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title: **Heavy metals removal from contaminated groundwater using PRB with immobilized membranes — the feasibility study**

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INTRODUCTION

Groundwater contamination with heavy metals caused by industrial waste storage and current and/or abandon mining activities is a widespread ecological problem in many industrialized countries worldwide. In Poland, especially in the Upper Silesia region, heavy metals (Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Zn(II), Cr (VI)) have been discharged into the environment causing soil and groundwater contamination, which is currently of great concern due to the threat it poses to drinking water and/or adjacent ecosystems (Lutyński, Suponik, 2008; Malina, Kwiatkowska, 2003; Suponik, 2009). Soil and groundwater remediation technologies have to deal with the reduction of this risk. Groundwater contaminated with heavy metals is typically treated by “pump and treat” that is neither cost-effective nor sustainable approach. Permeable reactive barriers (PRBs) (Fig. 1) seem to provide an effective and sustainable alternative for the *in situ* treatment of groundwater contaminated with heavy metals (Diels et al., 2002; Szewczyk et al., 2009; USEPA, 1998).

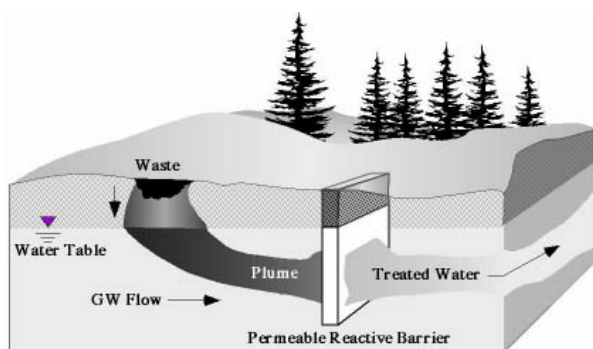


Figure 1. The concept of a permeable reactive barrier (PRB).

The PRB technology is considered as a part of the Enhanced Natural Attenuation (ENA) strategy, which is intensively developing in the EU countries. This strategy is based on the removal of heavy metals from the groundwater flow by enhancing natural geochemical processes, such as: adsorption, ion-exchange, chemical binding, redox reactions, precipitation etc (Fronczyk, 2006).

APPROACH

Our study evaluates the potentials of immobilized polymer inclusion membranes (PIMs) application within a PRB. The tubular modules formed from immobilized membranes provide rapid metal ions transport with high selectivity, as well as easy setup and operation (Nghiem et al., 2006). PIMs can be used for: (i) treatment of landfill leachates to minimize the risk of groundwater contamination, and (i) reduction of heavy metals concentrations in the groundwater flow (Malina, 2007). The PIMs are formed by casting cellulose triacetate (CTA) from an organic solution to form a thin, stable film. This solution contains also an ion carrier and a membrane plasticizer (mostly *o*-nitrophenyl alkyl ethers). The resulting membrane is used to separate source and receiving phases; it does not contain, however, an organic solvent to maintain the transport of ionic species through PIM (Kozłowski, Walkowiak, 2002).

The presented feasibility study concerns the studies of chromium(VI) removal from groundwater through PIMs containing: CTA as a support, *o*-nitrophenyl pentyl ether as a plasticizer, and Aliquat 336 as an ion carrier.

MATERIALS AND METHODS

The PIMs were prepared according to following procedure. First, a solution of CTA as a support, ONPPE as a plasticizer, and Aliquat 336 as an ionic carrier in dichloromethane as an organic solvent was prepared. Then, a specified portion of this solution was poured into a membrane mold comprised of a 9.0 cm glass ring attached to a plate glass with CTA—dichloromethane glue. Dichloromethane was evaporated overnight and the resulting membrane was separated from the glass plate by immersion in cold water.

The experiments were carried out in a permeation cell, in which the membrane film (4.9 cm² effective surface) was tightly clamped between a source and receiving phase. The source phase was a synthetic groundwater contaminated with chromium(VI). Samples of the aqueous receiving phase were removed periodically via a sampling port with a syringe, and analyzed directly afterwards with plasma atomic emission spectroscopy (ICP-AES) to determine chromium(VI) concentration.

PRELIMINARY RESULTS

The concentration of ion carrier plays an important role in the metal ions transport through PIMs. The influence of ion carrier (Aliquat 336) concentration on chromium(VI) transport is presented in Fig. 2. The optimal Aliquat 336 concentration was 1.0 M.

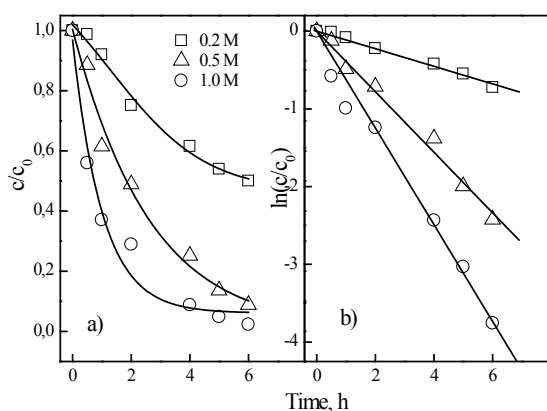


Figure 2. Chromium(VI) concentration in the source phase vs. time of transport through PIMs at different Aliquat 336 concentrations.

The results (Table 1) indicate that the rate of transferred mass of chromium(VI) through PIM depends on the equilibrium of Cr(VI)-Aliquat 336 in the aqueous phase/membrane boundary layer, and the source/receiving phase volume ratio.

Table 1. Chromium(VI) removal from synthetic groundwater using PIM with Aliquat 336.

Number of run	Initial concentration of Cr(VI) in source phase (ppm)	Volume of source phase (cm ³)	Volume ratio of source/receiving phase	Time of process (h)	Residual Cr(VI) concentration in source phase (ppm)
1	54.0	50	1:1	6	1.0
2	1.0	1500	30:1	3	0.001

With the source/receiving phase volume ratio equal to 1.0, it was possible to reduce the Cr(VI) concentration from 54.0 to 1.0 ppm in 6 h. Results of run no. 2, where the source/receiving

phase volume ratio was of 30:1, showed the possibility to reduce the Cr(VI) concentration 1000 times, i.e. from 1.0 to 0.001 ppm already after 3 h (Fig. 3).

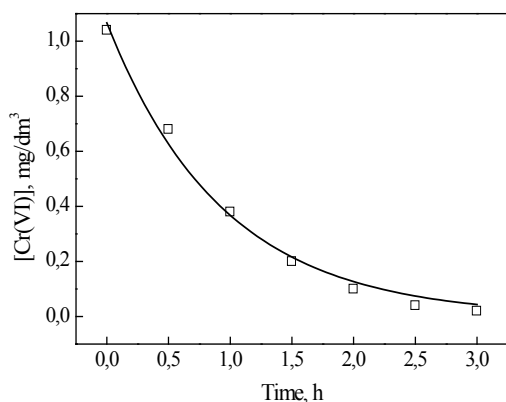


Figure 3. The changes of Cr(VI) concentration in groundwater.

CONCLUSION

This feasibility study showed that the groundwater transport through PIM allows for reducing chromium(VI) concentration in the source aqueous phase to 0.001 ppm, which is below the permissible limit for drinking water in Poland. Thus, the application of PIMs can be effective for heavy metals removal from contaminated groundwater, and the immobilization of specific ion carriers on the reactive material within PRB — a novel approach in groundwater remediation at contaminated sites.

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