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## HYDROCARBONS REMOVAL FROM UNDERGROUND COAL GASIFICATION WATER BY ORGANIC ADSORBENTS

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**Abstract:** The main problems in the case of the underground coal gasification process is the possible pollution of surrounding aquifers. The underground gasification cavity is a source of both gaseous and liquid pollutants and these are mainly aromatic hydrocarbons, phenols, heavy metals and others. In order to prevent underground water from pollution a permeable reactive barrier was proposed. The filling was granulated activated carbon and SPILL-SORB (peat) – two commonly available sorbents adequate for hydrocarbons removal. The wastewater (synthetic solution which simulated groundwater contaminated with the UCG products) was prepared by mixing distilled water with desired amounts of substances such as phenols, benzene, toluene, xylene, naphthalene etc. Batch tests were performed in order to measure sorption of phenols and benzene from the post-UCG water on the mentioned sorbents. Experimental results were fitted with linear and non-linear Freundlich and Langmuir isotherm models. The obtained data showed that removal of phenols and benzene in case of GAC was much more efficient. However, sorption was lower than in the case of literature data and can be explained by complex composition of the solution and pre-treatment of the samples. The Langmuir model gave a better fit in the case of GAC, whereas Freundlich isotherm model was matching the data better in case of SPILL-SORB.

**Keywords:** *underground coal gasification, permeable reactive barrier, Langmuir adsorption isotherm*

### Introduction

Underground coal gasification (UCG), the technology which dates back to the beginning of the XX century is an alternative technology of energy extraction from coal. Despite the fact that various field and laboratory tests were performed, it has never been implemented on a full technical scale. The main drawback of UCG is the environmental risk associated with water pollution in surrounding aquifers. The underground gasification cavity is a source of both gaseous and liquid pollutants which may get into contact with water and in future cause threat to water aquifers. The substances leached from the gasification zone are mainly mono- and polycyclic

aromatic hydrocarbons, phenols, heavy metals, cyanides, ammonium, chloride, sulphate (Humenick et al. 1980; Stuermer et al. 1982; Humenick 1984; Liu et al. 2006; Kapusta et al. 2010; Kapusta and Stanczyk 2011). Among many water treatment technologies the PRB (Permeable Reactive Barrier) is one of the considered method of UCG water treatment. It is a passive technology where contaminants are removed from an aquifer by flowing through a “reactive material” (Puls et al. 1998; Gavaskar et al. 2000; Gavaskar et al. 2003; ITRC 2005; Suponik 2011).

As the contaminated groundwater moves through the reactive barrier, the contaminants are removed by physicochemical, chemical and/or biological processes (Puls et al. 1998; Meggyes et al. 1998; Gavaskar et al. 2000; Meggyes et al. 2000; Suponik and Lutynski 2009, Suponik 2013). The mechanism involved in contaminant removal are listed below (Roehl et al. 2005; ITRC 2005; Suponik 2011).

- Biochemical reactions which lead to:
  - biodegradation of organic compound
  - precipitation of heavy metals by sulphate-reducing bacteria.
- Redox reactions which lead to:
  - chemical detoxification
  - precipitation of heavy metals.
- pH control (precipitation).
- Adsorption.

The type of mechanism which removes contaminants depends on the material used for filling and on the contaminant to be removed. In case of this study it was assumed that for removing aromatic hydrocarbons the filling for PRB would be granulated activated carbon or peat. These materials were selected based on literature review (U.S. DOE 1998, Gavaskar et al. 2003). In both cases the leading reaction which retains contaminants is adsorption. The uptake of adsorbate by the adsorbent can be described by various models where the most commonly applied are Freundlich and Langmuir isotherm models.

In this study results of batch tests of benzene and phenols removal from synthetic solution of post-UCG water by granulated activated carbon and peat are presented. Experimental results are fitted with linear and non-linear forms of Freundlich and Langmuir models.

