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REMOVAL OF PESTICIDES AND INORGANIC POLLUTANTS BY REVERSE OSMOSIS

Contamination of soil and groundwater with pesticides is mainly caused by old ecological burdens. This study focuses on the treatment of groundwater contaminated with chlorinated pesticides. The contaminants mainly include α -HCH, β -HCH, γ -HCH, HCB, DDE, DDD and DDT. Reverse osmosis technology using RO98pHt polyamide membranes was used to remove the pollutants under batch process conditions. The observed rate of removal ranged from 98.4% to 99.7%. Total dissolved content solids decreased from 1.35 g/dm³ to below 0.05 g/dm³.

1. INTRODUCTION

There are about 160 locations in the Czech Republic that have previously been contaminated with pesticides. Most of them have never been remediated, thus these contaminated areas represent a threat to the environment. Chlorinated pesticides like DDT have a very long average life. In addition, DDT metabolites to DDE, which tends to persist far longer in the body [1]. Long term DDT contamination has a negative influence on biological properties of soil [2].

The investigation of new contamination removal processes is currently a centre of attention. Membrane separation processes seem to be a viable choice for pesticide removal when surface or ground water is contaminated. The molecular weight of chlorinated pesticides ranges between 200–400 Da. Cut-off effectiveness of nanofiltration membranes is 200 Da, while for reverse osmotic membranes it is below 100 Da.

Nanofiltration is an economically attractive process and this led to its adaptation by many water suppliers [3]. Reverse osmosis is preferred for high retention parameters. High rejection rates of pesticides and micropollutants were shown in the study

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dealing with cellulose-acetate, polyamide and ultra-low pressure membranes [4]. The long-term application of reverse osmotic membranes exhibited rates higher than 99.5% in the removal of pesticides and herbicides, when ozonation was applied as a pre-treatment [5]. Nanofiltration can be effectively combined with other processes such as coagulation and adsorption [6].

The water matrix has a significant influence on the rejection of pesticides and the pressure normalized flux [7]. DDT is easily absorbed by humic acid and can be removed, when applied along with the nanofiltration process [8]. The results of the removal of pesticides from contaminated water by nanofiltration and reverse osmosis are reported and related work has been reviewed in recent papers. Pesticide removal by reverse osmotic membranes is a complicated process in which several membrane and solute parameters, as well as feed water composition and process conditions play a role. A significant aspect is also membrane fouling. Fouling alters the surface properties of the membrane and thus rejection of pesticides can be drastically changed in comparison with virgin membranes [9]. Electrostatic charge on the membrane also influences the rejection of pesticides having a dipole moment [10].

In the Czech Republic, a few studies were done dealing with the environmental application of membrane separation processes, mostly in the form of laboratory tests or semi-pilot experiments [11]. These studies provide information on the removal of chlorinated pesticides from contaminated groundwater by reverse osmosis. The effect of the high content of total dissolved solids (between 1.35 and 14.1 g/dm³) on the efficiency of pesticide separation was reported.

The study site was located in Central Bohemia. Tons of hazardous waste were deposited in the former open-cast mine in the past. Wastes were deposited without records, their origins in industry (residues of chemical processes, residues of hardening salts) and agriculture (residues of pesticides and herbicides). There were no waterproof barriers between waste and bedrock. Pollutants were spread into the environment by leaching through the soil and cracks in the granite bedrock. Severe contamination of groundwater was detected in the vicinity of the mine after the excavation of waste. Samples of groundwater, pumped from the central part of the mine, were taken for membrane separation experiments.

2. EXPERIMENTAL

Materials and methods. Membrane unit LAB M-20 was used for laboratory experiments. This unit is equipped with a plate and frame module and is designed to test small scale separations.

The membrane modul – LabStack M20 – characterized by nominal product rate of 30 dm³/h was used in the experiments. The module can operate at a maximum pres-

sure of 6.0 MPa. Reverse osmotic membranes RO98pHt (a thin-film composite on polypropylene) were used. A total of 30 membrane sheets were mounted in the module. The active area of each membrane was 0.0174 m². Therefore, the permeate flux corresponded to a total active membrane area of 0.522 m². The unit was equipped with digital pressure gauges A-10 (Greisinger Electronic).

