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Ion exchange membrane bioreactor for treating groundwater contaminated with high perchlorate concentrations

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HIGHLIGHTS

- Synthetic groundwater highly contaminated with perchlorate was effectively treated in an IEMB system.
- High perchlorate concentrations affect the permeability of the anion membrane in the IEMB.
- Glycerol was successfully used as a low cost & effective C source for perchlorate biodegradation.
- Bacterial activity in the biofilm facing the bio-compartment enhanced trans-membrane perchlorate flux.

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ABSTRACT

Perchlorate contamination of groundwater is a worldwide concern. The most cost efficient treatment for high concentrations is biological treatment. In order to improve and increase the acceptance of this treatment, there is a need to reduce the contact between micro organisms in the treatment unit and the final effluent. An ion exchange membrane bioreactor (IEMB), in which treated water is separated from the bioreactor, was suggested for this purpose. In this study, the IEMB's performance was studied at a concentration as high as 250 mg L^{-1} that were never studied before. In the bioreactor, glycerol was used as a low cost and nontoxic carbon and energy source for the reduction of perchlorate to chloride. We found that high perchlorate concentrations in the feed rendered the anion exchange membrane significantly less permeable to perchlorate. However, the presence of bacteria in the bio-compartment significantly increased the flux through the membrane by more than 25% in comparison to pure Donnan dialysis. In addition, the results suggested minimal secondary contamination (<3 mg C L^{-1}) of the treated water with the optimum feed of carbon substrate. Our results show that IEMB can efficiently treat groundwater contaminated with perchlorate as high as 250 mg L^{-1}.

1. Introduction

In recent years, perchlorate, which is used in rocket fuel, explosives, and match-producing industries, has become a major concern as a contaminant of surface and groundwater around the world [1,2]. The main health concern regarding perchlorate is its interference with the uptake of iodine by the thyroid gland, which could affect the nervous and skeletal system development in fetuses and young babies [3–6].

Presently, the USEPA suggests a health reference level (HRL) of 15 μg L^{-1} as the highest permissible concentration in drinking water [7]. Where it occurs, perchlorate ground water contamination varies in the range of a few micrograms per liter [8,9] to hundreds of milligrams per liter, leading to the termination of water production from highly contaminated wells. This is, in fact, the case in Israel's coastal aquifer [10].

Several methods are available for the removal of perchlorate from water and waste water. These utilize either physical removal or the degradation of perchlorate to form less hazardous species [2]. Ion exchange is an effective removal method for perchlorate concentrations below 1 mg L^{-1} [11–13]. However, when other anions, such as nitrate and sulfate, are present, the efficiency is substantially reduced [2,14]. Furthermore, regeneration of the resin is difficult and results in high concentrations of perchlorate in the regenerant solution, which needs further treatment [12,15]. Perchlorate reduction (degradation) can be achieved by chemical [16–18], electro-chemical [19,20] or bio-reduction [21,22], either *in situ* or in bio-reactors [1]. The last process is the most prevalent

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in practice. At present, chemical and electro-chemical reduction have only been demonstrated in small scale studies and currently are not cost effective [2].

Microbial reduction was found to be an effective method for treating high loads of perchlorate. Both heterotrophic and autotrophic perchlorate-reducing bacteria (PRB) use perchlorate as an electron acceptor under anaerobic conditions [21,22]. Heterotrophic PRBs use different carbon and electron donors, such as acetate, ethanol, and glycerin [23–26]. Autotrophic bacteria can use CO_2 and H_2 as carbon and electron donors, respectively [27].

Different types of bioreactors, such as fluidized bed reactors (FBR) and packed bed reactors (PBR) [1], are used for the *ex-situ* reduction and removal of perchlorate from different water sources. Biological treatment was capable of treating perchlorate contamination levels ranging from 50 μg L^{-1} up to 1000 mg L^{-1} using bioreactors with different removal rates and removal efficiencies [25,28–31].

However, these methods present some drawbacks when the effluent ought to meet the high quality standards of drinking water. These bioreactors are based on a flow through concept, where the water is in contact with the bacteria, the carbon source, and the bio-reduction byproducts. When dealing with drinking water, strict health regulations and restriction are applied, resulting in the need for costly post-treatment for the removal of the biomass and residual carbon.

The ion exchange membrane bioreactor (IEMB) [32] is an integrative technology that combines physical perchlorate removal, using an anion exchange membrane contactor, with perchlorate reduction in a bioreactor. By isolating the bioreactor-compartment treatment from the feed stream, the process minimizes the need for additional treatment to make the water suitable for drinking water. IEMB was also found to be effective in removing other anionic and cationic micro-pollutants from contaminated water. Extensive research has also been done on the removal and reduction of nitrate and low concentrations (<1 mg L^{-1}) of perchlorate in tap water [26,32–39]. Nevertheless, the potential for using IEMB for removal of perchlorate concentrations above 100 mg L^{-1} was never studied.

