The adsorption and biodegradation processes used in PRB (Permeable Reactive Barrier) Technology are presented in the paper. These processes were selected to assess the possibility of removal of benzene and phenols from groundwater contaminated by a dumping site located in a city in Upper Silesia, Poland. In these processes, a special material called reactive material must be used for efficient treatment of groundwater.

To design the PRB properly, a few parameters, called PRB parameters, such as: reactive material parameters, groundwater treatment parameters and geometrical PRB parameters should be determined. Groundwater treatment parameters for GAC (granulated active carbon) as a reactive material in adsorption process were measured with the Freundlich isotherm, and for a mixture of coarse sand and granulated peat in biodegradation process they were determined with the first-order kinetics equation.

The results of groundwater treatment parameters for GAC ($k_{\text{phen}} = 20.7 \text{ l/g}; n_{\text{phen}} = 0.51; k_{\text{ben}} = 3.9 \text{ l/g}; n_{\text{ben}} = 0.48$) and for the mixture of coarse sand and granulated peat ($\lambda_{\text{phen}} = 0.0369 \text{ 1/hr}; t_{1/2\text{phen}} = 18.72 \text{ hr}; \lambda_{\text{ben}} = 0.0142 \text{ 1/hr}; t_{1/2\text{ben}} = 48.72 \text{ hr}$) show high efficiency of phenols and benzene removal from groundwater. Since high concentration of phenols may be toxic for microorganisms in the case of a biodegradation process, GAC seems to be a better material for designed PRB.

1. INTRODUCTION

The treatment and protection of groundwater and surface water are the significant problems in Poland which need to be resolved as fast as possible. Groundwater can be polluted mainly with pollutants from dumping sites, municipal landfills, petrol stations, airports, agriculture, chemical plants, etc. Contaminants from the above mentioned sources flow downward in the unsaturated zone, reach the groundwater and in the form of diluted solution flow horizontally and can pollute surface water like rivers, lakes, etc.

There are more than 30 types of technologies for treating groundwater and contaminated soil. Each of them is effective in particular conditions. PRB technology is an interesting method for groundwater remediation and is used when contaminants are in the

* Faculty of Mining and Geology, Silesian University of Technology, ul. Akademicka 2, 44-100 Gliwice, Poland. E-mail: Tomasz.Suponik@polsl.pl
saturated zone. This novel technique of groundwater remediation is a passive one, contaminants are removed from an aquifer by the flow through a reactive barrier filled with a reactive material [1], [2], [3], [4], [5]. The illustration of this process is shown in figure 1.

![Diagram of groundwater treatment with PRB technology]

Fig. 1. The rule of groundwater treatment with the use of PRB technology

The four primary goals of this study were:
- Presenting the adsorption and biodegradation processes used in PRB technology,
- Presenting reactive materials used most often for adsorption and biodegradation processes,
- Evaluating adsorption parameters for GAC to estimate its potential for the efficient removal of benzene and phenols from groundwater,
- Evaluating biodegradation parameters for a mixture of coarse sand and granulated peat to estimate its potential for the efficient removal of benzene and phenols from groundwater.

Phenols and benzene were selected as contaminants in this study due to their presence in the groundwater located under the chosen dumping site and their highest concentration compared to other compounds. Table 1 presents the allowable values of pH, phenols, benzene, toluene, xylene (BTX) and other compounds in accordance with the legal regulations [6], compared to their real values in the groundwater [7].

