



# Soluble organic compounds in oil shale sour water are degradable only after being adsorbed to combusted oil shale



Ngai Man Ho<sup>a,\*</sup>, Lindsay Sly<sup>b</sup>, William P. Clarke<sup>a</sup>

<sup>a</sup>Centre for Solid Waste Bioprocessing, Schools of Chemical and Civil Engineering, The University of Queensland, Queensland 4072, Australia

<sup>b</sup>School of Chemistry and Molecular Biosciences, The University of Queensland, Queensland 4072, Australia

## HIGHLIGHTS

- A very effective and simple trickle filter process for oil refining wastewater.
- Biodegradation of complex and biorefractory organics is enhanced on substrata with adsorption capacity.
- A combined effect of adsorption and biofilms on degrading biorefractory organics.

## ARTICLE INFO

### Article history:

Received 4 December 2012

Received in revised form 12 February 2014

Accepted 23 April 2014

Available online 24 May 2014

### Keywords:

Biofilm

Biorefractory

Shale

Packed column

Wastewater Treatment

## ABSTRACT

This study demonstrates that the degradation of the organics of oil shale processing wastewater is promoted by shale ash. The wastewater TOC was approximately 4800 mg/L with at least 40% being biorefractory compounds. Sampling of effluent from a 1 m column packed with shale ash showed that over 96% of the TOC was removed at an influent flowrate of 40 L/m<sup>2</sup>/d. On-line CO<sub>2</sub> measurements showed that 86 ± 2% of the TOC was biodegraded to CO<sub>2</sub>. Control experiments included a packed column with glass beads with no TOC adsorption capacity; and stirred sequencing batch reactors with and without 5–10% (w/w) shale ash suspensions. Less than 65% of the TOC was found degraded in the controls and neither extending the hydraulic retention time nor reducing the organic loading enhanced the TOC removal efficiency. The results suggest the optimum degradation environment for the wastewater is within a biofilm with shale ash as a substratum.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

The wastewater from oil processing industries such as refineries, oil shale and oil sand processing is complex, containing a range of compounds with varying degradability, from carboxylic acid, N- and S-heterocyclic compounds, to sparingly soluble humic substances. Conventional activated sludge systems only removed 52–67% total organic carbon (TOC) from oil shale processing wastewater with a 6–8 days hydraulic retention time (HRT) and a 20–65 days sludge retention time (SRT) [1,2]. In comparison, biofilm systems have been shown to render compounds that are otherwise bio-refractory in suspended growth systems biodegradable. Clarke et al. [3] reported that over 98% of TOC was removed from oil shale processing wastewater in a 0.7 m column packed with mining waste (overburden and shale ash) and at least 80%

of the removed TOC was converted to CO<sub>2</sub>. In addition to the mono and dibasic aliphatic acids and benzoic acids degraded in the suspended growth systems, the packed column could degrade aromatic nitrogenous compounds. Despite this study, it was not clear whether the enhancement of organic removal was primarily attributed to the beneficial effect of biofilm growth, or whether the substratum plays a role in the removal process.

There are only a few studies that have explored the effect of substratum adsorption on organic biodegradation in biofilms. Some authors [4–6] demonstrated that adsorption onto a substratum improved the degradation of slowly biodegradable compounds compared to suspended growth systems, and proposed this to be the result of increasing the residence time of organics in the reactor. Some other authors [7,8] found that biodegradation of some toxic compounds such as benzylamines and herbicides was promoted by the addition of activated carbon or clay minerals to suspended growth systems. They suggested that adsorption alleviated the impact of toxic compounds on a biofilm by reducing the concentrations of these compounds in the biofilm and aqueous phases.

\* Corresponding author. Tel.: +61 (853) 8297 5517; fax: +61 (853) 2871 9254.

E-mail addresses: [angelho@dspa.gov.mo](mailto:angelho@dspa.gov.mo) (N.M. Ho), [l.sly@uq.edu.au](mailto:l.sly@uq.edu.au) (L. Sly), [b.clarke@eng.uq.edu.au](mailto:b.clarke@eng.uq.edu.au) (W.P. Clarke).

This paper examines the significance of substratum adsorption in the biodegradation of complex organic compounds in wastewater by comparing treatment in a trickle fed column packed with the solid residue (shale ash) from oil shale processing, which has adsorption capacity, and with a glass bead column with no adsorption capacity. The glass bead column was inoculated with a microbial enrichment from the shale ash and wastewater. Comparisons are also made with a sequencing batch reactor (SBR) operating with and without a dilute slurry of shale ash.

## 2. Materials and methods

### 2.1. The characteristics of oil shale processing wastewater and oil shale ash

The shale wastewater and shale ash used in this study were generated from the Southern Pacific oil shale processing pilot plant that processed oil shale from a deposit located 15 km north of Gladstone (Queensland) on the east coast of Australia from 1999 to 2004. The shale wastewater was generated during the preheating stages in a rotary kiln where moisture from the oil shale was evaporated and then condensed, and also in the oil refining process where steam used to scrub nitrogen and sulphurous compounds from shale oil was condensed. The shale wastewater in this study was stream stripped on site, with pH adjustment to enhance the removal of ammonia and H<sub>2</sub>S. The pilot plant produced approximately 0.5 m<sup>3</sup> wastewater per m<sup>3</sup> oil produced.