The IEMB combines continuous Donnan dialysis of the pollutant from the feed (water compartment), through a non-porous, anion exchange membrane, perm-selective for monovalent species, with a bio-compartment where it is bio-reduced to harmless products by a suitable microbial culture (Fig. 1). The Donnan dialysis process requires the presence of a driving counter-ion (e.g., chloride) in the bio-compartment, enabling the exchange with the trace counter-ions (perchlorate), while removing them from the water stream, thus keeping the electro-neutrality on both sides of the membrane [40]. Steady state perchlorate flux (J) from the water compartment to the receiving bio-compartment can be described by the following expression [35,37,40,41]:

$$J = \frac{\frac{C_{ClO_4^-,1}}{C_{Cl^-,1}} - \frac{C_{ClO_4^-,2}}{C_{Cl^-,2}}}{\frac{L_m}{P_m Q_m} + \frac{\delta_1}{DC_{Cl^-,1}} + \frac{\delta_2}{DC_{Cl^-,2}}} \quad (1)$$

The numerator of Eq. (1) represents the driving force of the process for a given membrane thickness and is mainly affected by the perchlorate concentration in the water compartment bulk. The denominator represents the total mass transfer resistance to perchlorate transport contributed by the boundary layers together with the membrane. C (mol m^{-3}) represents the different ion concentrations in the water and bio-compartments denoted with the suffixes 1 and 2, respectively. The mass transfer resistance of the membrane is given by the membrane thickness (L_m,(m)) divided by the permeability (P_m,(m^2 s^{-1})) and the membrane ion capacity (Q_m,(mol m^{-3}). The two boundary layer resistances are controlled

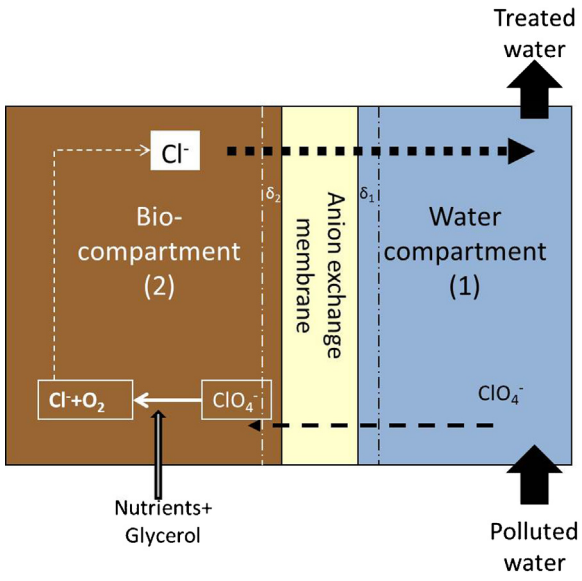

Fig. 1. Schematic diagram for perchlorate transport in an IEMB. Modified from Fonseca et al. 2000 [33].

by the boundary layer thicknesses ($\delta_{1,2}$,(m)), the diffusion of perchlorate in water (D,(,(m^2 s^{-1})) and the different Cl^- concentrations on both sides of the membrane ($C_{Cl^-,1,2}$, (mol m^{-3})).

Once perchlorate crosses the membrane, it enters the anaerobic bio-compartment, enriched with PRBs. A carbon and energy source and other essential nutrients are continuously fed to the bio-compartment, allowing effective perchlorate degradation [26]. In previous studies, ethanol was chosen as a carbon and energy source for treating drinking water since it is non-toxic and has a low diffusion rate through a monovalent selective anion exchange membrane [42] (i.e., Neosepta ACS). On the other hand, ethanol is a relatively expensive carbon source.

As noted above, IEMBs have previously only been applied to treating waters with relatively low perchlorate contamination levels (<1 mg L^{-1}). Because the flux of perchlorate across the membrane depends on its concentration, it is important to examine the performance of the IEMB at a higher range of concentrations (1–250 mg L^{-1}). The aim of the present study was to characterize the IEMB for the removal of perchlorate from highly contaminated groundwater containing several hundreds of mg per liter. In addition, glycerol was evaluated as an efficient, safe, and cost-effective carbon source alternative to ethanol, which has been used to date in IEMB studies.

2. Experimental section

The experimental setup for the IEMB used in this study is illustrated in Fig. 2. The IEMB module was constructed from Plexiglas and had two identical rectangular ducts that were separated by an ion exchange membrane (Neosepta ACS, manufactured by Tokuyama Soda, Japan). The duct dimensions were: 0.3 cm in height, 25 cm in length, and 1.5 cm in width. The active membrane area used was 37.5 cm^2. Both compartments were connected to reservoirs from which synthetic contaminated water and bio-media were fed to the water and bio-compartments, respectively, by two peristaltic pumps (Cole Parmer MasterFlex 7550-60 Computerized Drive and Miniplus 3 Peristaltic Pump, Gilson, respectively). In addition, each side was connected to a gear pump (DGMO9, Fluid-o-Tech, Italy) that recirculated the liquid from the reservoir through the module compartments. The flow regime near the membrane on both sides was turbulent, so