The presence of these compounds in groundwater was caused by an improperly protected dumping site situated in a city in Upper Silesia, Poland. This groundwater was used in the laboratory tests presented in the paper. The main types of wastes which were stored at the dumping site are: fly-ash, toxic chemical wastes in the form of fluid and semi-fluid (the main fluid waste contains phenols) and furnace slag [4]. Between 1993–1994 the dumping site was surrounded by a cut-off wall. However, in 2004 it was found out that this wall did not work properly. Hence the idea to resolve
Adsorption and biodegradation in PRB technology

problems connected with the contaminated groundwater by using PRB Technology. The reactive barrier might be located in this case in the place where the cut-off wall does not work properly, i.e. where the plume flows out from the surrounded area. The aquifer, in which contaminated groundwater flows, is made up of fine sand and clayey sand (hydraulic conductivity of ca. $1 \cdot 10^{-5} \text{ m/s}$), while the aquitard, located ca. 10 m under the contaminated area, is made up of dusty clay and sandy clay (hydraulic conductivity of ca. $8 \cdot 10^{-11} \text{ m/s}$). The thickness of aquitard is 1–2 m [4], [7].

Table 1

<table>
<thead>
<tr>
<th>Compounds and parameters</th>
<th>Unit</th>
<th>Allowable value</th>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>–</td>
<td>6.5–9</td>
<td>7.6</td>
</tr>
<tr>
<td>Chloride</td>
<td>mg/dm$^3$</td>
<td>1000</td>
<td>128.0</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg/dm$^3$</td>
<td>500</td>
<td>8000.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>mg/dm$^3$</td>
<td>0.06</td>
<td>0.148</td>
</tr>
<tr>
<td>Arsenic</td>
<td>mg/dm$^3$</td>
<td>0.1</td>
<td>0.020</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/dm$^3$</td>
<td>2</td>
<td>0.210</td>
</tr>
<tr>
<td>Chromium</td>
<td>mg/dm$^3$</td>
<td>0.5</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Nickel</td>
<td>mg/dm$^3$</td>
<td>0.5</td>
<td>0.496</td>
</tr>
<tr>
<td>Lead</td>
<td>mg/dm$^3$</td>
<td>0.5</td>
<td>0.391</td>
</tr>
<tr>
<td>BTX</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>0.1</td>
<td>12.684</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td>5.640 mg/dm$^3$</td>
</tr>
<tr>
<td>Xylene</td>
<td></td>
<td></td>
<td>1.242 mg/dm$^3$</td>
</tr>
<tr>
<td>Phenols</td>
<td></td>
<td>0.1</td>
<td>2861.6 mg/dm$^3$</td>
</tr>
</tbody>
</table>

As the contaminated groundwater moves through the reactive barrier, the contaminants are removed by physicochemical, chemical and/or biological processes [1], [2], [3], [4], [5]. Many reactive materials can be used as a filler in PRB. The processes applied here are [8]: redox reaction, pH control, adsorption, biodegradation. It is well known that for the removal of phenols and benzene from water, it is good to use adsorption and biodegradation [4], [5], [9], [10]. This led to the idea to use these processes in PRB technology to treat groundwater located under the chosen dumping site.

Adsorption is a process that occurs when a liquid solute accumulates on the surface of a solid adsorbent, forming a molecular or atomic film (the adsorbate) [11]. With regard to the strength of fixation between adsorbent and adsorbate, the adsorption process can be divided into [12]:

- physical adsorption – the adsorbate adheres to the surface only through Van der Waals interactions (weak fixation of molecules or atoms);
- chemisorption – the adsorbate adheres to the surface through the formation of a chemical bond (higher strength of fixation than physical adsorption).
The manner and strength of fixation are of great importance in relation to the possibility of remobilisation, and are strongly influenced by parameters such as concentration, solubility and speciation of the contaminants and co-solvents as well as the prevalent pH, Eh and temperature conditions [13], [14].

There is a large number of materials that are able to immobilize contaminants by sorption, including GAC, coal, charcoal, zeolite, activated aluminium oxide, silica gel, montmorillonite, kaolinite, peat, compost, sawdust, ion-exchange resins. Hence, it was found out that they can be used as a reactive material in the PRB technology, especially for contaminants which are not susceptible to Eh or pH changing processes. When selecting the right and effective sorption material for PRB it should be taken into account that it must meet the following conditions: high sorption capacity, high selectivity for target contaminants, fast reaction kinetics, high hydraulic permeability, long-term effectiveness, it also needs to be non-harmful to the environment, available at a reasonable cost [14], insoluble, not biodegraded and easy to apply. Unfortunately, sorption material should be frequently replaced and regenerated due to the effects of potential desorption or reversed ion-exchange. This aspect makes adsorption barrier rather expensive and not attractive compared to other types.