## Materials and methods

Two reactive materials were selected for the study, i.e. granulated activated carbon (GAC) and peat in form of the commercial adsorbent SPILL-SORB. The granular activated carbon was WACC 8X30 made from coconut shells by steam gas-method. SPILL-SORB (peat) is a fully organic industrial adsorbent of high moisture adsorbancy. Properties of GAC and peat are presented in Table 1. Methodology of the tests was typical for experiments of sorption from aqueous solution (Gulgonul 2012).

Table 1. Properties of sorbents used in the study  
(SPILL-SORB MSDS 2012, ELBAR Katowice MSDS 2013)

Property, unit	GAC Value	SPILL-SORB Value
Particle size distribution, mm	0.6–2.4	–
Specific surface, m <sup>2</sup> /g	min. 1000	200
Iodine number, mg/g	min. 1000	–
Moisture, %	max. 5	10%
Ash, %	max. 12	6
pH	ca. 8	4–6
Hardness, %	min. 98	–
Bulk density, g/dm <sup>3</sup>	480±30	150±2

The wastewater (synthetic solution which simulated groundwater contaminated with UCG products) was prepared by mixing distilled water with desired amounts of the following pure substance: phenols, benzene, toluene, xylene, naphthalene, fluorene, phenanthrene, pyrene, anthracene, CuSO<sub>4</sub>·5H<sub>2</sub>O, NiSO<sub>4</sub>·7H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, NaCl, K<sub>2</sub>CrO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KCN. The concentrations of contaminants in the solution were similar to the values reported in the literature (Liu et al. 2006; Kapusta and Stanczyk 2011). Chemical composition of solution is presented in Table 2. The initial conductivity and pH of the solution was 22 mS/cm and 7.9 respectively. Since pH after adding the substances was 5.5, it was adjusted to the intentional value by slow titration with ultra-pure sodium hydroxide.

Table 2. Initial chemical composition of synthetic UCG wastewater used for the test

Parameter/ chemical compound	Value	Unit
pH	7.9	–
Conductivity	22	mS/cm
TOC	4.48	mg/dm <sup>3</sup>
Phenols	15.4	mg/dm <sup>3</sup>
NH <sub>4</sub> <sup>+</sup>	3280	mg/dm <sup>3</sup>
CN <sup>-</sup>	1.84	mg/dm <sup>3</sup>
Benzene	0.540	mg/dm <sup>3</sup>
Toluene	0.141	mg/dm <sup>3</sup>
Xylene (sum)	0.121	mg/dm <sup>3</sup>
Cr <sup>6+</sup>	0.091	mg/dm <sup>3</sup>
Cu	0.55	mg/dm <sup>3</sup>
Ni	1.24	mg/dm <sup>3</sup>
Zn	0.16	mg/dm <sup>3</sup>
SO <sub>4</sub> <sup>-</sup>	550	mg/dm <sup>3</sup>
Cl	784.1	mg/dm <sup>3</sup>

The concentration of contaminants in wastewater during the tests was measured with the use of:

1. UV-Vis Spectrophotometer DR5000 HachLange – diazotised 4-nitroaniline method, wavelength 550 nm (phenols)
2. HPLC – UVD 340u Gynkotek, column RP-18 Hypersil Gold, flow 1 cm<sup>3</sup>/min in gradient analysis Me/H<sub>2</sub>O (benzene).

The installation in which batch tests were carried out was a programmable rotator equipped with 50 cm<sup>3</sup> plastic tubes. In the rotator, the 2 minutes reciprocal rotation was used for every sample (with turning angle 90° and speed range 50 rpm) after which a short pause (15 second) followed. The solutions were poured into plastic tubes (50 cm<sup>3</sup> to every sample) and then a specified mass of reactive material was added to every sample. Later, the tubes were closed with corks. After shaking the samples for 2 hours, the solutions were flowed through thick filters and the concentrations of particular chemicals were measured. The temperature in laboratory air and in tested water was about 19 °C.

The amount of solute adsorbed per unit weight of material (mg/g) was calculated with the use of the following formula:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium adsorbate concentrations (mg/dm<sup>3</sup>), respectively,  $V$  is the volume of solution (dm<sup>3</sup>) and  $W$  is the weight of the adsorbent (g).

