Characterization of oil shale kerogen semi-coke and its application to remove chemical pollutants from aqueous solutions

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Abstract. *An alternative adsorbent from oil shale semi-coke material for removing chemical pollutants from aqueous solutions was investigated. For this purpose, enriched oil shales with different kerogen contents (57, 79 and 90 wt%) were pyrolyzed in nitrogen atmosphere at 600–900 °C at a heating rate of 10 °C/min and a hold time of 60 min. The surface properties of semi-cokes, namely Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution (PSD), were determined by nitrogen adsorption. The studied semi-cokes were found to be micro- and mesoporous. The highest semi-coke BET surface area, 160 m²/g, was obtained at a pyrolysis temperature of 700 °C, which corresponds to 519 m²/g of char, excluding the minerals. This porous carbon material was tested as an adsorbent to remove pesticides and phenolic compounds from aqueous solutions. Three kinds of phenolic compounds (resorcinol, 5-methylresorcinol, 4-nitrophenol) and three kinds of organophosphorus pesticides (dimethoate, parathion, malathion) were tested to study the adsorption on the semi-coke material. Different contact times were tested for the adsorption of the compounds of interest. The results showed that with an adsorbent dosage of 10 mg/mL over 98% of pesticides were removed from the solution within 30 min at an initial concentration of 100 µM (corresponding to 23–33 mg/L depending on the compound). More than 97% of the phenolic compounds were adsorbed from water within six hours at an initial concentration of 10 µM (1.1–1.4 mg/L).*

Keywords: *Estonian oil shale, kerogen, semi-coke, pyrolysis, adsorbent.*

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1. Introduction

The development of low-cost sorbents from industrial waste is an important aspect of circular economy. The use of waste materials can make different production processes more sustainable and environmentally friendly. It is proposed that a good low-cost adsorbent has a high carbon content and advanced pore structure capable of removing contaminants within few hours. In addition, such an adsorbent should be readily available and accessible [1]. A waste material that meets these criteria is discussed in the present paper. This solid waste material is called semi-coke, which is generated in large quantities during oil production. Over the decades, a vast amount of semi-coke waste has been deposited in open landfills, which is an environmental blight. In Estonia, the volume of these semi-coke deposits is estimated to be somewhere between 83 and 300 million tons [2, 3]. To date, it has found limited alternative uses only. Semi-coke is a solid residue obtained by carbonization containing relatively large amounts of unburnt carbon, making it attractive for sorbent production [1, 4]. The possible conversion of semi-coke to sorbent material not only improves the environmental benefits but is also economically viable [5].

Adsorption is considered to be a cost-effective and efficient technology for the purification of contaminated drinking water, wastewater and soil [1]. Phenolic compounds are a group of chemicals of concern because they persist in the environment for a long time, accumulate and have toxic effects on human beings and animals [6]. Their entry into the aquatic environment results from natural, industrial, domestic and agricultural activities [6]. Another group of major pollutants is pesticides, which have the potential to contaminate drinking water supplies. Organophosphorus pesticides are widely used as insecticides in agriculture, which are known to be toxic and cause severe and long-term effects in humans and animals [7].

The potential of using semi-coke as an adsorbent from various sources has been studied before. The application possibilities of coal semi-coke have been investigated more than those of oil shale. Recent research progress on semi-coke adsorption applications is well summarized in a review article by Lartey-Young and Ma [1]. Different studies have shown that semi-coke can be used for removal of gaseous pollutants from air [8–11] as well as inorganic ions [12–14] and organic compounds [15] from aqueous solutions. In addition, oil shale semi-cokes have been tested to remove dyes from aqueous solutions [14, 16, 17]. In most of these articles, chemical activation with H_2SO_4, HCl, H_3PO or KOH has mainly been used to improve the properties of semi-coke. Regarding physical activation, oil shale from the Kendyrlyk Deposit was pyrolyzed and steam-activated to obtain an activated shale with a Brunauer-Emmet-Teller (BET) surface area of 131.7 m^2/g. The obtained porous carbon material was successfully tested as an adsorbent for the purification of wastewater, which worked best for the removal of petroleum products (100%), phosphates

(95.5%), suspended matter (81.7%), biochemical oxygen demand (81.3%), and surfactants (78.8%) [18].