High dissociation constant of phenols ($pK_a = \text{ca.}10$) indicates that they are not dissociated at neutral pH. So both phenols and benzene are mainly sorbed by hydrophobic bonding to organic material. Therefore large amounts of organic material (less polar and more aromatic) are required for high sorption degree of phenols and benzene at neutral pH.

In groundwater, there are microorganisms which can decay hazardous hydrocarbons using them as a source of carbon and/or energy. Biodegradation of an organic compound is a molecular hydrocarbon alteration due to enzymes, leading to the formation of less or non-toxic compounds such as CO$_2$, H$_2$O [15], inorganic compounds and biomass. Benzene and phenols can be biodegraded according to the following reactions:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O,$$  \hspace{1cm} (1)

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O.$$  \hspace{1cm} (2)

Sustained conditioning of the aquifer system is generally important for biological processes in PRB. A biodegradation process runs slowly and in order to accelerate it favourable conditions should be created in the reactive barrier. The most important factors that biodegradation is dependent on are:

- concentration of oxygen in water ($>0.2$ g O$_2$/m$^3$),
- concentration of nutrients in water (C:N:P = 120:10:1),
- temperature (15–45 °C),
- redox potential (Eh >50 mV),
- pH (acceptable pH range, i.e. 5.5–8.5).
Therefore bio-barriers can be optimized by adding: nutrients, air, oxygen and an electron donor [13].

Bio-barriers can consist of a zone containing barrier material or may simply be a zone in the native soil where degradation is stimulated. Examples of materials that can be applied in PRB to promote bioremediation enhancement include the following:

- solid oxygen-releasing compound (e.g. ORC® – Oxygen Releasing Compound) – material which is able to supply enough O₂ over a period of 6 to 12 months to support aerobic biodegradation [16],
- solid carbon (e.g. sawdust, compost, peat and GAC – used as a bio-filter) – organic compounds are first adsorbed on the surface of an adsorbent, and after increasing the number of microorganisms, they can be desorbed and oxidized by them [17].

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>Reactive material Type of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>activated alumina, bauxite</td>
</tr>
<tr>
<td>Molybdenum (Mo), uranium (U), technetium (Tc), cesium (Cs)</td>
<td>activated carbon</td>
</tr>
<tr>
<td>Uranium (U), technetium (Tc)</td>
<td>exchange resins</td>
</tr>
<tr>
<td>Molybdenum (Mo), mercury (Hg), uranium (U), arsenic (As), phosphorus (P), selenium (Se), copper (Cu)</td>
<td>ferric oxides and oxyhydroxides</td>
</tr>
<tr>
<td>Molybdenum (Mo), uranium (U), aluminium (Al), barium (Ba), cadmium (Cd), manganese (Mn), mercury (Hg), nickel (Ni), uranium (U),</td>
<td>magnetite</td>
</tr>
<tr>
<td>Molybdenum (Mo), uranium (U), chromium (Cr), arsenic (As), lead (Pb), sulphate</td>
<td>peat, lignite, coal</td>
</tr>
<tr>
<td>Molybdenum (Mo), uranium (U), technetium (Tc), lead (Pb), cadmium (Cd), zinc (Zn)</td>
<td>phosphates</td>
</tr>
<tr>
<td>Aluminium (Al), barium (Ba), cadmium (Cd), manganese (Mn), mercury (Hg), nickel (Ni), uranium (U), strontium-90 (Sr), arsenic (As), chromium (Cr), lead (Pb), selenium (Se)</td>
<td>zeolite</td>
</tr>
<tr>
<td>Chlorinated volatile organic compound (cVOC)</td>
<td>ferrous minerals</td>
</tr>
<tr>
<td>Fuel hydrocarbons</td>
<td>ORC® compound</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>ultramicrobacteria</td>
</tr>
<tr>
<td>Benzene, toluene, ethylbenzene, xylene (BTEX), naphthalene, phenols, creosote-contaminated groundwater, coal-tar contaminated groundwater, chlorinated aliphatic compounds</td>
<td>GAC, compost, peat – used as biofilter; native soil</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>zeolite-activated carbon clays</td>
</tr>
<tr>
<td>Benzene, toluene, ethylbenzene, xylene (BTEX), phenols, volatile organic compound (VOC), polycyclic aromatic hydrocarbon (PAH)</td>
<td>GAC</td>
</tr>
</tbody>
</table>