The experiments were conducted on a 1 m<sup>3</sup> sample of shale wastewater which was stored at 4 °C. The wastewater had the following composition: total suspended solids 100 ± 4 mg/L, TOC 4870 ± 96 mg/L, TKN 629 ± 12 mg/L, ammonia 43 ± 1 mg/L and pH 9.0 ± 0.2. The organic fraction was mainly comprised of carboxylic acids, phenols, ketones and aromatic nitrogenous compounds and humic substances. Phosphorus in the shale wastewater was less than 0.5 mg/L, insufficient to support microbial growth, and was therefore supplemented to achieve a mass ratio of 31 to 1 (TOC to phosphorous) in the shale wastewater [9].

The shale ash is the solid residue from oil shale after extraction of the volatilisable organics and combustion of the residual char at 800 °C. 79% of the shale ash sample used in the experiments was retained on a 1.18 mm sieve and 18% passed a 75 µm sieve. It had a neutral pH and an organic carbon content of 4.8 ± 0.7% (dry basis). The composition of shale ash was primarily haematite and gypsum [10].

### 2.2. Batch adsorption experiments

An adsorption isotherm of shale wastewater organics onto shale ash and glass beads (1.26 mm average diameter, Potters A120, USA) was determined by mixing the respective solid with diluted shale wastewater at a ratio of 1:7.5 (w/w) for 5 days at 22 ± 2 °C in 300 ml glass flasks sealed with TFE caps [11]. Ten flasks were prepared at an initial TOC concentration ranging from 45 to 4500 mg/L. The amount of TOC adsorbed was taken to be the amount of TOC lost from solution over 5 days. A blank control with shale wastewater solution replaced with Milli-Q water was used to estimate the amount of TOC dissolved from the shale ash. A quality control with shale wastewater only was used to evaluate any shale wastewater TOC loss due to volatilisation and sorption to the flask.

### 2.3. Reactor design

The packed column studies were conducted in two 1 m × 0.24 m (height × internal diameter) acrylic columns (Fig. 1). Each column had 24 liquid sampling ports made with sintered

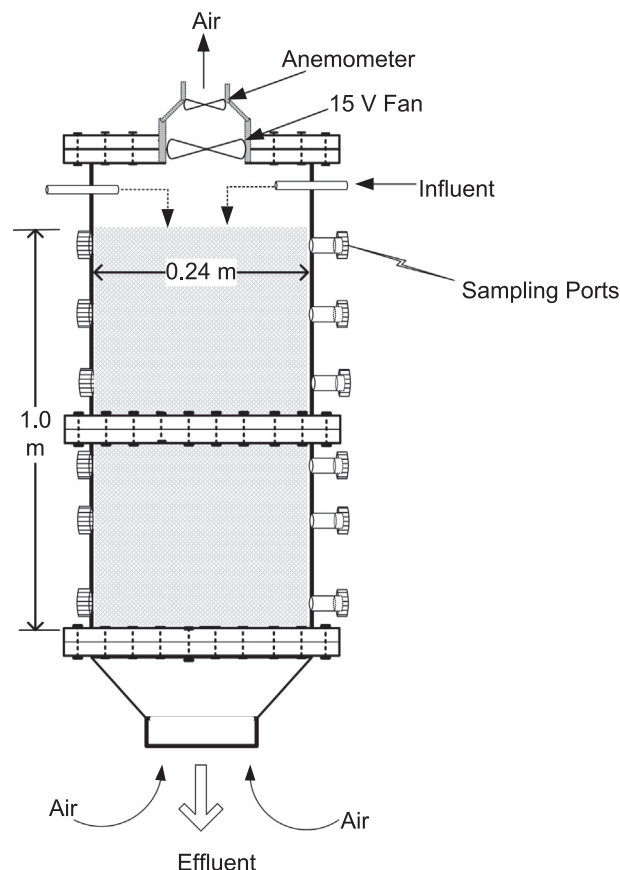


Fig. 1. The packed-column reactor.

glass (20–40 µm pore size) and 24 stainless steel mesh cylinders (1 cm in diameter and 8 cm long) that were packed with the same bedding material as the rest of the column and inserted into the column for solid sampling. The shale wastewater influent was delivered through four Norprene tubing lines (Cole Parmer, USA) fed by a four head peristaltic pump (Cole Palmer, USA) to four equally spaced feed ports around the column. The feed dripped onto a 0.20 m diameter rotating disc suspended 0.05 m above the surface of the packing material. The rotating disc was evenly drilled with 16 × 5 mm diameter holes. Glass fibre wicks were hung down through the holes to break surface tension on the hole, allowing the influent to drip down evenly across the column surface. The column base was supported by a 1.5 mm stainless steel mesh and ambient air was drawn upwards through the column by a 12 V fan centrally positioned in the headspace outlet 0.20 m above the surface of the column (Fig. 1). The velocity of the gas leaving the column was recorded using a 0.020 m nominal internal diameter vane anemometer (Rototherm® D5000, UK).

The shale ash column was packed with 24.4 kg (dry weight) of shale ash to a depth of 0.81 m, and the glass bead column was packed with 57.6 kg (dry weight) of 1.26 mm average diameter glass beads (Potters A120, technical quality, USA) to a depth of 0.80 m. Both columns were first fed with Milli-Q water for a week to obtain baseline levels of headspace CO<sub>2</sub> concentration before starting the shale wastewater feed. The pH of shale wastewater fed to the glass bead column was adjusted to pH 7.5 ± 0.2 to avoid pH inhibition to microbial growth. A pH adjustment was not required in the shale ash column because of the high buffering capacity of the shale ash. The operating parameters for the shale ash column and glass bead column are listed in Table 1.

The continually-stirred sequencing batch studies were conducted in two acrylic reactors with 4 L maximum working volume

Download English Version:

<https://daneshyari.com/en/article/6637211>

Download Persian Version:

<https://daneshyari.com/article/6637211>

[Daneshyari.com](https://daneshyari.com)