Study of application of alginite in the treatment of pesticide contaminated groundwater

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ABSTRACT
The Hungarian chemical industry produces large amounts of chloro acetamide and phenoxy-acetic-acid type herbicides for the agriculture. The study of the environmental fate of the compounds is very important and can help in pollution prevention. The aim of this work was to find a method to reduce the groundwater contamination caused by organic compounds (main pollutants are acetochlor, propisochlor and 2,4-DCP). The applicability of alginite (special oil shale) as an adsorbent was tested. Static equilibrium experiments were carried out in order to study the efficiency of alginite. GC/ECD, HPLC and TOC were used as analytical methods. The data fit to a Langmuir-like isotherm within the concentration range of 0 and 100 mg/l. Concerning the amounts added, 80-90 % of contaminants were bounded by alginite. Similar experiments were carried out with bentonite, too because this clay mineral has already been used in environmental protection as an adsorbent. On the other hand, the bentonite is the main component of alginite. About 40% of the investigated chemical was adsorbed by this adsorbent. Our results showed that the alginite can be used efficiently in the treatment of natural waters polluted by herbicides, and it works better than bentonite.

INTRODUCTION
Pesticides, especially herbicides, are an important part of the chemicals used. Some persistent pesticides and their degradation products have been found to accumulate and transport between different environmental compartments, leading to contamination of atmosphere, ground- and surface water, soils as well as foods. Numerous investigations have proved the various pesticides and their degradation products in ground water or even drinking water. To estimate the ecological impact of pesticides for the protection of environment and human health, a deep understanding of pesticides' behaviour in different environmental compartments. Pesticides undergo a series of reactions and transports in the environment, where soil takes a central position when considering the fate of the pesticides. Soil has relatively high tolerance against natural and anthropogenic contamination. Pesticide residues undergo a series of complex physical and biological process in soil. They are often a combination of process such as chemical and biological degradation, adsorption, desorption and leaching. The fate of a given pesticide in soil depends on it's physical-chemical properties and the soil properties.

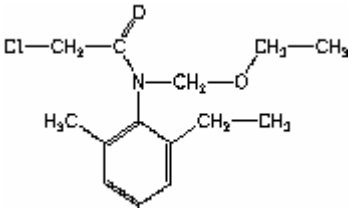
In natural substance the adsorption increases the concentration of contaminate compounds. Of this knowledge can be worked out a directed to reduction of contaminate technology. The base of this technology can be the applicability of alginite as adsorbent.

METHODOLOGY

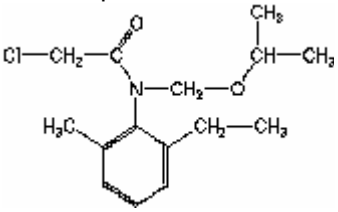
Materials

After the identification of contaminating compounds in groundwater we chose the main components which were used in experiments:

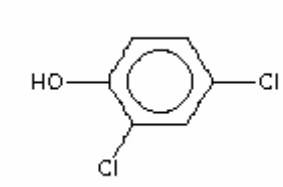
Acetochlor: 99,3 %



Propisochlor: 99,8 %



2,4-DCP: 99 %



The solutions were made with 0,1 M NaCl/0.1 M phosphate-buffer.
We used alginite as adsorbent:

pH	7,4
Organic matter	33 %
Surface	31,88, m2/g
Pore diameter	3,4 nm

Methods

- Static equilibrium experiments (adsorption and desorption)
  - adsorbent: 5 g alginite
  - concentration range: 10-100 mg/l

- Analysis: after equilibration were carried out

- We use the next analytical methods after the right sample preparation in examinations:

HPLC (High Pressure Liquid Chromatography)

Merck LaChrom

eluens:	acetonitrile:H2O= 65:35
wavelength:	=218 nm
colonna:	Lichrospher (125 m); RP-18 (5 m)
time:	10 min
detector:	*UV*

TOC (Total Organic Carbon)

Heraeus TOC

- determination on low temperature with sodium peroxo disulphate oxidation and UV detection

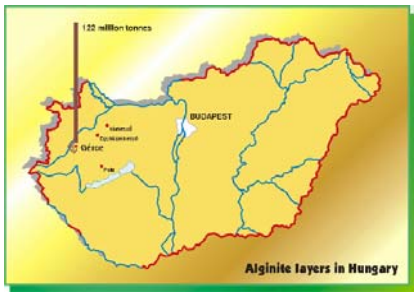
The organic matter content of alginite disturbs the analysis. As the solute interacts with the humic solutions in the liquid as well as in the solid phase.