Table 2

Reactive materials used in laboratory or field tests for different kinds of contaminants [1], [8], [13], [18], [19]
Groundwater contains low concentration of oxygen. Apart from the use of solid oxygen-releasing compounds, oxygen can be supplied to groundwater by biosparging.

The type of contaminants is the most important factor during the selection of reactive material. A compilation of laboratory and field research into chemicals treated with reactive material by adsorption and biodegradation is provided in table 2 [1], [8], [13], [18], [19]. It is divided into the contaminant groups (inorganic and organic), the reactive material type and finally into the type of the principal reaction which allows contaminants to be removed from groundwater.

On the basis of table 2 and papers [13], [16], [20], [21], [22], [23], [23] a decision was made to choose GAC and a mixture of coarse sand and granulated peat as reactive material in PRB for phenols and benzene adsorption and biodegradation, respectively. Peat mixed with sand was used to reduce the risk of developing anaerobic conditions in the barrier. Peat and sand were applied in bio-barriers to combine biodegradation and sorption as the removal mechanisms for organic compounds. These materials were used in the field and at a laboratory scale in Norway for BTX and phenols removal from groundwater [13]. A reactive barrier filled with GAC was applied as a full-scale sorption barrier in Austria where groundwater also contains phenols and benzene [20].

2. METHODOLOGY FOR DETERMINATION OF GROUNDWATER TREATMENT PARAMETERS

To properly design the PRB a few parameters, called PRB parameters, should be determined: reactive material parameters, groundwater treatment parameters and geometrical PRB parameters (table 3) [25].

<table>
<thead>
<tr>
<th>Optimization of PRB parameters</th>
<th>Reactive material parameters</th>
<th>Groundwater treatment parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• hydraulic conductivity</td>
<td>adsorption parameters</td>
</tr>
<tr>
<td></td>
<td>• effective porosity</td>
<td>and/or</td>
</tr>
<tr>
<td></td>
<td>• bulk density</td>
<td>decay kinetic parameters</td>
</tr>
<tr>
<td></td>
<td>• dispersion parameters</td>
<td></td>
</tr>
<tr>
<td>Geometrical PRB parameters</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

At the beginning of the design procedure reactive material parameters and groundwater treatment parameters need to be measured (table 3). Groundwater treatment parameters for both tested materials (i.e. for GAC and the mixture of coarse sand and granulated peat) were determined by laboratory tests presented in this part of the paper. The reactive material parameters were also determined on the basis of laboratory tests but the methodology and discussion were presented in the following articles.
The results of the process of determination of reactive material parameters of the tested materials are presented in Table 4.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>GAC</th>
<th>Mixture of coarse sand and granulated peat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity (m/s)</td>
<td>$5.42 \times 10^{-4}$</td>
<td>$5.84 \times 10^{-4}$</td>
</tr>
<tr>
<td>Bulk density (kg/m$^3$)</td>
<td>559</td>
<td>1680</td>
</tr>
<tr>
<td>Effective porosity (–)</td>
<td>0.31</td>
<td>0.22</td>
</tr>
<tr>
<td>Longitudinal dispersivity [m]</td>
<td>0.76</td>
<td>0.76</td>
</tr>
<tr>
<td>Transverse dispersivity (m)</td>
<td>0.076</td>
<td>0.076</td>
</tr>
</tbody>
</table>