Similarly to this article, phenolic compounds have been previously removed from aqueous solutions but using coal semi-coke, which is somewhat different in composition from oil shale semi-coke. In this regard, Gao et al. [19] prepared activated semi-coke by KOH activation with a BET surface area of 347.4 m^2/g. The researchers tested five different phenolic compounds (phenol, *p*-benzenediol, *p*-nitrophenol, resorcinol, *o*-dihydroxybenzene) for studying the adsorption properties of the activated coal semi-coke. Their results showed that the adsorption efficiency of the activated semi-coke for phenolic compounds increased with contact time and adsorbent dosage [19]. In addition, Yang et al. [20] prepared porous carbon from coal semi-coke via K_2CO_3 catalytic steam activation and tested it for *p*-nitrophenol adsorption from aqueous solution. The BET surface area of the obtained material was 121 m^2/g and it demonstrated good affinity for *p*-nitrophenol, with the maximum adsorption capacity of 192.1 mg/g.

The present study is focused on locally available oil shale and its semi-coke, the high availability and low cost of which lead to its consideration as a suitable source for the production of adsorbent materials. The aim of this work is to broaden the possible applications of oil shale pyrolysis waste products. For this purpose, a semi-coke adsorbent was prepared from the enriched Estonian oil shale kerogen by a simple heat treatment. Understandably, the direct use of industrial oil shale semi-coke by-product would be of greatest interest. However, the present study focused on an enriched oil shale semi-coke as a model that helps to explain the potential of the carbon fraction in these materials. The authors believe that this kerogen semi-coke material has the same properties as the carbon in industrial semi-cokes and will provide insight into the potential that the carbon fraction can offer in industrially produced semi-cokes. In addition to focusing on the most valuable fraction (i.e. kerogen) in semi-cokes, there is also the possibility that the carbons produced directly from oil shale may be of interest in their own right. Unlike most of the other previously published research articles, this work did not use chemical activation with harsh acids or bases involved in the process (also not in the enrichment procedure) or physical activation. The prepared material was tested as an adsorbent for purifying water from chemical contaminants, such as phenols and pesticides. To the authors' best knowledge, oil shale semi-coke has not been previously tested for the adsorption of pesticides and phenols.

2. Materials and methods

2.1. Materials

Kerogen concentrates from oil shale were prepared in Virumaa College, Oil Shale Competence Centre of Tallinn University of Technology. Three enriched oil shale samples with different kerogen contents were prepared to see how the surface properties of these samples act and change during pyrolysis experiments. Oil shale was enriched using the flotation method. First, the oil shale sample was ground to a particle size less than 125 µm. After that, the sample was mixed with $CaCl_2$ in an aqueous solution at a volume ratio of roughly 1:1 to separate organic and mineral matter. The organic part of oil shale has a lower density and rises to the surface of a denser $CaCl_2$ solution ($\rho \approx 1.5$ g/cm³). The obtained mixture was centrifuged for 10 minutes and the procedure was repeated 2–3 times to obtain a concentrate containing about 50–60%, and 4–5 times to obtain a concentrate containing about 80–90% by mass kerogen. For obtaining over 90% kerogen, the sample was additionally treated with 5% HNO_3 and left overnight to remove the remained deeper mineral fractions. After each centrifugation procedure, the resulting kerogen was filtered and thoroughly washed with distilled water, and finally dried. The ash content, calorific value, elemental composition, total organic carbon (TOC) and total inorganic carbon (TIC) contents of the kerogens are shown in Table 1. The kerogen content of the obtained materials was estimated by two ways: from thermogravimetric analysis (TGA) data in air atmosphere and by a calculation using a formula:

$$Q = 35 \text{ K, MJ/kg [21],}$$

where Q is calorific value and K is kerogen fraction (100% = 1).

As can be seen from Table 1, the agreement between the two methods was very good.

Table 1. The ash content, calorific value, elemental composition, total organic carbon and total inorganic carbon contents, and BET surface area of the unpyrolyzed oil shale kerogens. All calculations were made on a dry matter basis

Sample	Ash content, 815 °C, wt%	Calorific value, MJ/kg	C_{total}, wt%	H, wt%	N, wt%	S, wt%	TIC, wt%	TOC*, wt%	Calculated kerogen content, wt%	Kerogen content from TGA, wt%	BET surface area, m^2/g
K60	32.3	20.0	46.1	5.1	0.1	1.5	3.1	43.1	57.1	56.5	5.8
K80	18.9	28.0	61.4	7.4	0.2	1.4	1.2	60.2	80.1	78.9	4.5
K90	8.9	33.0	71.0	8.7	0.3	1.2	0.0	71.0	94.2	90.1	3.3