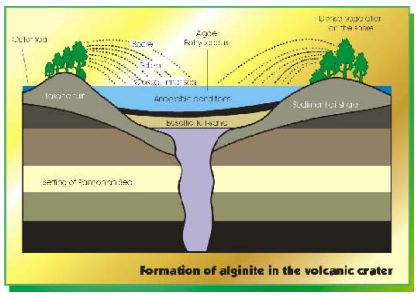
THE ALGINITE

Millions of years ago green algal a relatively rare species (Botryococcus bravnii) proliferated in the closed ring-shaped volcanic crater-cone which arose from the Pannonian sea. The sea algae settled down with other floating particles on the bottom of the interior hollow. The mineral resource originated from this settled and fossilised algal-biomass is known as alginite. It developed in anaerobic conditions.

Alginite belongs to the category of oil shales but it has got unique and individual attributes which can cause an alteration to the oil shales not only in physico-chemical characteristics but in the potential usage of the product. So far alginite was discovered exclusively in Hungary, or more precisely in the Carpathian Basin. It can be found and mined solely in this area of the world.

Alginite is a mineral containing in high concentration such components as humus, limestone and other macro- and micro elements, these among **62 different components** so for identified in it, all deriving from the region of Gérce and Pula, Hungary. Alginite is a mineral of **natural origin which contains neither any artificial additives nor chemicals**. It is neutral, sometimes slightly basic in pH value – measured in water – of between 7.16–7.78; measured in solutions of KCl it is between 6.92–7.50.

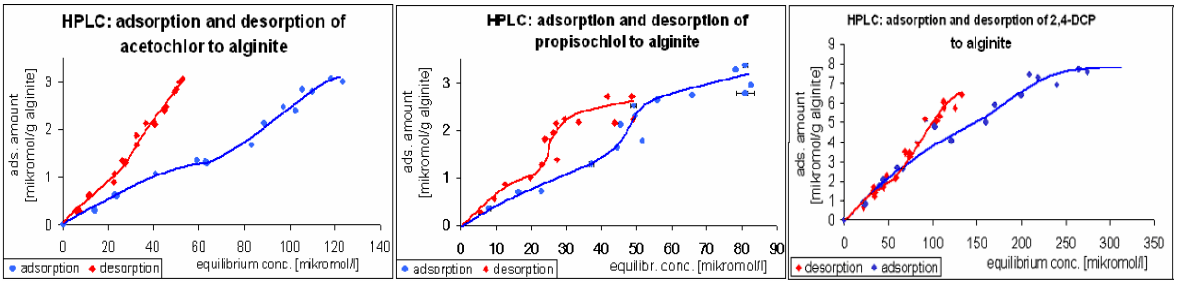




RESULTS

Adsorption and desorption

Adsorption and desorption process affect the behaviour of pesticides in soil. They determine the bioavailability, phytotoxicity, persistence, and mobility of pesticides. Adsorption can lead to an accumulation of pesticides and a decrease of pesticide concentration in soil and solutions, resulting diminished bioavailability, reduced degradation and mobility. Through desorption pesticides become available for process such as further chemical and biological degradations, transport with surface water, and distribution in the soil and leaching into groundwater. Because of the variable and complex nature of soils, accompanied by a number of adsorption-desorption and degradation process.



Isotherms show that the adsorption and desorption processes consist of more steps.

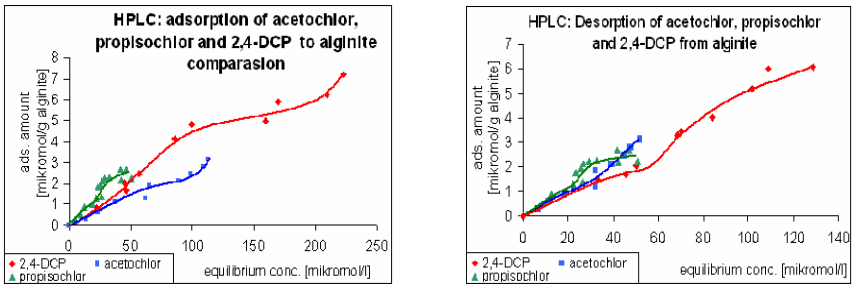
Explanation:

- •Adsorbate establishes a second layer or they form different associates either in the solution or on the surface.
- •Alginite is a heterogeneous adsorbent (organic and mineral parts)

Desorption isotherms are above the adsorption isotherms.

- •Explanation: Capillary condensation

Results show that alginite strongly binds the contaminants studied.