### 2.1. METHODOLOGY FOR DETERMINATION OF ADSORPTION PARAMETERS

The laboratory tests carried out to determine groundwater treatment parameters for the adsorption process were conducted by placing GAC and contaminated groundwater in septum-capped vials and shaking them on the vibratory machine for 4 hours. The batch tests were carried out in two separate series: benzene and phenols. The initial concentration of benzene and phenols in water was 20.01 mg/l and 2208.4 mg/l, respectively [26]. Due to the fact that the temperature of groundwater at the depth of 5–15 m below ground level in Poland is ca. 10 °C, the temperature of air in the laboratory and in tested water was the same.

In the batch tests, the cooled water was poured into six septum-capped vials in each series and then 103.6, 195.1, 302.2, 397.6, 491.0, 612.7 mg of GAC was added to every vial respectively in the benzene series, and 400.7, 501.0, 591.0, 704.6, 790.8, 906.7 mg of GAC respectively in the phenols series. After shaking the vials for 4 hours on the vibratory machine, the water was poured through thick filters and the concentrations in the machine were measured with UV-Vis spectrophotometer for phenols and with gas chromatograph for benzene.

It is common knowledge that increasing the pH value reduces organic compounds adsorption. Since batch tests were conducted at pH 7.9, the next measurement for higher pH value needs to be done. It may give some information about what can happen if groundwater pH increases.

### 2.2. METHODOLOGY FOR DETERMINATION OF BIDEGRADATION PARAMETERS

The laboratory test carried out to determine groundwater treatment parameters for biodegradation process was conducted in a glass column packed with a mixture of
coarse sand and granulated peat at a volume ratio of 8/2 (figure 2). Groundwater was circulated in the column from bottom to top with the use of a peristaltic pump and then the biodegradation process was conducted in it. The groundwater Darcian velocity was 0.55 m/day which means that conditions in the column corresponded to the conditions in the aquifer in the chosen area (the Darcian velocity in the aquifer located under the dumping site is 0.3–0.7 m/day). There were three sampling points along the column in order to draw water out and to measure the concentration of benzene and phenols with UV-Vis spectrophotometer for phenols and with gas chromatograph for benzene.

![Fig. 2. Installation for the simulation of flow and the treatment process of contaminated groundwater in reactive barrier; 1, 2, 3, 4, 5 – sampling points](image)

The biodegradation of phenols and benzene is particularly related to the oxidation state. Although the degradation of these compounds is possible under anaerobic conditions, the aerobic conditions are probably necessary to achieve high removal efficiencies [23], [24]. In order to create aerobic conditions in the column filled with mixture of sand and peat, the water was continuously aerated in a bulb with an aquar-
ium pump. In this test, peat as solid carbon accumulated organic compounds like phenols and benzene, and after increasing the number of microorganisms in reactive material, it desorbed these contaminants and at the same time microorganisms oxidized them. The main bacterial strains in groundwater were: *Bacillus cereus*, *Pseudomonas putida*, *Staphylococcus sciuri* and *Corynebacterium*. In accordance with the papers [22], [23], hydrocarbons decay under the influence of these microorganisms.

It is common knowledge that high and low pH values as well as high concentration of heavy metals are unfavourable for microorganisms. Since the column test was conducted at a pH 7.5 and the concentration of heavy metals was less than 10 mg/dm³, it was necessary to conduct more measurements in conditions which were worse for microorganisms.

The main objective of the column test was to calculate the reaction rate and the half-life of biodegradation. In order to do it properly, the steady state of this process had to be achieved, it was obtained 35 days after the beginning of the test.