Conductivity and pH were measured using devices GMH 3430 and GMH 3530, respectively (Greisinger Electronic). Chlorinated pesticides in water samples were determined as follows: 20 cm³ of sample was extracted with 10 cm³ of hexane in a separating funnel for a period of 15 min. Subsequently, the concentration of pesticides in hexane extract was measured with a GC HP 5890 gas chromatograph, equipped with a capillary column HP-5MS (length: 60 m, stationary phase: 5% diphenyl and 95% dimethylsiloxan) and an electron capture detector.

The GC method programme was as follows: initial temperature 50 °C, hold 1 min, rate 25 °C·min⁻¹ to 195 °C, hold 0 min, rate 1 °C·min⁻¹ to 205 °C, hold 5 min, rate 3 °C·min⁻¹ to 280 °C, hold 5 min. The concentration of metals was determined by using a SensAA (GBC Scientific Equipment) atomic absorption and emission spectrometer. Concentration of anions was measured by a DIONEX ICS 100 (Thermo Scientific) ionic chromatograph, equipped with an IonPac AS4A-SC 4 mm Analytical Column. Total dissolved solids (TDS) were determined by the gravimetric method at 105 °C. The TOC values of samples were measured with TOC/TNb analyzer liqui-TOC II (Elementar Analysensysteme GmbH). The technological parameters for batch process were described by the following parameters.

- Concentration factor (c_F), defined as:

$$c_F = \frac{V_I}{V_C} \quad (1)$$

where: V_I is the input volume of batch, and V_C is the volume of remaining concentrate in batch.

- Pressure normalized flux (permeability) P , which is the transport flux per unit transmembrane driving force and can be described by:

$$P = \frac{V_t}{At\Delta p} \quad (2)$$

where: V_t is the total volume transported throughout the membrane, m³, A is the membrane area, m², t is the time unit, s, and Δp is the pressure difference between the upstream and downstream sides of a membrane, kPa.

- Retention factor r_{F_i} for individual components:

$$r_{F_i} = 1 - \frac{(c_i)_P}{(c_i)_C} \quad (3)$$

where: $(c_i)_P$ is the concentration of a component i in permeate, and $(c_i)_C$ is the concentration of a component i in the concentrate.

Experimental conditions. A series of experiments, using reverse osmosis technology, were performed to determine the removal efficiency of pesticides and inorganic pollutants from contaminated groundwater. Separation experiments were carried out in a batch mode in one stage. The input volume of the leachate was 20 dm³. All experiments were performed at a transmembrane pressure of 2.0 MPa. The operating temperature was set to 20 °C. The cross-flow velocity was 17.4 dm³/min for the module arrangement used.

The permeate flow intensity was measured during the experiments to determine the pressure normalized flux. After each experiment, the membranes were flushed with tap water and both alkaline and acidic cleaning was performed. First, Ultrasil (Henkel) alkaline detergent was added until pH 12 was reached, to remove organic foulants. Then the device was again rinsed with tap water and diluted hydrochloric acid was added to the flush-water to acidify it to pH 2. The cleaning effectiveness was confirmed by measurement of the pure water flux under standard conditions of 2 MPa and 20 °C. Collected samples were stored at 4 °C before analysis. Permeate was collected during the separation process and samples of mixed permeate were taken for analysis. Samples of feed solutions and technological streams (mixed permeate and concentrate) were analyzed for inorganic components, TOC and pesticides. In addition, 10 samples of the solution in each batch were analyzed for pesticides.

3. RESULTS AND DISCUSSION

The hydraulic efficiency of the separation process may be described by the permeability values, with utilization of flux volume measurement (Fig. 1). The concentration factor of $c_F = 12$ was achieved during the experiment.

The main factors affecting pressure normalized flux values are the osmotic pressure of treated solutions, membrane scaling and the composition of the treated solutions (Tables 1 and 2). Solubility of inorganic components can be exceeded, due to concentration polarization or increasing concentration in bulk solutions (in the case of batch process). No abrupt decrease in pressure normalized flux was observed, decreas-

ing steadily during the concentration of batch. The decrease was 79% when concentration factor $c_F = 12$ was achieved.

