Polymer mats for reactive/sorptive barrier remediation of diverse contaminants in groundwater

B. M. PATTERSON, G. B. DAVIS
CSIRO Land and Water, Private Bag no. 5, Wembley, Western Australia 6913, Australia
e-mail: bradley.patterson@csiro.au

M. E. GRASSI & A. J. MCKINLEY
Department of Chemistry, The University of Western Australia, Nedlands, Western Australia 6907, Australia

Abstract A new reactive/sorption barrier technique using polymer tubing mats is reported, which promises to provide remediation benefits for biodegradable and volatile contaminants. The mats consist of narrow diameter polymer tubing woven onto a mesh. These are placed in the subsurface and flushed with gaseous or liquid amendments to stimulate biodegradation, or to “strip” volatile contaminants from the target contaminated zone. Laboratory “proof of concept” experiments have been carried out for a diverse range of contaminants, including atrazine, nutrients (ammonium and nitrate), and for volatile contaminants, e.g. benzene. Field testing has commenced.

Key words ammonium; atrazine; bioremediation; BTEX; in situ; mats; permeable reactive barriers; polymer tubing; volatilization

INTRODUCTION

Hollow fibre polymer tubing coiled as mats and flushed with gases or liquids has been evaluated as a permeable reactive barrier (PRB) for a range of groundwater contaminants. PRBs were made popular by Gillham & O’Hannesin (1994). Recent reviews of the more general applicability of PRBs are found in Blowes et al. (2000) and Davis & Patterson (2002).

The successful application of PRB technology relies on several factors: the implementation of a “reactive” zone that effectively treats the target contaminant; the longevity of the technology; and minimal maintenance costs long-term. The polymer mat technology offers the potential to satisfy these requirements where delivery of gaseous or liquid amendments is required to generate the reactive zone of a PRB, or where volatilization remediation is appropriate.

OVERVIEW OF OTHER STRATEGIES

There are many subsurface strategies that could be or have been engineered to behave as PRBs. For example, anaerobic/cometabolic strategies have been used for aliphatic and other chlorinated compounds (Cole et al., 1998; Gregory et al., 2000; Kao & Lei, 2000; Zenker et al., 2000; Lee et al., 2001); oxidation, aeration or alternate electron
acceptor strategies have been applied to petroleum hydrocarbon contaminants, such as
the BTEX (benzene, toluene, ethylbenzene and xylene isomers) range of compounds
(Bianchi-Mosquera et al., 1994; Borden et al., 1997; Kao & Borden, 1997); nitrification/denitrification strategies have been used for nitrogen-nutrients (Robertson
& Cherry, 1995; Volokita et al., 1996; Schipper & Vojvodić-Vuković, 2000); and pH
buffering and sulphide precipitation strategies have been used for metal contaminants
(Benner et al., 1997, 1999). Sequential PRB treatment for mixed contaminant plumes
has also been reported by Fiorenza et al. (2000) and Morkin et al. (2000).

Groundwater is neither turbulent nor well mixed, so creation of a reactive zone and
delivery of amendments can be problematic. Typically, an immobilized, permeable
amendment needs to be delivered into the path of the contaminated groundwater to
provide intimate contact between the contaminant and the amendment. Affixed, solid-
phase carbon may be one solution where anaerobic processes are to be induced (as per
Benner et al., 1999). However, under certain circumstances this may not be possible,
or replenishment of the amendment may be an issue. Lee et al. (2001) evaluated the
use of a NAPL and an emulsified vegetable oil to achieve an immobilized carbon
source.

Here we show via laboratory experimentation that the polymer mat technology can
be successfully used to deliver a variety of amendments to treat atrazine, ammonium
(and nitrate) and BTEX hydrocarbons in groundwater. Other contaminants, such as
metals and chlorinated solvents, can equally be addressed using the technique. Limited
field testing data are also presented, along with plans for future testing. Initial results
are presented in Patterson et al. (2000a, 2000b), Davis & Patterson (2002) and
Patterson et al. (2002a, 2002b).

POLYMER MAT LABORATORY EXPERIMENTS

In each of the experiments described below, hollow polymer (dimethylsiloxane or
silicone) tubing coiled and shaped as mats were emplaced in 2-m long columns, with
influent groundwater to the columns spiked with the target contaminant. Each mat
consisted of a 5-m length of polymer tubing (2.0 mm i.d., 3.0 mm o.d.), with a
stainless steel spring inserted into the centre of the polymer tubing to provide support
and eliminate twisting or collapsing. The polymer tubing was then woven through a
0.14-m diameter coarse mesh support to form a polymer mat. During treatment,
amendment gases (e.g. oxygen, hydrogen) or liquids (e.g. ethanol) were flushed
through the inner volume of the polymer tubing. The flushed gas or liquid diffuses
through the walls of the polymer tubing into the groundwater flowing past the outside
of the tubing, to effect the "reactive" remediation strategy.

