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# SORPTION OF COMMERCIAL HERBICIDE "FONDO" CONTAINING GLYPHOSATE BY VARIOUS CARBON MATERIALS

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***Abstract***
*Glyphosate, one of the organophosphate herbicides, has been widely used in the world. The removal of glyphosate was comparatively investigated by various methods. Low cost materials, such as carbon materials are preferred for sorption processes. Carbon materials, in contrast to the other sorption materials (e.g. zeolites, clays, inorganic sorbents) are able to be easily disposal, e.g. by incineration. The aim of this paper is to describe the sorption of glyphosate (commercial product – FONDO) from aqueous solutions by various carbon materials (from charcoal to coke).*

***Key words***
*Sorption, glyphosate, active carbon, charcoal, coal, coke*

## Introduction

Glyphosate [N-(phosphonomethyl) glycine] is a post-emergence nonselective herbicide, used for the control of a wide variety of weeds. Three salts of glyphosate are used as an active ingredients in common pesticide products [1]:

- the isopropylamine salt is used as a herbicide to control broadleaf weeds and grasses in many food and non-food crops and a variety of other sites including ornamentals, lawns and turf, residential areas, greenhouses, forest plantings and industrial rights of- way. It is formulated as a liquid, solid or pellet/tablet, and is applied by using ground or aerial equipment.
- the sodium salt is used as a plant growth regulator for peanuts and sugarcane, to modify plant growth and hasten the ripening of fruit. It is applied as a ground spray to peanut fields and as an aerial spray to sugarcane.
- the monoammonium salt of glyphosate is also sprayable herbicide used to control annual and perennial weeds in agriculture.

The presence of glyphosate in the environment has led to the need of developing techniques for its removal from water sources. Existing water treatment methods include microfiltration, ultrafiltration, reverse osmosis, adsorption by activated charcoal, filtration using sand and biological degradation. Some of these procedures are expensive and/or require large infrastructure investments, and some are specific to particular contaminants. [2] As a result, there is increasing interest in alternative low-cost techniques. The use of carbon membranes is potentially an attractive option because they are inexpensive, easy to produce, and have/after various activation processes has good adsorption characteristics.

## Materials and methods

All of the experiments were performed with modelled water solutions prepared from commercial product FONDO (concentration of glyphosate 360 g $L^{-1}$). The carbon materials (crushed to a size of 0.05 – 0.25 mm) were used [3]:

- *Charcoal* – water content in its original state max. 28.0 %, ash content in anhydrous state max. 12.0 %, content of fixed carbon max. 80 %, volatile content of max. 12.0 %,
- *The brown coal ("orech")* – water content in its original state max. 30.2 %, ash content in anhydrous state max. 9.8 %, dust content (<10 mm) max. 3.0 %, volatile content of max. 51.0 %, sulphur content max. 0,77 %, minimum calorific value 17.6 MJ $kg^{-1}$.
- *The brown coal ("kostka")* – ash content in anhydrous state max. 9.8 %, dust content (<10 mm) max. 13.0 %, sulphur content max. 0.77 %, minimum calorific value 13.0 MJ $kg^{-1}$.
- *Active carbon (mikroCHEM)* – ash content in anhydrous state max. 3.5 %, dust content (<10 mm) max. 20.0 %, minimum calorific value 25.0 MJ $kg^{-1}$.
- *Coke (US Steel)* – water content in its original state max. 13.5 %, ash content in anhydrous state max. 12.0 %, dust content (<10 mm) max. 9.0 %, volatile content of max. 1.2 %, sulphur content max. 0.6 %, minimum calorific value 26.0 MJ $kg^{-1}$.

Glyphosate adsorption isotherms were obtained by batch equilibration experiments. They were performed by adding 5.0 mL of the stock solution to 0.05 g of carbon material in glass centrifuge tubes. The tubes have been shaken for 6 hour and then the supernatants were separated by centrifugation. The concentration of glyphosate in the supernatants was measured by the UV–VIS spectrophotometric method proposed by Rasul Jan et al. [4] by using a Genesys 8 UV-VIS spectrophotometer equipped with a 1 cm quartz cell.