Adsorption of chlorophenol is better. A small 2,4-DCP molecule can enter easily into the small pores than bigger chloroacetanilides.

- *Adsorption depends on the size of molecule.*

Adsorption of propisochlor is adsorbed in highest amounts than acetochlor.

- *Adsorption depends on the structure of the molecule.*

The isopropyl group (propisochlor) links to alginite stronger than ethoxymetyl (acetochlor)

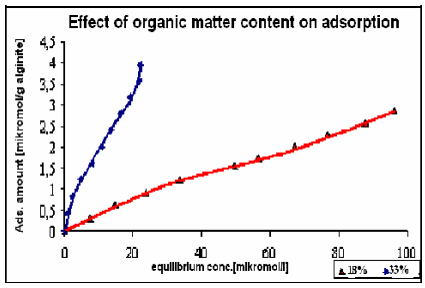
No significant differences between the desorption and adsorption of the chemicals

Effects of different parameters on adsorption

Effect of organic matter

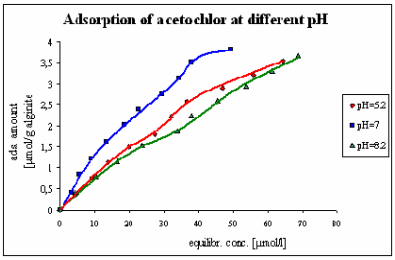
We investigated two types of alginites with different organic matter content :

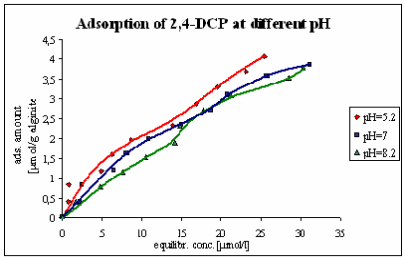
a.) 18 % b.) 33%

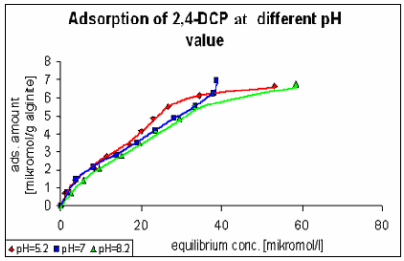


Adsorption is determined by organic matter

Effect of pH

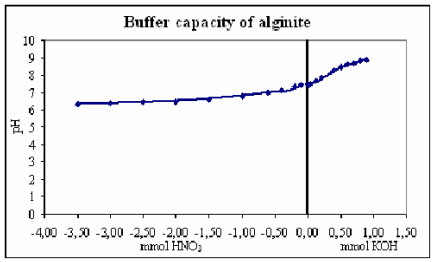




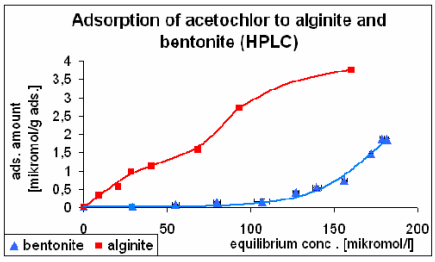


The pH doesn't influence the adsorption. The isotherms of chemicals are similar, there aren't significant differences.

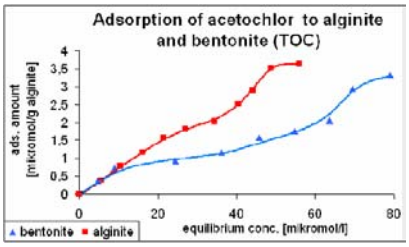
Cause: Good buffer-capacity of alginite



Comparison of alginite and bentonite as adsorbent



Alginite can bound more acetochlor (acetochlor can be found large amount in contaminated water) than bentonite. Isotherm of alginate takes place above the isotherm of bentonite in low concentrations, too.



There aren't differences in low concentration, but above 10 mg/l equilibrium concentration the alginate proves to be better adsorbent than bentonite.

CONCLUSIONS

- The alginite works as a good adsorbent for contaminated waters.
- Alginite strongly adsorbs the contaminants the bounded chemicals can not be eluted from the adsorbent biodegradation
- The pH doesn't influences significantly the adsorption (because of good buffer capacity of alginite).

- Efficiency of alginite is similar to bentonite but alginite is a better adsorbent. (Bentonite is widely applied as an adsorbent in environmental protection.)

- Experiment data can be used in transport models of contaminants.

- The results show that alginite is usable as an adsorbent in order to treat the contaminated groundwater.

REFERENCES

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