* TOC is calculated from the difference of total carbon (C) and TIC

2.2. Preparation of the semi-coke adsorbent

Pyrolysis was carried out in an electrically heated quartz tube furnace (Fig. 1). For pyrolysis experiments, 1.5 g of oil shale kerogen was weighed in the crucible and inserted into the quartz tube, which was maintained at temperatures from 600 to 900 °C under a nitrogen flow of 200 mL/min. The heating rate of 10 °C/min and the sample holding time of 60 minutes at the desired temperature were kept constant in all experiments. After the experiments, semi-coke was mechanically milled using a mortar. The mass loss was determined from the weight difference before and after pyrolysis.
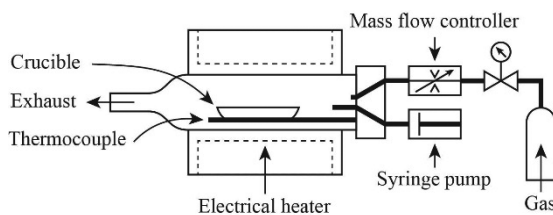
Fig. 1. Simplified scheme of the pyrolysis reactor.

2.3. Instrumentation

The analysis of the specific surface area and porosity was performed by using Quantachrome Autosorb iQ-c instrument. For the analysis, approximately 0.1 g of the kerogen semi-coke sample was placed into a vial and degassed

for 17 h at 300 °C. The N_2 adsorption-desorption isotherms of semi-coke were obtained by recording altogether 86 nitrogen adsorption and desorption data points at relative pressures (P/P_0) from 4×10^{-3} to 1. The BET method was used for calculating the specific surface area. The pore size distributions (PSD) of samples were determined from the nitrogen adsorption isotherms at –196 °C (77 K) using the density functional theory (DFT). The pore sizes discussed in this work are presented according to the IUPAC classification, which defines micropores as pores less than 2 nm wide, pores between 2–50 nm as mesopores, and pores above 50 nm as macropores. The micropore volumes of samples were determined by applying the Dubinin-Radushkevitch (DR) model. The mesoporosity of the semi-coke samples was determined by subtracting the DR microporosity value from the porosity value determined at an isotherm relative pressure of 0.95. The macroporosity of the semi-coke sample was determined by subtracting the porosity value at a relative pressure $P/P_0 = 0.95$ from the porosity value at a relative pressure $P/P_0 = 0.99$ [2]. The BET surface area of the semi-coke organic char was calculated by dividing the surface area of the whole semi-coke sample by the organic fraction present in oil shale semi-coke [2]. The proportion of the mineral part and its specific surface area (4.0 m^2/g) were taken into account too.

Elemental analysis was carried out on a Vario MACRO CHNS analyzer. The calorific values were measured using the bomb calorimeter IKA C5000 according to ISO 18125:2017. The moisture and ash analysis was carried out using Nabertherm TR 120 drying oven according to ISO 18134-2:2017 and a Nabertherm Muffle Furnace L9 according to ISO 18122:2022, respectively.

Thermogravimetric analysis of the previously described kerogen samples was performed using a NETZSCH STA 449 *F3* Jupiter® thermal analyzer. For pyrolysis experiments, a high purity N_2 (99.999%), and for combustion, a simulated air atmosphere (80% N_2, 20% O_2) were used. 2–5 mg of the previously homogenized material was weighed into Al_2O_3 crucibles without lids. Depending on the sample, a heating rate of 10 or 20 °C/min was used. For pyrolysis, a heating rate of 10 °C/min was chosen to compare the results from TGA with those obtained by using the pyrolysis reactor. For combustion, a higher heating rate was applied, as the combustion analysis results were solely used for analyzing the amount of organic char and carbonate minerals in the samples. Parallel measurements were carried out for both environments and these showed excellent reproducibility (differences between mass change steps < 2%).

Reversed-phase high-performance liquid chromatography (HPLC) analysis was performed on an Agilent Technologies 1260 Infinity II instrument (Agilent Technologies, Waldbronn, Germany) equipped with a diode array detector (DAD). The separation was carried out on an Agilent InfinityLab Poroshell 120 EC-C18 column (4.6 × 100 mm, 2.7 µm particle size) at a flow rate of 0.4 mL/min. The mobile phase consisted of Milli-Q water and acetonitrile (ACN). The following gradient elution program was employed for

the analysis: a linear gradient of water/ACN (50:50, v/v) to ACN (100%) over 3 minutes, ACN (100%) held from 3 to 9 min, followed by the 9–15 min linear gradient of H_2O-ACN (50:50, v/v) to return to the initial conditions and for the chromatograph column re-equilibration. The injection volume was 5 µL and during analysis, the samples were kept in a thermostated autosampler at 15 °C. The column temperature was set to 30 °C and the detection wavelength was 200 nm.