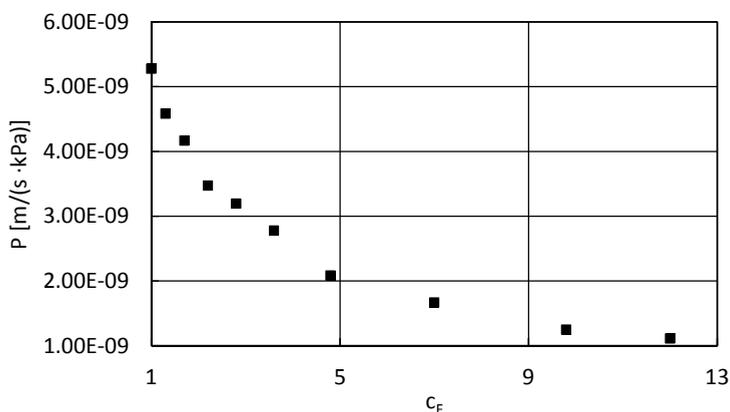


Fig. 1. Dependence of pressure normalized flux on the concentration factor for the batch process; $\Delta p = 2.0$ MPa, $t = 20$ °C

Alkaline and acid flushing was effective for membrane cleaning, confirmed by pure water flux measurements before and after experiments. The pure water flux decreased from 5.59×10^{-9} $\text{m}/(\text{s} \cdot \text{kPa})$ to 5.31×10^{-9} $\text{m}/(\text{s} \cdot \text{kPa})$, representing a decrease of 3%. Flux was fully recovered after the cleaning procedure.

The total concentration of HCH isomers expressed as the sum of α -HCH, β -HCH, γ -HCH and the total concentration of DDT and its derivatives expressed as the sum of DDE, DDD and DDT was determined in samples of batch concentrate (Fig. 2).

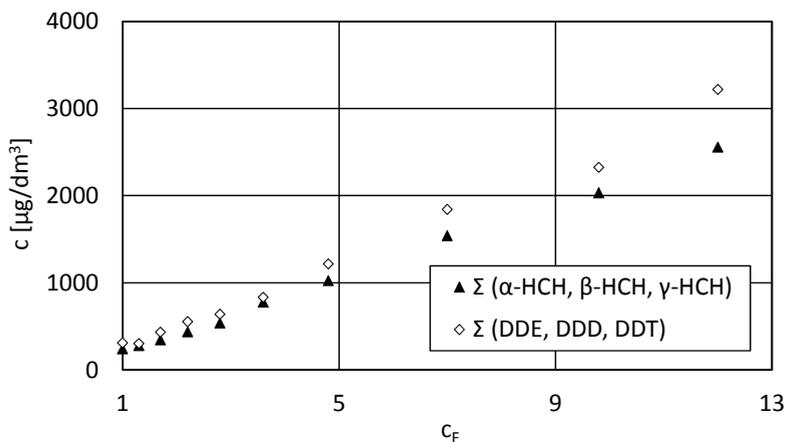


Fig. 2. Concentrations of pesticide in the batch concentrate during the separation process

Results of the quality analysis of leachate and process streams are given in Tables 1 and 2.

Table 1

Analysis of an individual stream. Content of chlorinated pesticides

| Pesticide | Input [$\mu\text{g}/\text{dm}^3$] | Permeate [$\mu\text{g}/\text{dm}^3$] | Retention factor [%] | Concentrate [$\mu\text{g}/\text{dm}^3$] |
|---------------|--|---|-------------------------|--|
| α -HCH | 135 | 0.8 | 99.4 | 1430 |
| β -HCH | 67.2 | 0.6 | 99.1 | 723 |
| γ -HCH | 37.2 | 0.6 | 98.4 | 402 |
| HCB | 9.0 | < 0.2 | > 97.8 | 98.0 |
| 2,4'-DDE | 0.7 | < 0.2 | – | 7.3 |
| 4,4'-DDE | 3.5 | < 0.2 | – | 33.4 |
| 2,4'-DDD | 39.1 | < 0.2 | >99.5 | 415 |
| 4,4'-DDD | 0.8 | < 0.2 | – | 8.5 |
| 2,4'-DDT | 63.3 | 0.2 | 99.7 | 625 |
| 4,4'-DDT | 201 | 0.6 | 99.7 | 2130 |
| Total | 556.8 | 3.0 | 99.5 | 5872.2 |

The average separation efficiency (retention factor) for chlorinated pesticides was 99.5%. Molecular weights of studied pesticides are as follows: HCH = 290.83 g/mol (formula $\text{C}_6\text{H}_6\text{Cl}_6$), HCB = 284.83 g/mol (formula C_6Cl_6), DDE = 318.02 g/mol ($\text{C}_{14}\text{H}_8\text{Cl}_4$), DDD = 320.04 g/mol (formula $\text{C}_{14}\text{H}_{10}\text{Cl}_4$) and DDT = 354.49 g/mol (formula $\text{C}_{14}\text{H}_9\text{Cl}_5$). The separation efficiency was slightly higher for DDT and its derivatives than for isomers of HCH. This can be related to their molecular weight [9].

