THE EFFECT OF ORGANIC MATTER TYPE OF HUNGARIAN OIL SHALE IN SORPTION OF ACETOCHLOR

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Abstract
The development of efficient methods for the removal of different type of organic contaminates of natural waters is an ever challenging task in the modern environmental technology. The paper reports the physical characterization and adsorption properties of a Hungarian oil shale (OSR). Static equilibrium experiments were carried out to study the adsorption of acetochlor from aqueous solution. The obtained equilibrium data were satisfactorily fitted by a multistep adsorption isotherm within the concentration range of 0 to 100 mg/l. More than 90 % of the added acetochlor was adsorbed by the studied oil shale. The contaminants are bound strongly by the sorbent therefore they cannot be washed out by the groundwater flow which, in turn, favors to the natural bacterial decomposition process of the polluting compound. This is considered as a significant advantage of the adsorbent because no chemical regeneration of the inexpensive oil shale is required. The reported results indicate that the oil shale can be used efficiently for the treatment of natural waters to remove their organic contaminants.

Keywords: oil shale, adsorption, acetochlor

Introduction
Water pollution problems caused by organic contaminants emitted by the chemical industry and agricultural activity are especially severe because they threaten both soil and aquatic live too. They are present in surface and subsurface waters as a result of natural degradation of different pollutants released by the agriculture and by various industrial plants [1]. Chloroacetanilide are persistent in the environment [2] and can cause toxicity especially by bioaccumulation in animals and plants whereby threatening human health too [3]. The removal of these compounds from contaminated raw water is a difficult task.
The studied oil shale adsorbent contains considerable amounts of clay minerals as well as organic matter too which is finely dispersed in the macro- and micropores of the inorganic matrix. Oil shale sources are located at several places of the Carpathian Basin, and especially large amounts can be found in the Hungarian mines. It is an algae based biomass fossil fine-grained sedimentary rock containing large amounts of organic matter, clay volcanic ash and calcium carbonate. The shale originates from the biomass of yellow green algae – genus *Botryococcus braunii* – accumulated in the volcanic craters over 4 to 5 million years [3]. The organic matter (OM) in oil shale is composed of bitumen and large amount of kerogen [4].
The aim of our work is to investigate the sorption properties of Hungarian oil shale as an adsorbent for the removal of acetochlor from model water samples, under laboratory conditions. The effect of organic material content and type of the oil shale were examined.

Materials and methods
Analytical grade sodium chloride, sodium dihydrogen phosphate and disodium hydrogen phosphate were obtained from Reanal Chemical Co. (Hungary). The HPLC grade solvent

(acetonitrile) was provided by VWR Ltd. (Hungary). The acetochlor standard reference material (>99%) was the product of Sigma Aldrich.

Hungarian oil shale sample was first air-dried, then milled for 1 hour and sieved (particle size below 360 μm was used). Particle size distribution of OSR was measured using Mastersizer 2000 laser diffraction system (Malvern Instruments Ltd). Total organic carbon content (TOC) of adsorbents were determined by Apollo 9000 (TEKMAR DOHRMAN) TOC Analyzer. Nitrogen gas adsorption isotherms (BET surface) and pore size were obtained with ASAP 2000 apparatus.

The main mineral fraction of adsorbents was analyzed using the PHILIPS PW3710 X-ray diffractometer (K filter, Cu radiation (50 kV, 40 mA)). The crystalline phases were identified using the X'Pert Highscore Plus software. Scanning electron microscopy for oil shale samples was conducted using Thermo Fischer APREO SEM attached with EDX units, with accelerating voltage 20 kV. The pH of OSR were measured by a Radelkis pH meter (OP-211) using a combined glass electrode (Radelkis, OP-0808P).

The measured physical and chemical properties of the studied OSR are summarized in Table 1.