After this time the measurement series were started. The concentration of benzene and phenols in groundwater before it flowed into the column was 40 mg/l and 211.1 mg/l, respectively. The lower concentration of phenols in comparison with the adsorption tests arose from the fact that groundwater was diluted in this test because phenols could be toxic for microorganisms if their concentration exceeded 500 mg/l [22]. In this case, the concentration of benzene in water had to be increased (because water was diluted). The temperature in laboratory air and in the tested water was ca. 10 °C in this study, similarly to the adsorption tests.

3. RESULTS AND DISCUSSION

3.1. GROUNDWATER TREATMENT PARAMETERS FOR ADSORPTION

The concentration of benzene in water for every vial was 2.49, 1.33, 0.32, 0.21, 0.19, 0.10 mg/l, and the concentration of phenols was 95.0, 60.6, 51.9, 37.5, 25.0, 20.9 mg/l. Phenols and benzene are probably sorbed mainly by hydrophobic bonding to GAC.

Groundwater treatment parameters for GAC as an adsorbent for benzene and phenols were measured with the Freundlich isotherm:

\[ C_g = k \cdot C^n, \]  

where:
- \( C_g \) – the amount of contaminant adsorbed by weight of GAC (mg/g),
- \( C \) – the equilibrium concentration in water after performing a batch test (mg/l),
The isotherm is a measure of the amount of a soluble organic compound that is adsorbed per unit weight of media at a constant concentration and at constant temperature.

The data collected from the batch test were plotted on a log-log graph to form a straight line based on the empirical Freundlich equation: \( \log C_g = \log k + n \log C \) (figure 3).

![Figure 3. Freundlich isotherm for: a) benzene, b) phenols in two-phase system of GAC–water, at a temperature of 10 °C](image)

Table 5 presents the results of the determination of groundwater treatment parameters for GAC as a reactive material. The results show that GAC can be used as an adsorbent in PRB technology for treating groundwater located under the selected dumping site. Thus these parameters and reactive material parameters (table 4) will be used as input data in, e.g., the numerical model for the determination of geometrical PRB parameters and for assessing whether adsorption in PRB technology used for groundwater located under a dumping site is effective enough to protect the environment. Unfortunately, the adsorbing capacity of GAC is limited and active carbon must be replaced from time to time. To facilitate the temporary replacement of GAC, the reactive barrier should be made of prefabricated units or filter columns filled with this reactive material.

The coefficient of determination \( R^2 \) for benzene series and phenols series was equal to: \( R^2 = 0.96 \) and \( R^2 = 0.98 \), respectively. These values indicate that the Freundlich isotherm was well fitted to the experimental data.

The results obtained in the batch tests of phenols are similar to the results presented on the website [21] where \( k_{\text{phen}} \) and \( n_{\text{phen}} \) are 17.18 l/g and 0.23, respectively. In
the book [28], the same parameters for phenols and benzene are $k_{\text{phen}} = 21$, $n_{\text{phen}} = 0.54$ and $k_{\text{ben}} = 1$, $n_{\text{ben}} = 1.60$, respectively.

Table 5

<table>
<thead>
<tr>
<th>Parameters, unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$ – Freundlich sorption equilibrium constant (l/g)</td>
<td>3.9</td>
</tr>
<tr>
<td>$n$ – Freundlich exponent (-)</td>
<td>0.48</td>
</tr>
</tbody>
</table>

## 3.2. GROUNWATER TREATMENT PARAMETERS FOR BODEGRADATION

Figure 4 presents the results of the column test, i.e. the values of benzene and phenols concentration in water drawn out from the sampling points shown in figure 2.

![Fig. 4. Benzene and phenols concentration obtained in the column test carried out in the installation shown in figure 2](image)

Groundwater treatment parameters for the mixture of coarse sand and granulated peat as a reactive material for benzene and phenols removal were calculated using the first-order kinetics equation:

$$C = C_0 e^{-\lambda t},$$

(4)

where:

- $\lambda$ – the reaction rate (decay coefficient) (1/hr),
- $t$ – the time of the biodegradation process (hr),
\[ C_0 \] – the initial concentration of phenols and benzene in water (mg/l),  
\[ C \] – the concentration of phenols and benzene in water in time \( t \) (mg/l),  
\[ C/C_0 \] – the relative concentration of organic compounds.