## Results and discussion

Sorption of benzene on GAC and SPILL-SORB is shown in Fig. 1, whereas sorption of phenols on GAC and SPILL-SORB is shown in Fig. 2. The mechanism of adsorbate removal in both cases is the hydrophobic adsorption to GAC and peat. Therefore, it was decided to fit Freundlich and Langmuir models in order to explain interactions between the adsorbate and adsorbent and to compare the constants with literature data.

The isotherms were fitted with linear and non-linear forms of Freundlich and Langmuir isotherm models. These two models are the most common and fairly accurate ones that describe sorption of substances from aqueous solutions (McKay et al. 1985; Kumar 2006). The intention was to assess if the non-linear forms give a better fit than commonly applied linear forms. In case of linear forms, the sum of square residuals is not minimized as it is in formulas presented below for the Freundlich and Langmuir model respectively:

$$\sum_i (q_{ei} - K_F C_e^n)^2 \quad (2)$$

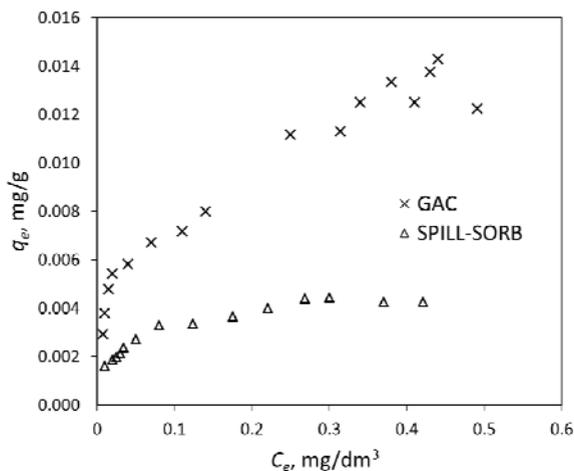


Fig. 1. Adsorption isotherms of benzene from UCG wastewater solution on GAC and SPILL-SORB at 19 °C

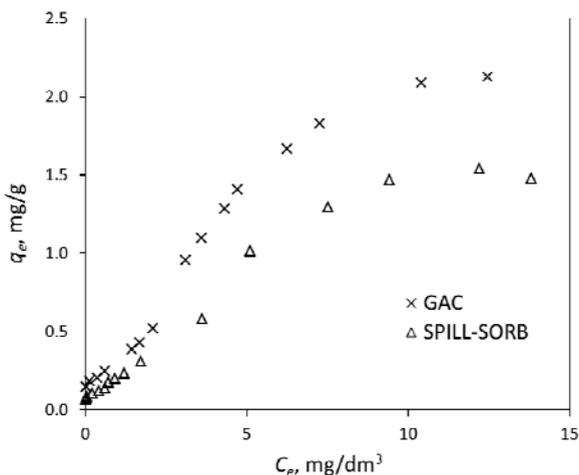


Fig. 2 Adsorption isotherm of phenols from UCG wastewater solution on GAC and SPILL-SORB at 19 °C from wastewater

$$\sum_i \left( q_{ei} - \frac{QK_L C_e}{1 + K_L C_e} \right)^2 \tag{3}$$

Langmuir model has four linear forms and all of them were assessed in terms of best model fit to the experimental results. The linear and non-linear forms of equations assessed in the study are presented in Table 3.