Table 1. Characterization of the oil shale (OSR) sorbent

Properties	***OSR***
pH (1 mol/L KCl)	7.21
BET*, m^2/g	31.87
Typical pore size, nm	3.4
Main fraction, %	80.8
Particle size, μm	50-150
Organic content, %	9.79
Carbonate content, %	41.2
Main mineral phases, %	
	23.0
Calcite	7.3
Quartz	1.6
Siderite	6.2
Dolomite	2.5
Albite	1.8
Caolinite	0.6
Montmorillonite	38.7
Illite	0.7
Amorphous material	17.7

*Specific surface obtained by BET nitrogen adsorption method

Samples having different amounts of organic matter were used in order to investigate the effect of OM on adsorption of acetochlor on oil shale. Therefore humic substances (HS) were removed from OSR according to the Kézdi's method [5]: the oil shale was treated with hydrogen-peroxide (30 % w/w) solution, then dried and milled.

Since montmorillonite is the main mineral in OSR, bentonite from Egyházaskesző (Hungary) containing 81 % clay mineral (mostly montmorillonite) was used as an adsorbent too.

Adsorption studies

The adsorption isotherms were obtained in a series of batch experiments. The procedure is summarized in the scheme shown in Fig. 1. Static equilibrium experiments were carried out in a solution containing 0.1 mol/l NaCl and 0.01 mol/l phosphate buffer (pH=7). 5-5 g of adsorbent were left to swell in 5 ml distilled water for 24 h at room temperature, then 65 ml of acetochlor (solute) in appropriate buffer solutions (0-100 mg/l) was added. The suspension

was shaken for 1 hour in an orbital shaker then separated by centrifuge at 6000 rpm for 20 min. The supernatant was filtered then analyzed by HPLC.
In the supernatant, the concentration of acetochlor was determined by a MERCK LaChrom HPLC system equipped with a LiChospher 100 column filled with 5 □m RP-18 packing material (125 mm x 4 mm) and with programmable UV detector. Samples of 10 □l injected by an autosampler were isocratically eluted by a hydro-organic eluent containing 65 % acetonitrile and 35 % water; flow rate: 0.7 ml/min; □=218 nm.

Results and discussion
The adsorption isotherms are important to describe the solute-adsorbent interaction. A multi-step isotherm model [6] was employed for the numerical fitting of the isotherm data to Equ. (1) by the Microcal TM, Origin 6.0 software.

$$q = \sum_{i=1}^{s} \left\{ \frac{q_{Ti} K_i (c - b_i + |c - b_i|)^{n_i}}{2^{n_i} + K_i (c - b_i + |c - b_i|)^{n_i}} \right\} \qquad (1)$$

where
c is the equilibrium concentration of solution, [□mol/l],
s is the number of steps of the isotherm (i = 1...s),
q_{Ti} is the adsorption capacity, [□mol/g],
K_i is the equilibrium constant, [(l/□mol)^{n_i}],
b_i is the critical concentration limit, [□mol/l],
n_i is the average degree of association assigned to the i-th step of the adsorption curve.

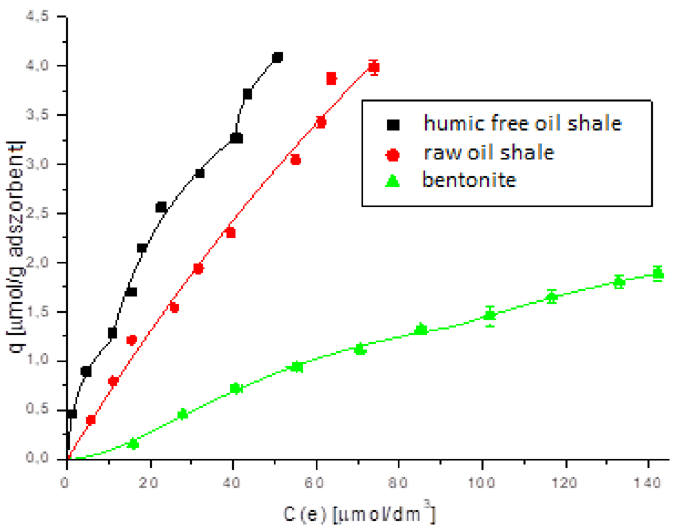

Figure 1. Effect of organic matter content of oil shale on sorption of acetochlor

Adsorption isotherms for the acetochlor on oil shale (OSR) at different organic matter content values of the solution are shown in Fig. 1.