In order to achieve groundwater treatment parameters, the relative concentrations of organic compounds \( (C/C_0) \) were plotted against time in hours (figure 5). The slope of the fitted line is the reaction rate, \( \lambda \) (hr\(^{-1}\)).

![Graph](image)

**Fig. 5.** Pseudo first-order degradation rate of phenols and benzene

The coefficient of determination \( (R^2) \) for benzene and phenols was equal to: \( R^2 = 0.81 \) and \( R^2 = 0.91 \), respectively. These values indicate that pseudo first order model fitted the experimental data. Table 6 presents the results of groundwater treatment parameters determination for the mixture of coarse sand and granulated peat as a reactive material.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzene</td>
</tr>
<tr>
<td>Half-life ( t_{1/2} ) (hr)</td>
<td>48.72</td>
</tr>
<tr>
<td>Reaction rate ( \lambda ) (1/hr)</td>
<td>0.0142</td>
</tr>
</tbody>
</table>

The results obtained in this part of the article show that even at such a low temperature, biodegradation proceeded quite quickly. Surely, at the field scale the conditions may be worse for biodegradation and the reaction rate can be lower, too.

Later the reaction rate \( (\lambda_{\text{phen}} = 0.0369 \text{ 1/hr}; \lambda_{\text{ben}} = 0.0142 \text{ 1/hr}) \) used as a groundwater treatment parameter and reactive material parameters (table 4) will be used as
input data in, e.g., the numerical model for the determination of geometrical PRB parameters and for assessing whether biodegradation process in PRB technology used for specific region is effective enough to protect the environment.

However, it is well known now that biodegradation will be very difficult to use in PRB technology for the treatment of specific groundwater due to the high concentration of phenols which are very toxic for microorganisms. In the laboratory test, water was diluted and it would be very difficult to do this at the field scale. This problem in connection with the possibility of increasing pH in water as well as the possibility of higher concentration of heavy metals means in fact that the mixture of coarse sand and granulated peat cannot be used as a reactive material in PRB technology for specific groundwater.

4. CONCLUSIONS

- Biodegradation parameters obtained for phenols and benzene, with the use of the mixture of coarse sand and granulated peat as a reactive material, are $\lambda_{\text{phen}} = 0.0369$ l/hr and $\lambda_{\text{ben}} = 0.0142$ l/hr, respectively. The biodegradation process used in PRB is efficient and interesting due to the fact that no other contaminants are generated and it is not necessary to replace the reactive material unless the barrier blocks up. Unfortunately, the biodegradation process proceeds slowly and suitable conditions for microorganisms must be created in the reactive barrier (e.g. the concentration of oxygen in water should be higher than 0.2 g O$_2$/m$^3$).

- Since there is a high concentration of phenols in the examined groundwater, it could be toxic for microorganisms, the water in the laboratory test was diluted. Such a solution would be very difficult to apply at the field scale. Thus the mixture of coarse sand and granulated peat would be very difficult to use as reactive materials in PRB technology for removal of phenols and benzene from groundwater located under the improperly protected dumping site located in a city in Silesia, Poland.

- The adsorption parameters obtained with the use of GAC as an adsorbent for phenols and benzene are $k_{\text{phen}} = 20.7$ l/g, $n_{\text{phen}} = 0.51$ and $k_{\text{ben}} = 3.9$ l/g, $n_{\text{ben}} = 0.48$, respectively. Because of the limited adsorbing capacity of the GAC bed, active carbon must be replaced and regenerated. In order to facilitate the temporary replacement of GAC, the reactive barrier should be made of prefabricated units or filter columns. The GAC applied in PRB technology can make it possible to remove phenols and benzene (effectively) from groundwater located under the dumping site located in a city in Silesia, Poland.

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REFERENCES


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