2.4. Dispersive solid phase extraction

For the extraction of compounds, the dispersive solid phase extraction (dSPE) was used. Resorcinol, 5-methylresorcinol, 4-nitrophenol, dimethoate, malathion and parathion were of analytical grade (purity > 98%) and were obtained from Sigma-Aldrich (Germany). Deionized water was supplied from a Milli-Q water purification system (Millipore S. A. Molsheim, France). For the experiments, 10 mg of sorbent was added to a 1 mL water sample spiked with standards in a 2 mL Eppendorf tube. Experiments with different times of contact between the adsorbent and analytes were performed over a six-hour period at 300 rpm at room temperature. A separate tube was used for each experiment, so that the volume of the solution was kept constant for analysis, which otherwise would alter the results. The same procedure was followed for the 1 mL standard solution in the Eppendorf tube for comparison and for calculating the efficiency of the adsorbent. The sorbent and the eluate were separated by centrifugation at 14,000 rpm for 10 min. Finally, the eluate was filtered with a Whatman syringe filter (0.45 µm, nylon) and used for HPLC analysis.

3. Results and discussion

3.1. Characterization of the pyrolysis process by thermogravimetric analysis

In order to characterize the thermal behavior of the investigated samples and to compare the obtained results with data received using other equipment (i.e. the batch reactor), TGA analyses were performed in both pyrolysis and combustion conditions (Fig. 2a and 2b, respectively).

As can be seen from Figure 2a, the samples exhibited different properties, as expected. Namely, the mass loss corresponding to the amount of organic material and the one corresponding to the amount of calcite minerals were noticeably different. In the pyrolysis experiments, sample K60 exhibited a 48.3% mass loss that corresponded to the loss of organic matter. The main mass loss took place in the temperature range from about 200 to 520 ºC for all the samples. In comparison, samples K80 and K90 exhibited the respective
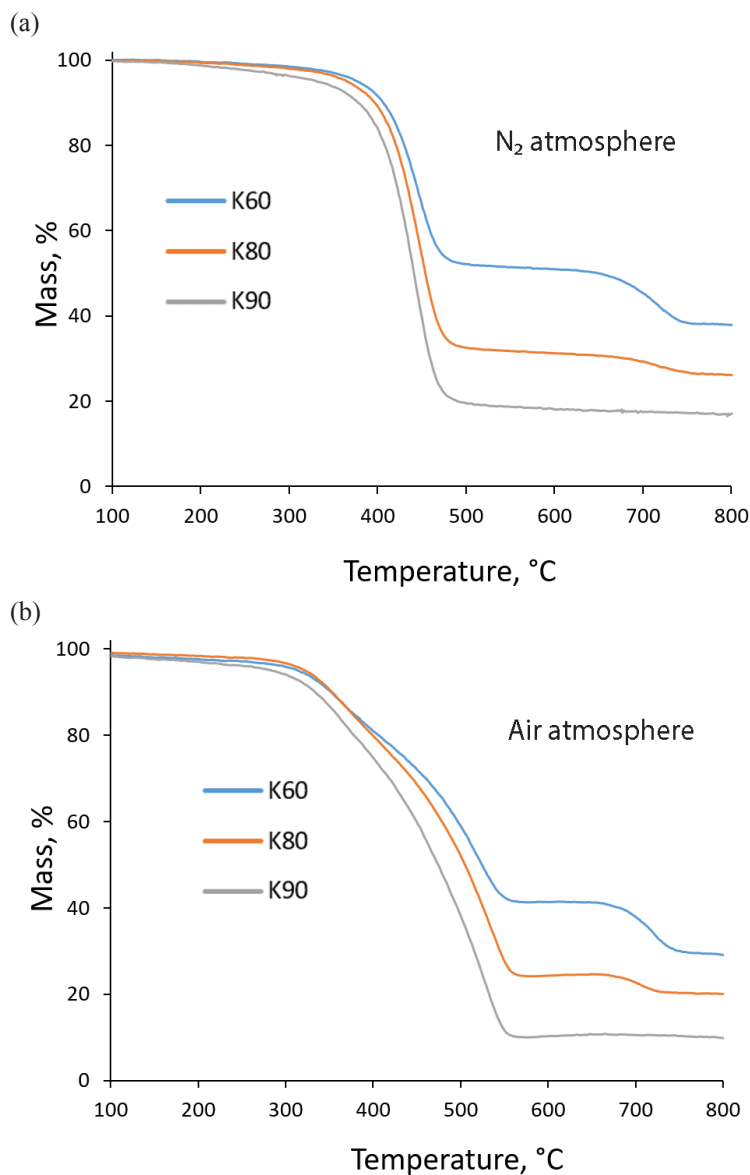
(a)