The theoretical cross-sectional area of a mat was 150 cm², giving a cross-sectional
coverage of the column of 97%. Due to the weaving and overlapping of the tubing, the
thickness of the mats was up to 15 mm and the density of the coverage was reduced.
Hydraulic testing of the mats (data not presented here) showed that the mats provided
less or equivalent resistance to water flow than the aquifer sands used in the soil
columns. This enabled water to flow past the mats without restriction.
Polymer mats were tested to generate aerobic, bioactive conditions by delivering oxygen into anaerobic groundwater contaminated with 500 μg l⁻¹ of atrazine. Air was flushed through the mats at a rate of 40 ml min⁻¹. Downgradient of the mat, dissolved oxygen concentrations in groundwater in the columns increased from <0.1 mg l⁻¹ to approximately 4 mg l⁻¹. Whilst air (oxygen) was delivered to the groundwater, atrazine concentrations decreased significantly (Fig. 1). However, when nitrogen gas was flushed through the mats and not air, to re-create anaerobic conditions in the flowing groundwater, atrazine concentrations rebounded to influent concentration levels (Fig. 1). Aerobic degradation (as opposed to mineralization) rates of atrazine were relatively rapid with a zero-order rate of 240-400 μg l⁻¹ day⁻¹ or a half life, $t_{1/2}$, of 0.34 days (Patterson et al., 2000a, 2002a).

![Fig. 1](image-url) Dissolved oxygen and atrazine ratios between sampling ports B and C (20 cm apart and either side of the polymer mat) during air and nitrogen purging of the mat.

### Ammonium- and nitrate-contaminated groundwater

A dual-reactive system of polymer mats was tested to remediate ammonium-contaminated groundwater in 2-m long soil columns. The strategy was for the first set of polymer mats to deliver oxygen to induce bacterial nitrification of the ammonium to nitrite/nitrate as the groundwater moved past, and for the second set of polymer mats to deliver hydrogen or a carbon source, such as ethanol, to induce bacterial denitrification of the nitrite/nitrate to produce nitrogen gas. Both air and oxygen were tested to induce nitrification, and hydrogen and ethanol were tested to induce denitrification—earlier results are in Grassi (2000) and Patterson et al. (2000b).

When oxygen was delivered to the groundwater via the polymer mats, nitrification half-lives in the range 0.07–0.25 days were induced in the aerobic zone of the soil columns (Figs 2 and 3). With hydrogen delivery via the polymer mats, a denitrification half-life (nitrate plus nitrite removal) of 3.5 days was induced (Fig. 2). Denitrification rates were significantly enhanced when ethanol was delivered via the polymer mat, with denitrification half-lives in the range 0.12–0.34 days (Fig. 3).
Fig. 2 Changes in NH$_4^+$-N, NO$_3^-$-N and NO$_2^-$-N concentrations along the length of the oxygen- and hydrogen-amended column.

Fig. 3 Changes in NH$_4^+$-N, NO$_3^-$-N and NO$_2^-$-N concentrations along the length of the oxygen- and ethanol-amended column.

BTEX-contaminated groundwater

Laboratory column experiments were also conducted on BTEX contaminated groundwater using the polymer mats (Patterson et al., 2002b). The main aim was to assess the removal of the BTEX hydrocarbons by volatilization, rather than biodegradation. As such, the experiments were conducted under sterile conditions using sodium azide to eliminate loss of the organic compounds due to biological processes. Air was flushed through the mats. The polymer mats proved efficient in physically removing (stripping) benzene and naphthalene from groundwater (Fig. 4). Removal efficiencies from the groundwater flowing past a single polymer mat were 85% for benzene and 75% for naphthalene. In field applications, air flushing of the polymer mats would also deliver oxygen to the groundwater inducing biodegradation, providing a dual remediation benefit.
Polymer mats for reactive/sorptive barrier remediation of diverse groundwater contaminants

Fig. 4 Aqueous benzene concentrations in the soil-column after gas purging of the polymer mats commenced. Sampling ports: 1 = column influent; 2 = downgradient of the first polymer mat; 3 = downgradient of the second polymer mat; and 4 = downgradient of the third polymer mat. Error bars are 95% confidence intervals.

FIELD APPLICATION

In laboratory experiments the mats have shown promise in providing a fixed delivery mechanism capable of semi-passive delivery of amendments to alter subsurface geochemical conditions or as a stripping mechanism for contaminants. The polymer mats have been tested at a field site in Perth, Western Australia to deliver oxygen to an atrazine-contaminated groundwater plume. Oxygen concentrations measured 8 cm downgradient of some of the mats, placed 10 m below the water table, increased from below detection limits (i.e. anaerobic conditions) to 5 mg l\(^{-1}\). Detailed results of this trial are yet to be published. The dual mat delivery system for ammonium remediation is to be evaluated in the field in 2001/2002.

CONCLUDING COMMENTS

The use of polymer mats is a promising technology for controlled and targeted treatment (or extraction during volatilization) of contaminants. It can also provide a somewhat stable environment for microbial activity. The mats have scope for innovation and delivery of more complex subsurface treatment options where the amendments partition through polymer materials (i.e. most gases and some liquids). Since the delivery of amendments is effectively through an air phase, costs are projected to be lower in comparison to direct injection into groundwater of aqueous phase amendments. Where a PRB is hydrologically and geochemically viable, then the long-term, cost-effective delivery of amendments and sustainability of the subsurface reactive zone is the key to the applicability of the technology for groundwater cleanup. The polymer mats may aid in achieving this for PRB systems.

Acknowledgements Monika Brill is acknowledged for her assistance with the ammonium research. Nathan Innes and David Briegel fabricated the columns, and Terry Power and Dean Coad provided technical assistance. The Water and Rivers Commission of Western Australia provided part funding of the research.
REFERENCES


