</td>
<td>8.3</td>
<td>14.8</td>
<td>16.1</td>
<td>10.1</td>
</tr>
<tr>
<td>Removal (%)</td>
<td>-482*</td>
<td>13.3</td>
<td>80.3</td>
<td>-63.7</td>
<td>-66.0</td>
<td>71.5</td>
</tr>
<tr>
<td>SD</td>
<td>15.1</td>
<td>20</td>
<td>16.8</td>
<td>7.5</td>
<td>11.7</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Removal of organic contaminants. As with BOD and turbidity, the attenuation of petroleum hydrocarbons was principally achieved by the primary reed bed (B1). The remaining three beds further reduced influent concentrations to well below 4mg L\(^{-1}\). This resulted in an average removal of 96% for the three years of operation regardless of the variation in influent concentration. The oil in water was eliminated by three major retention mechanisms: (i) Soil matrix retained about 15 mg kg\(^{-1}\) without any further significant accumulation over time. (ii) Sediment layer and above ground parts of growing reeds retained oil by as much as 36±9 and 43±13% of their weight. (iii) Macrophytes were also found to uptake and translocate hydrocarbons in a sequential manner to above ground vegetative parts averaging approximately 10 mg kg\(^{-1}\).

It seems clear that the well-developed sediment layer and the vigorously growing reeds were primarily acting as efficient filters. They physically entrap and sequester most of the incoming hydrocarbons introduced in production inlet water and, with time, they became the major sinks within this ecosystem. This limited the hydrocarbons from reaching the original mineral soil matrix and probably facilitated their rapid dissipation by various biotic and abiotic processes. This signifies that hydrocarbons retained by the sediment layer and the creeping on the stem of the reeds are subjected to active aerobic biodegradation and intense weathering processes such as volatilisation and photooxidation that are usually greater in summer than in winter\(^{19,20,21}\). The common reed appears to uptake and degrade hydrocarbon compounds through various metabolic pathways within the plant, transforming and mineralising them into less toxic forms through phyto-oxidation similar to other phytoremediative plant species\(^{22}\). It is also believed that reeds facilitate the volatilisation of hydrocarbons particularly the lower molecular compounds through their high evapotranspiration rates, a process known as “phytovolatilisation”, if this is the case then it might be even more significant under desert conditions\(^{23}\). In addition, the role of the root-associated bacteria in enhancing the metabolism of organic contaminants has long been recognised as rhizosphere-enhanced biodegradation. Roots appear to provide an ideal environment for the associated bacteria by supplying them with various readily utilizable substrates, water, oxygenation, and other nutrients. The high input of organic matter and simple substrates, nutrients like NPK, ample hydrocarbons, warm temperatures are expected to have provided a favourable environment for bacterial populations to flourish. These findings are supported by laboratory respirometric tests which revealed that the process of biodegradation is achieved by the active indigenous bacterial populations inhabiting the ecosystem. They seem to become adapted to the environmental conditions including the chemistry of the production water without signs of suppression. In fact their activity was enhanced with time and was probably favoured by the high and diverse input of organic substrates and nutrients within the system (Fig. 2).

Fig.2: Bacterial activity for 100g reed bed matrix, where O is the original sample and 2m, 4m & 6m referring to the distance at which soil samples were collected from water inlet ditch towards the drain conduit after one year of operation. The error bars indicate ± the standard deviation of the duplicate samples.

Generally, the water regime and redox status observed in the Nimr system proved a greater potential for aerobic biodegradation to take place within the primary reed bed (B1). However anaerobic biodegradation cannot be excluded due to the anoxic conditions down the soil profile suggesting the co-existence of aerobic-anaerobic biodegradation. This was clear as an increase in soil moisture content reduced bacterial activity within the ecosystem\(^{23,24}\).

Reed Growth and Development. The ability of Phragmites to grow, develop and uptake inorganic and organic contaminants as well as tolerate high salinity and the extreme desert environmental conditions was a key success factor of this technology. They have grown to significant heights (>2.5m) and formed very dense stands reflecting their healthy status, which in turn contributed significantly to the formation and development of the crucial sediment layer. Thus the continuous input and incorporation of organic matter into the system will maintain and sustain the system efficiency and capacity, particularly with regard to contaminants removal. Reeds also play another important role in oxygenating the rhizosphere, a process which enhances metal precipitation and facilitates the aerobic biodegradation process at a much faster rate\(^{7}\). As the system became mature i.e. towards the end of the three years, it was observed that the removal of some contaminants like hydrocarbons and Fe, Mn and Li had improved.