(b)

Fig. 2. Thermogravimetric analysis of oil shale kerogens: (a) in N$_2$ atmosphere (pyrolysis) and (b) in air atmosphere (combustion).

organic mass losses of 68.0% and 80.9%. According to pyrolysis results, K60 and K80 contained about 13.0% and 5.0% carbonate minerals, whereas sample K90 did not exhibit any such components.

The combustion experiments, the results of which can be seen in Figure 2b, yielded a more interesting outcome. As expected, the combustion of the organic matter in the samples took place in two somewhat overlapping steps. We have previously attributed this to the specific combustion mechanism of the complex organic matter present in oil shale [22]. The mass loss that accounted for the combustion of organic matter was found to be a bit different from the respective amounts during pyrolysis. The mass losses for samples K60, K80 and K90 during the organic matter decomposition were 56.5, 78.9 and 90.1%, respectively (see Table 1). A comparison of these results with those obtained from pyrolysis experiments showed the mass losses to exhibit higher values. The difference between the two environments was approximately 10% (absolute) for all samples. As previously described by Aarna and Rikken [23], when kerogen is decomposing, the forming products tend to acquire their most stable form, which then causes the H/C ratio to decrease with increasing pyrolysis time. This leads to the increase in the relative number of aromatic carbons compared to hydrogen atoms and supports the results of this work – the mass loss during pyrolysis tends to be smaller than that in combustion in the course of which most of the carbon is burned and CO_2 is formed [24]. The presence of fixed carbon after the pyrolysis experiments allows the production of the semi-coke adsorbent. The total kerogen content was also determined by TGA combustion experiments (Table 1). The total amount of calcite and dolomite could be estimated from the TGA graphs as well. Samples K60 and K80 contained about 11.7% and 4.2% carbonate minerals, while sample K90 did not contain those minerals. These results are in good agreement with the elemental analysis results given in Table 1, i.e. the TIC contents correlate well enough with the mass losses recorded by TGA, when recalculated to CO_2 (11.4% and 4.4%, respectively). The small difference between the two methods can be attributed to the fact that the analysis principles are different and also the heterogeneity of the sample might play a role.

3.2. Surface characterization of kerogen semi-cokes

The choice of starting material makes an enormous difference for the nature of any carbon considered as a sorbent candidate. The important characteristics of any carbonaceous adsorbents are the surface area and porosity that carbon exhibits. Therefore, this unconventional kerogen semi-coke sorbent was first characterized. The effect of pyrolysis temperature (600–900 °C) on various kerogen characteristics, such as organic char and carbonate contents, surface area, porosity and total mass loss, was investigated. The pyrolysis conditions were described in Section 2.2 and the obtained results are presented in Table 2.

The organic char contents of the semi-cokes measured by TGA showed that the char contents remained fairly similar and did not depend on the pyrolysis temperature. This confirms that only fixed carbon remains in the solid residue and the volatile matter has been removed already at 600 °C.

The results also indicated that the mass loss slightly increased with rising temperature, but remained more or less constant in case of sample K90. The increase in the total mass loss with increasing pyrolysis temperature is due to the decomposition of carbonates, which were not present in the K90 sample. The average mass losses of samples K60, K80 and K90 were approximately 55, 70 and 80 wt%, respectively. These results are in good accordance with TGA results, where the mass losses at 800 °C in N_2 atmosphere were 62, 74 and 83 wt%, respectively (see Fig. 2a).