**Results and discussion**

Experimental data obtained by sorption experiments, were evaluated by using Freundlich isotherm and Langmuir isotherm. As the most efficient adsorbent for the adsorption of glyphosate from the model aqueous solutions seems to by charcoal (adsorption capacity of 0.8486 $mg^{-1}$ g at $c_{eq}$ = 100 mg $L^{-1}$) and active carbon (adsorption capacity of 0.8385 $mg^{-1}$ g at $c_{eq}$ = 100 mg $L^{-1}$).

Both materials have a large active surface with plenty of active functional groups on surfaces that are likely to have a significant impact on adsorption of glyphosate.
On the other hand the lowest adsorption capacity, was observed in the case of coke (0.1350 mg $g^{-1}$).
We assume that during a process of coke preparation a decrement of the adsorption surface area and removal of the available functional groups, which would be available for adsorption of polar herbicide will occur.

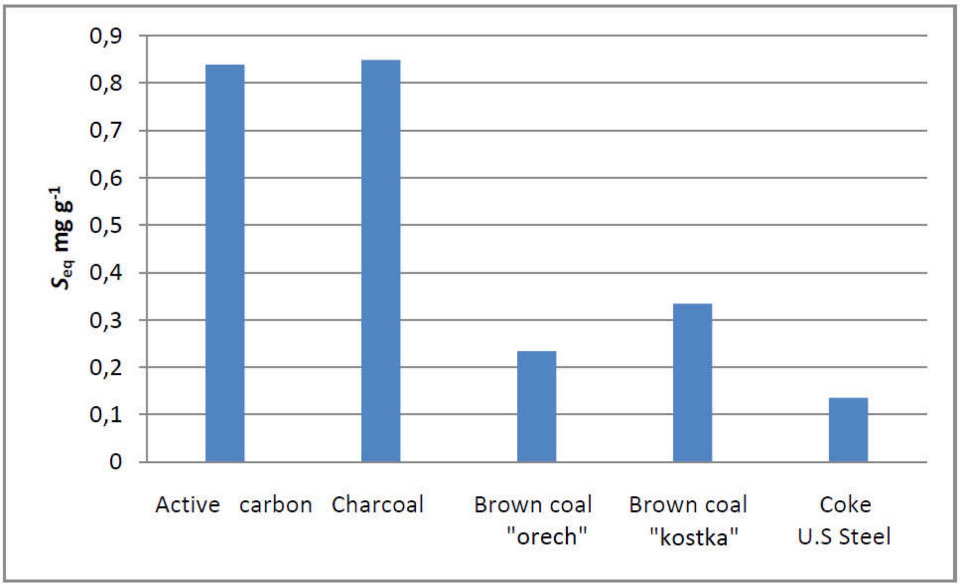


*Fig. 1 Adsorption capacity of the studied materials at glyphosate equilibrium concentration 100 mg $L^{-1}$*

Freundlich isotherm model correlates well with the experimentally obtained data in the case of activated carbon with a correlation coefficient of 0.9583, 0.8927 for charcoal, brown coal “orech” 0.9988 and 0.9925 “kostka”. In the case of US Steel coke Pearson correlation coefficient was 0.9318. As shown in the Fig. 2, *n* is in each case greater than 1, what means predominant adsorption processes were indicated. This increased concentrations of the molecules of the organic sorbate in the water phase and this decreased the relative share of the captured solid phase sorbent. This phenomenon is particularly marked in the case of coke.