Table 3. Linear and non-linear forms of Freundlich and Langmuir models

Isotherm model	General equation (non-linear form)	Linear form
Freundlich	$q_e = K_F C_e^n$	$\log q_e = \log K_F + n \log C_e$
Langmuir-1		$\frac{C_e}{q_e} = \frac{1}{Q} C_e + \frac{1}{K_L Q}$
Langmuir-2	$q_e = \frac{Q K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \frac{1}{K_L Q} \frac{1}{C_e} + \frac{1}{Q}$
Langmuir-3		$q_e = Q - \left( \frac{1}{K_L} \right) \frac{q_e}{C_e}$
Langmuir-4		$\frac{C_e}{q_e} = K_L Q + K_L q_e$

Experimental data were plotted in linear forms and fitted with regression lines. Constants for each model i.e.  $K_F$  and  $n$  for Freundlich and  $K_L$  and  $Q$  for Langmuir were calculated based on the general form of the linear equation of regression line. Coefficients for the non-linear forms of the models were calculated by minimizing residual sum of squares to the experimental values. The coefficient of determination was calculated for each form of the models and summarized for GAC and SPILL-SORB in Table 4 and 5 respectively. Table 3 and 4 present Freundlich and Langmuir constants calculated by using linear and non-linear forms of the equations for benzene and phenols adsorption on GAC and SPILL-SORB at 19 °C.

Table 4. Freundlich and Langmuir constants calculated using linear and non-linear forms of the equations for benzene and phenols adsorption on GAC at 19 °C

Isotherm	Benzene			Phenols		
	$K_F$ dm <sup>3</sup> /mg	$n$	$R^2$	$K_F$ dm <sup>3</sup> /mg	$n$	$R^2$
Freundlich (linear)	0.0172	0.3343	0.9667	0.5668	0.4234	0.8421
Freundlich (non-linear)	0.0175	0.3443	0.9639	0.4510	0.6558	0.9604
	$K_L$ , dm <sup>3</sup> /mg	$Q$ , mg/g	$R^2$	$K_L$ , dm <sup>3</sup> /mg	$Q$ , mg/g	$R^2$
Langmuir-1	17.7436	0.0144	0.9667	0.1765	3.3333	0.6422
Langmuir-2	75.5384	0.0102	0.8647	31.6666	5.2632	0.5327
Langmuir-3	56.4972	0.0116	0.6476	12.3609	1.0619	0.1851
Langmuir-4	36.6690	0.0129	0.6476	2.2869	1.6796	0.1851
Langmuir (non-linear)	17.7260	0.0142	0.9810	0.1005	4.07291	0.9753

Table 5. Freundlich and Langmuir constants calculated using linear and non-linear forms of the equations for benzene and phenols adsorption on SPILL-SORB at 19 °C

Isotherm	Benzene			Phenols		
	$K_F$ dm <sup>3</sup> /mg	$n$	$R^2$	$K_F$ dm <sup>3</sup> /mg	$n$	$R^2$
Freundlich (linear)	0.00604	0.2865	0.9717	0.3462	0.3843	0.7792
Freundlich (non-linear)	0.00585	0.2702	0.9604	0.2836	0.6806	0.9650
	$K_L$ dm <sup>3</sup> /mg	$Q$ mg/g	$R^2$	$K_L$ dm <sup>3</sup> /mg	$Q$ mg/g	$R^2$
Langmuir-1	33.8750	0.0046	0.9914	0.0967	3.3333	0.6728
Langmuir-2	56.3111	0.0039	0.8671	4700	0.2128	0.3306
Langmuir-3	46.7289	0.0042	0.8054	113.6363	0.6009	0.0643
Langmuir-4	37.664	0.0044	0.8054	7.2998	1.2313	0.0643
Langmuir (non-linear)	31.8979	0.0046	0.9547	0.0945	2.8633	0.9895

Comparison of correlation coefficients for both linear and non-linear models shows that GAC adsorption equilibrium data follow predominantly the Langmuir non-linear model for benzene and phenols. In the case of SPILL-SORB the sorption data for benzene are described more accurately by Langmuir-1, whereas phenols follow the Langmuir non-linear model. In both materials the Freundlich model gives a slightly less accurate fit. In case of GAC some of the Langmuir non-linear models have unacceptable fitting and therefore should be rejected for further assessment. Experimental data with best-fit models are presented in Figs 3 and 4.