Nimr shortfalls and possible solutions. The continuous monitoring and database for the Nimr system confirmed that it has been operating below its expected capacity by = 65% and some metals do breakthrough at very low concentrations into the effluents. This is probably caused by soil settling and compaction during the early stages of bed
preparation including soil filling and the subsequent operation and watering. It is anticipated that finer particles, especially clays might have been translocated down the soil profile and then became compacted before the reed roots got established and reached maturity, thus restricting root-soil exploitation. This resulted in non-uniformity in the originally designed subsurface water flow and instead surface flow dominated the system. In such cases preferential flow might have been taking place that may well explain the breakthrough of some heavy metals and the low treatment capacity. To evaluate the possibility of overcoming these shortfalls, seven-months-small-scale pot experiments were conducted. In these experiments, Nimr reed bed matrix was ameliorated the with fine sand or peat at ratio of 1:1 to improve its hydraulic conductivity (Ks). The pots were planted with reeds and surface and subsurface water flow regimes were tested. These experiments collectively revealed that sandy loam matrix with surface flow regime outperformed the treatment efficiency and capacity of Nimr system. At present, train A has been renovated with coarser soil matrix and its treatment capacity is improved and train B has been treating production waters for the last five years and the effluents are used for growing halophytes such as Atriplex, henna and acacia. Our research over the three years has demonstrated that the use of reed bed technology is feasible and resilient for treating oil production waters. This judgment is based on the overall performance of the system including the quality of its treated effluents which meets the Omani guidelines for wastewater reuse in agriculture (Table 3).

Table 3: A comparison between influent and effluent quality change as compared to the quality discharge limits of Oman for irrigating vegetables and fruits that are likely to be eaten raw (Standard A).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard A</th>
<th>Range</th>
<th>Treated Effluents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>5000</td>
<td>10-1000</td>
<td>141</td>
</tr>
<tr>
<td>Ba</td>
<td>1000</td>
<td>0-800</td>
<td>93</td>
</tr>
<tr>
<td>Cr</td>
<td>50</td>
<td>10-100</td>
<td>5.2</td>
</tr>
<tr>
<td>Cu</td>
<td>500</td>
<td>5-100</td>
<td>16</td>
</tr>
<tr>
<td>Fe</td>
<td>1000</td>
<td>100-10000</td>
<td>1716</td>
</tr>
<tr>
<td>Pb</td>
<td>100</td>
<td>5-60</td>
<td>7</td>
</tr>
<tr>
<td>Mn</td>
<td>100</td>
<td>80-120</td>
<td>636</td>
</tr>
<tr>
<td>Zn</td>
<td>5000</td>
<td>1-640</td>
<td>31.8</td>
</tr>
<tr>
<td>Li</td>
<td>70</td>
<td>75-281</td>
<td>456</td>
</tr>
<tr>
<td>B</td>
<td>0.5 mg L⁻¹</td>
<td>2.7</td>
<td>9.2</td>
</tr>
<tr>
<td>Sr</td>
<td>500 mg L⁻¹</td>
<td>3.8-8.6</td>
<td>14</td>
</tr>
<tr>
<td>Na</td>
<td>200 mg L⁻¹</td>
<td>2000-2500</td>
<td>7370</td>
</tr>
<tr>
<td>TOC</td>
<td>N/A</td>
<td>70-140</td>
<td>&lt;12</td>
</tr>
<tr>
<td>BOD₅ @ 20°C</td>
<td>15 mg L⁻¹</td>
<td>40-160</td>
<td>&lt;40</td>
</tr>
<tr>
<td>EC</td>
<td>2 dS m⁻¹</td>
<td>12-15</td>
<td>28</td>
</tr>
<tr>
<td>pH</td>
<td>6-9</td>
<td>7-8.5</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3: A comparison between influent and effluent quality change as compared to the quality discharge limits of Oman for irrigating vegetables and fruits that are likely to be eaten raw (Standard A).

Conclusions
The three-year evaluation study of the Nimr reed bed project has demonstrated that the technology is viable for treating production waters under Oman environmental conditions and Nimr’s shortfalls can be surmounted. The quality of the treated effluents is better than most of the physiochemical parameters listed for Omani standards for wastewater reuse. It is important to emphasise that the success of reed bed technology depends on the correct combination of wastewater characteristics, the type of substrate, design and flow regime as well as the right macrophytes that can grow advantageously. The removal of metals was achieved by their partitioning onto the reed bed substrate and uptake by the vigorously growing reeds. Hydrocarbons were attenuated by the reed bed substrate, sediment layer, creeping on the growing reeds and macrophyte uptake, then dissipated via a complex of processes. Therefore, the current treatment performance of the reed beds seems sustainable especially if the level of calcium carbonate, the sediment layer and the vigour of macrophyte growth are maintained.

In the future, research investigations should be oriented to enhance root proliferation down the soil profile of B1 red bed and evaluating the implications of harvesting practice on the system’s performance. Finally, it will be necessary to continue the existing practice of monthly monitoring, which is important for regulatory agencies and will enhance understanding of the various processes involved in contaminant removal and sustainability.

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