Effect of organic material type of sorbent
In this work the adsorption capacity of three samples containing different amount and type of organic phase was compared. Several studies confirmed that the high organic matter content of the adsorbent significantly increases the adsorption of organic compounds [6]. In this study the organic matter values were as follows: bentonite<humic free oil shale<OSR (see Table 2).

Table 2. Organic material content of adsorbents

	OSR	humic free oil shale	bentonite
TOC (solid), %	14.4	10.5	0.09
HS, (%)	3.81	0.00	0.05
Kerogen (%)	10.5	10.5	0.04
DOC* (mgC/ l)	78.1	93.0	11.7

DOC: dissolved organic carbon

The Fig. 1 shows the adsorption isotherms of acetochlor on bentonite, humic free oil shale and raw oil shale. It can be seen that acetochlor was bound better by the humic free sample than by the HS containing sample. It seems that the higher organic content of OSR resulted in lower adsorbed amount of acetochlor. In this untreated sample the surface is covered by HS (Fig. 2), therefore it is just partially accessible for contaminants. The presence of humic substances increased the solubility of acetochlor, thus HS decreased its adsorbed amounts compared to the treated oil shale.

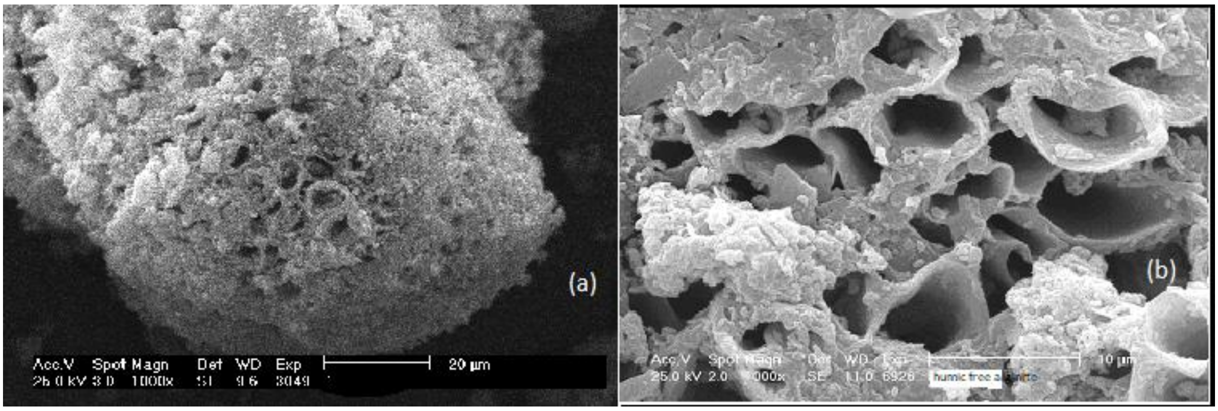

Fig. 2 SEM images of row oil shale (a) and humic free oil shale (b)

When HS was removed from the oil shale with hydrogen peroxide the kerogen and bitumen fraction remained unchanged on the surface [8]. Making a comparison among the adsorption isotherms in Fig. 1 proves that bitumen and kerogen are responsible for the relatively high solid TOC (see Table 2) and sorption capacity. The absence of organic matter (bentonite) resulted in the lowest adsorbed amount of acetochlor. This compound is better bound by the organic matter content of the adsorbent, while clay minerals do not play an important role in this adsorption process.

Conclusion

Laboratory scale study of adsorption properties of the Hungarian oil shale revealed that it can be used as a low-cost adsorbent for the efficient removal of acetochlor and similar organic contaminants from polluted raw waters. The results of static equilibrium studies were fitted by a multi-step isotherm equation. The adsorption is favored by the special organic matter content (bitumen, kerogen) of the adsorbent (raw oil shale) but lower values of HS (H_2O_2 treated oil shale, bentonite).

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