All three kerogen samples had the highest surface areas at 700 °C, while at temperatures 600 and 900 °C the samples' surfaces areas (and porosities) were lower. The highest BET surface area, 160.2 m^2/g, was obtained with K80 semi-coke, which corresponds to the 518.5 m^2/g-char recalculated onto char basis alone (calculation described in Section 2.3). In addition, the K80 semi-coke sample pyrolyzed at 700 °C revealed the largest total pore volume and micropore volumes – 0.11 and 0.06 cm^3/g, respectively. The microporosity increased significantly when increasing the pyrolysis temperature from 600 to 700 °C, but began to decrease again at higher temperatures (> 700 °C). The micropores accounted for the majority of the total pore volume of all samples (around 40–70%). In contrast, the mesoporosity increased with increasing temperature. The mesopores accounted for about 20–30% of the sample porosity. At 600 °C, the macropores of all samples were less developed. The macroporosity of samples K60 and K90 was not particularly affected by the pyrolysis temperature used (except 600 °C for sample K60). The macropores in samples K60 and K80 covered about 20–30% of the total pore volume, while in sample K90 the respective figure was only about 5–10%. It can be concluded that the studied kerogen semi-coke samples were mostly micro- and mesoporous, while the microporosity started to decrease at temperatures over 700 °C.

Pore size distribution determines the applicability of materials as sorbents, while those with different porosities are preferred for different applications. For example, it is known that the porous structure of carbon used to capture small gaseous molecules from the air is characterized by high microporosity, while many carbons used to capture larger molecules in water are designed to have higher micro- and mesoporosity. Generally, adsorbents with a higher surface area and porosity are preferred. Consequently, the K80 sample pyrolyzed at 700 °C was chosen as a model semi-coke sorbent for the adsorption experiments (Section 3.3). The N_2 adsorption-desorption isotherms (Fig. 3a) and pore size distribution (Fig. 3b) of the semi-coke of kerogen K80 sample reveal some information about the sorbent obtained. According to the IUPAC classification, the isotherm in Figure 3a is classified as Type II, which is usually characteristic for nonporous or macroporous adsorbents, however, this isotherm exhibits a steep rise at a low relative pressure, which indicates the presence of micropores. In addition, an H3 type hysteresis loop appeared in the isotherm, which refers to the slit-shaped pores. For the latter pores, a

Table 2. Kerogen semi-coke organic char and carbonate contents, BET surface areas, porosity values and mass loss of the three oil shale kerogen samples pyrolyzed in N_2 atmosphere at different temperatures

Sample	Temperature, °C	Organic char[a], %	Carbonates[a], %	BET surface area, m²/g	BET area m²/g, char	Total pore volume at $p/p_0 = 0.99$, cm³/g semi-coke	Microporosity, cm³/g semi-coke	Mesoporosity, cm³/g semi-coke	Macroporosity, cm³/g semi-coke	Total mass loss[b], %
K60	600	16.4	20.2	64.4	372.7	0.045	0.025	0.013	0.007	49.0
	700	14.4	18.2	108.6	732.8	0.099	0.042	0.023	0.034	49.0
	800	13.8	14.1	101.1	707.6	0.094	0.040	0.021	0.033	56.2
	900	14.2	12.4	67.6	451.6	0.087	0.027	0.028	0.032	61.2
K80	600	30.4	10.4	123.0	396.2	0.068	0.048	0.015	0.005	67.9
	700	30.4	8.5	160.2	518.5	0.108	0.062	0.018	0.020	71.3
	800	29.8	4.5	129.8	426.3	0.107	0.051	0.022	0.034	72.2
	900	30.0	2.9	77.7	250.2	0.071	0.031	0.022	0.018	72.9
K90	600	58.7	0	65.3	108.4	0.041	0.026	0.012	0.004	79.9
	700	59.3	0	144.2	240.4	0.081	0.056	0.021	0.004	79.3
	800	58.8	0	113.0	189.6	0.064	0.044	0.016	0.003	80.1
	900	59.5	0	52.0	84.7	0.063	0.020	0.036	0.007	80.7