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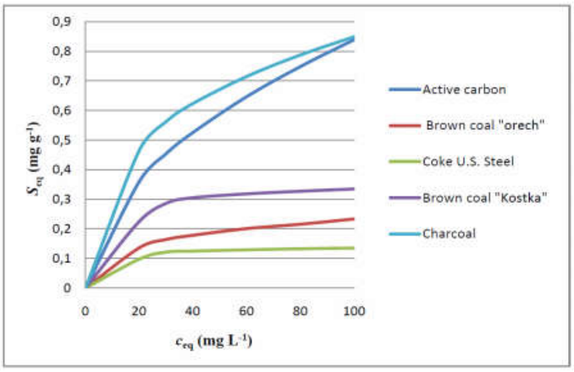
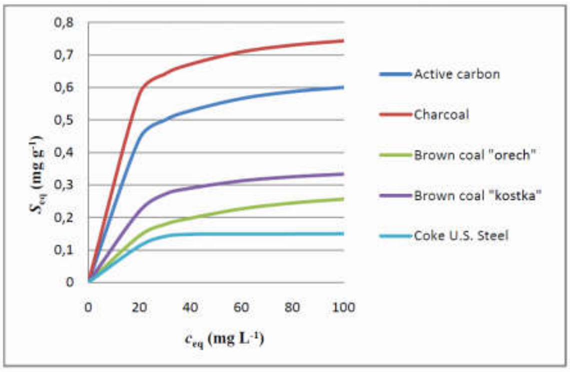



| Sorbent | $K_f$ | $n$ |
|---|---|---|
| Active carbon | 0.80 | 1.96 |
| Charcoal | 0.18 | 2.97 |
| Brown coal "orech" | 0.06 | 3.39 |
| Brown coal "kostka" | 0.21 | 9.91 |
| Coke U.S. Steel | 0.09 | 11.36 |

*Fig. 2 Freundlich isotherm of studied adsorption systems and their coefficients*

Langmuir isotherm model correlates well with the experimentally obtained data - in the case of activated carbon with a correlation coefficient of 0.8709, 0.8655 for charcoal, brown coal – "orech" 0.9999 and 0.9928 "kostka".

In the case of U.S. Steel coke Pearson correlation coefficient was 0.9414.




| Sorbent | $S_{max}$ | $b$ |
|---|---|---|
| Active carbon | 0.66 | 0.10 |
| Charcoal | 0.80 | 0.13 |
| Brown coal "orech" | 0.32 | 0.04 |
| Brown coal "kostka" | 0.37 | 0.09 |
| Coke U.S. Steel | 0.15 | 1.64 |

*Fig. 3 Langmuir isotherm of studied adsorption systems and their coefficients*

**Conclusions**

The work was focused on the study of carbon materials sorption properties for the removal of glyphosate from the modelled aqueous solutions. The model Freundlich isotherm shows that the highest adsorption capacity was experimentally determined for the sample of charcoal and active carbon. The lowest value of adsorption capacity was determined for the sample of coke from U.S. Steel and the brown coal "orech". They have proven to be less effective sorbents, but they would be activated in many ways, which we will be discussed in the near future. Langmuir isotherm follows the model best fitted to charcoal and active carbon. Least efficient sorption materials were shown to be the brown coal "orech" and coke from U.S. Steel.

**References**

[1] STENERSEN, J 2004: Chemical pesticides: mode of action and toxicology. CRC Press, 274 p. ISBN 0-7484-0910-6

[2] MORENO ESCOBAR, B., GOMEZ NIETO, M.A. and HONTORIA GARCÍA, E. 2005: Simple tertiary treatment systems. Water Supply 5, p. 35 - 41.

[3] ŽÁK, E. 2015: Possibilities of carbonaceous materials application for selected contaminant sorption [Graduate Theses] - Slovak University of Technology Bratislava. Faculty of Materials Science and Technology; Institute of Safety, Environment and Quality. Trnava: MTF STU, 50 p.

2015, Number 5, Volume 3, date of issue 28th Juni 2015 ISSN 1339-5270

[4] RASUL JAN, M., SHAH, J., MIHAMMED, M. and BEHISHT, A. 2009: Glyphosate herbicide residue determination in samples of environmental importance using spectrophotometric method. Journal of Hazardous Materials, 169. p. 742–745

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