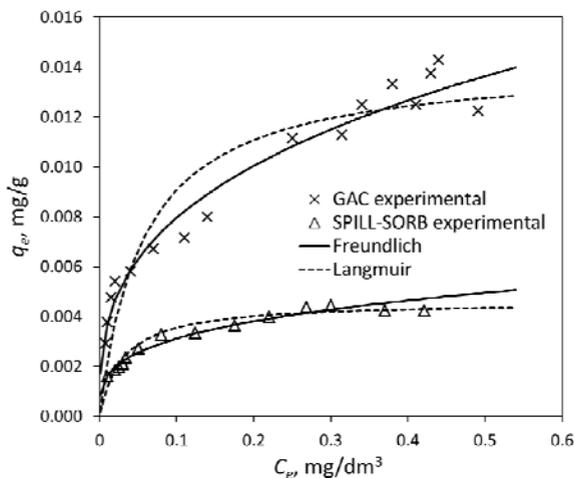


Fig. 3. Freundlich and Langmuir best model fitting for sorption of benzene on GAC and SPILL-SORB at 19 °C from wastewater

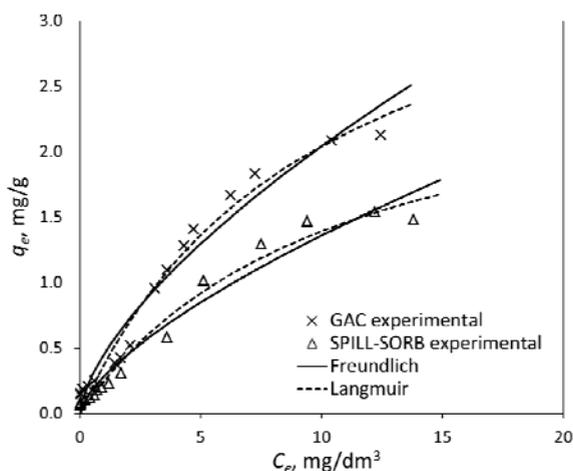


Fig. 4. Freundlich and Langmuir best model fitting for sorption of phenols on GAC and SPILL-SORB at 19 °C from wastewater

The isotherm data clearly show that removal of phenols and benzene in case of GAC is much more efficient. It can be explained by much larger specific surface of GAC and its pH which is more favorable for organic compounds sorption (Villacanas et al. 2006). Nevertheless, the Langmuir and Freundlich constants are significantly lower than those reported in literature (Maarof et al. 2004; Villacanas et al. 2006; Vijana and Neagu 2012). There might be several reasons of this phenomenon. The first one is the method of sample preparation. In our study the GAC and SPILL-SORB were not pre-treated neither by thermal nor chemical treatment (eg. with nitric acid). Those procedures could not be followed in case of PRB, therefore were rejected. Another explanation could be the fact that the experiments were not conducted under vacuum and in the access of oxygen. The tendency of carbon to chemisorb oxygen is greater than the tendency to adsorb any other species. Oxygen chemisorbs on the surface of GAC to form carbon–oxygen functional groups that may be acidic, neutral, or basic. These phenomena has been observed in other studies (Tessmer et al. 1997; Dabrowski et al. 2005). We can assume that this effect is not valid for peat. Low adsorption of these two measured compounds could be explained by the number of other chemical compounds in the solution which most probably occupy sorption sites of adsorbents. Therefore, the obtained values were lower than those reported in the literature for less complex solutions.

## Conclusions

Granulated activated carbon and peat were tested as possible filling for PRB installed around UCG site. The reason for choosing these materials was their accessibility and relatively high sorption properties of organic compounds. Sorption of phenols and

benzene was much higher on GAC than on peat (SPILL-SORB). In the case of GAC the model which describes more accurately sorption equilibrium is the Langmuir non-linear model whereas in case of SPILL-SORB a slightly better fit was obtained with Langmuir-1 linear isotherm model for benzene and as Langmuir non-linear for phenols. Calculated constants for the models were lower than usually reported in the literature which can be explained by the fact that the material were not pre-treated and the experiments were conducted in the access of oxygen. Another factor could be the complex composition of the synthetic solution used for the tests where other compounds were most probably adsorbed.

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