[a] Determined by TGA in air atmosphere
[b] Determined by weighing crucibles with samples before and after the batch reactor experiments

suitable calculation method for pore size distribution would be the density functional theory. The PSD graph indicates that this material is micro- and mesoporous, as the data in Table 1 also reveal. Most of the pores in the semi-coke sample ranged from 0.5 to 5 nm (Fig. 3b). The PSD graph shows many pores to have a size of 0.6 nm, and some pores to be with a width of 1.2, 1.4 and 3.8 nm. With all the pores at $P/P_0 = 0.99$ considered, their average pore diameter was found to be 2.6 nm.
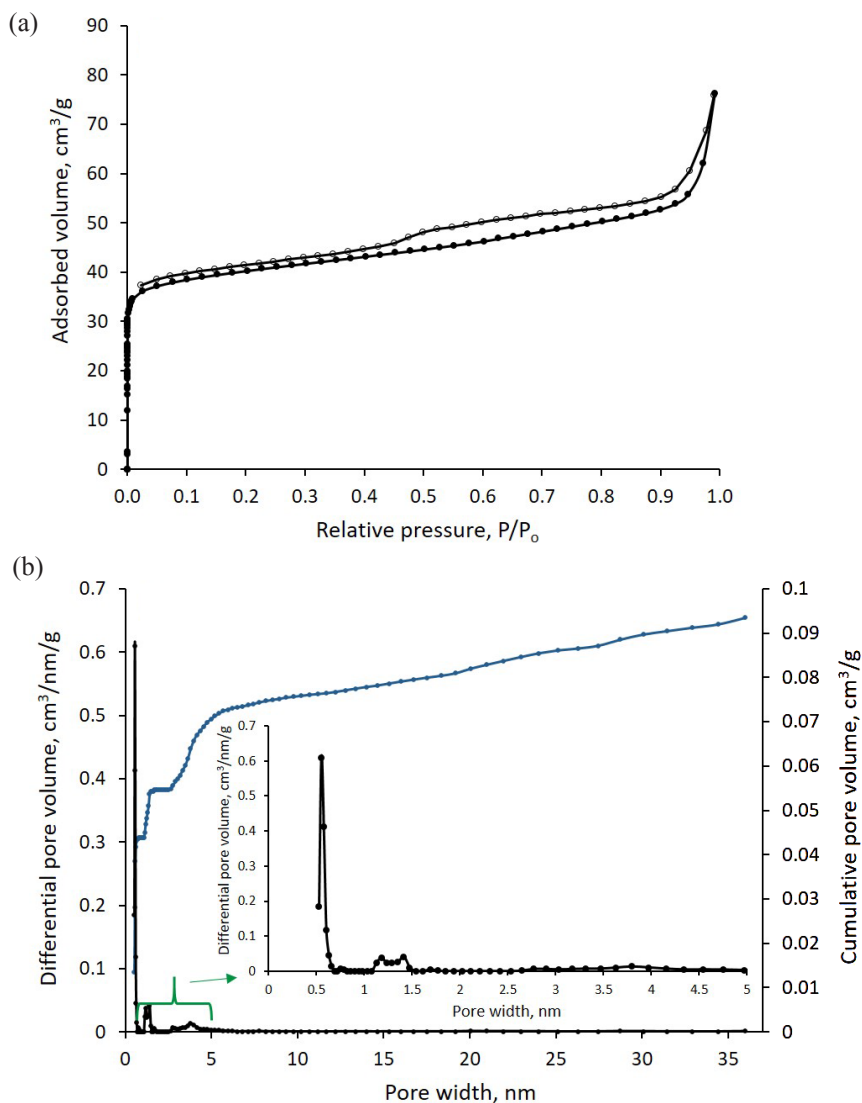

Fig. 3. N_2 adsorption-desorption isotherms (a) and DFT pore size distribution (b) of the semi-coke of kerogen K80 sample.

3.3. Adsorption tests with the semi-coke of kerogen sample

As already mentioned, the semi-coke of K80 kerogen sample pyrolyzed at 700 °C with the highest surface area and total pore volume was tested as a model adsorbent for the purification of water samples from common pollutants. It must be stated that the oil shale kerogen semi-coke material produced at this laboratory differs from the industrial semi-coke materials in carbon content. We have previously determined the total carbon contents of industrial semi-cokes, which varied between 7 and 12 wt%. At the same time, the carbon content of the studied kerogen semi-coke sample is around 30 wt%, i.e. the difference is about three times. However, the authors believe that this kerogen semi-coke material has the same characteristics as the carbon in industrial semi-coke materials and the results will provide insight into the potential that the carbon fraction can offer in industrially produced semi-cokes.

To demonstrate the suitability and adsorption capacity of the semi-coke sorbent of kerogen K80 sample, two different classes of substances with different molecular structures were chosen for the experiments – phenolic compounds and pesticides, which are shown in Table 3.