Table 2

Analysis of an individual stream. Content of inorganic substances and TOC

| Pesticide | Input [mg/dm^3] | Permeate [mg/dm^3] | Retention factor [%] | Concentrate [mg/dm^3] |
|--------------------|--------------------------------------|---|-------------------------|--|
| Na | 158 | 2.4 | 98.5 | 1753 |
| K | 209 | 3.5 | 98.3 | 2425 |
| Ca | 163 | 0.5 | 99.7 | 1860 |
| Mg | 41 | 0.1 | 99.8 | 398 |
| Mn | 3.6 | < 0.2 | > 94.4 | 32 |
| Cl^- | 47 | 1.3 | 97.2 | 511 |
| NO_2^- | 232 | 4.7 | 98.6 | 2120 |
| NO_3^- | 357 | 3.9 | 98.3 | 4150 |
| SO_4^{2-} | 36 | 0.3 | 99.1 | 373 |
| TDS | 1350 | < 50 | 98.6 | 14100 |
| TOC | 14.0 | 1.0 | 92.9 | 121 |

Mass balance of pesticides for technological streams is as follows: content in the input stream $\sum(\alpha\text{-HCH}, \beta\text{-HCH}, \gamma\text{-HCH}) = 4788 \mu\text{g}$ and $\sum(\text{DDE}, \text{DDD}, \text{DDT}) = 6168 \mu\text{g}$, content in the output stream (permeate and concentrate) $\sum(\alpha\text{-HCH}, \beta\text{-HCH}, \gamma\text{-HCH}) = 4295 \mu\text{g}$ (89.7% of the input weight) and $\sum(\text{DDE}, \text{DDD}, \text{DDT}) = 5387 \mu\text{g}$ (87.3% of the input weight). A significant portion of pesticides was adsorbed on the organic fouling layer, or on the membrane surface. The adsorption of pollutant onto the membrane surface can be physical or chemical in nature, or both [12]. Physical adsorption is a completely reversible process, while the latter can be irreversible for strong chemical bonds or reversible for weak secondary chemical bonds such as hydrogen bonding and complexation. It is possible that both chemical (hydrogen bonding) and physical (hydrophobic interactions) adsorption occurs during the separation process [8].

Determination of inorganic compounds, salts and total organic carbon (TOC) was carried out in mixed permeate and concentrate. Retention factors for inorganic components ranged from 97.2% to 99.8%, with an average retention factor for TDS 98.6%. The composition of input solution determines process parameters such as retention factors. These parameters should be determined for each component of the solution in the case of applied environmental studies, when complex solutions (solutions that contain a large number of different organic and inorganic constituents) are separated.

It was demonstrated that reverse osmosis is an effective technology for non-selective treatment of contaminated water. Both organic and inorganic substituents were retained in the concentrate stream. A significant reduction of input volume was performed. When concentration factor $c_F = 12$ was achieved, the volume of concentrate was only 8% of its original volume.

The permeate stream can be infiltrated in the vicinity of the contaminated site, because it meets the limits stipulated by the local authority.

4. CONCLUSIONS

The study dealt with removal of mixed contamination from groundwater. Groundwater was contaminated with chlorinated pesticides and other pollutants. Membrane separation technology was used to remove hazardous constituents that represented a threat to the environment, due to leaching through the soil and through cracks in the granite bedrock. Reverse osmosis was chosen because of the requirement for a high quality permeate.

The observed removal rates for chlorinated pesticides ranged between 98.4% and 99.7% in the presence of high salt content. Separation efficiency was slightly higher for DDT and its derivatives than for isomers of HCH. A significant advantage of the applied process is a volume reduction of contaminated water. This study demonstrated

that reverse osmosis is an effective tool for the remediation of targeted old ecological burdens.

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