Table 3. Results of the adsorption analysis of water samples before and after purification with the semi-coke sorbent for 6 hours
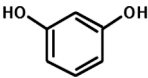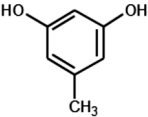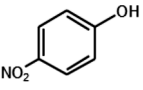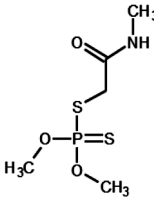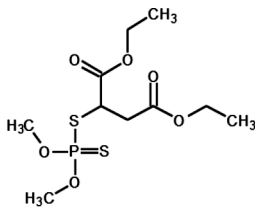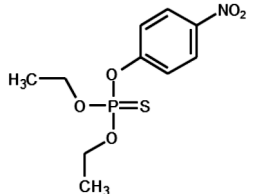
Compound	Molecule	Molecular weight, g/mol	Initial concentration,		Amount adsorbed, %, average ± SD, n = 3
			µM	mg/L	
Resorcinol		110.11	10	1.10	97.2 ± 0.6
5-Methyl-resorcinol		124.14	10	1.24	99.6 ± 0.4
4-Nitro-phenol		139.11	10	1.39	100
Dimethoate		229.26	100	22.93	100

Table 3 (continued)

Compound	Molecule	Molecular weight, g/mol	Initial concentration,		Amount adsorbed, %, average ± SD, n = 3
			μM	mg/L	
Malathion		330.36	100	33.04	100
Parathion		291.26	100	29.13	100

In order to estimate the time required for a complete adsorption of the compounds onto the semi-coke sorbent, experiments with different contact times were carried out. For this purpose, the experiments with spiked water sample before (control) and after contact with the adsorbent were carried out. The samples were collected and analyzed after every half an hour for 3 hours, and then after every hour until 6 hours (Fig. 4). It can be seen from Figure 4 that the pesticides dimethoate, malathion and parathion were almost completely adsorbed on the sorbent already within 30 minutes, while the adsorption of phenolic compounds resorcinol, 5-methylresorcinol and 4-nitrophenol required more time. More specifically, pesticides dimethoate, malathion and parathion were adsorbed on the semi-coke adsorbent within 30 minutes with 99.0, 97.9 and 99.5%, respectively, and were completely adsorbed (100%) within 1 hour. The adsorption of phenolic compounds took a little longer as their adsorption increased with exposure time. Phenolic compounds resorcinol, 5-methylresorcinol and 4-nitrophenol were adsorbed within 3 hours with 91.5, 96.2 and 100%, respectively, while within 6 hours the respective percentages were as follows: 97.2, 99.6 and 100%. In fact, 4-nitrophenol was completely adsorbed within 1.5 hours.
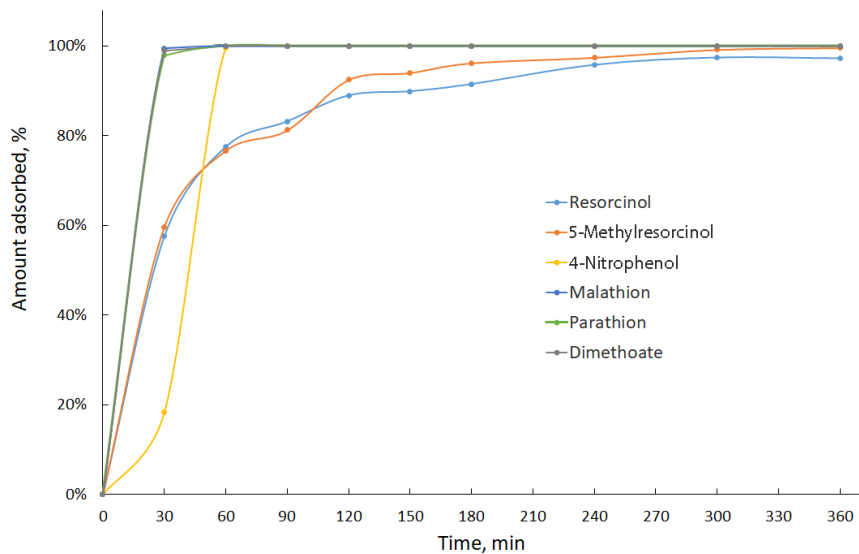
Fig. 4. Adsorption tests with the semi-coke of kerogen K80 sample at different exposure times on the compounds of interest.

These results are also illustrated in Figure 5, where HPLC chromatograms demonstrate a reduction in concentrations in water samples before and after exposure to the semi-coke sorbent for 3 and 6 hours.
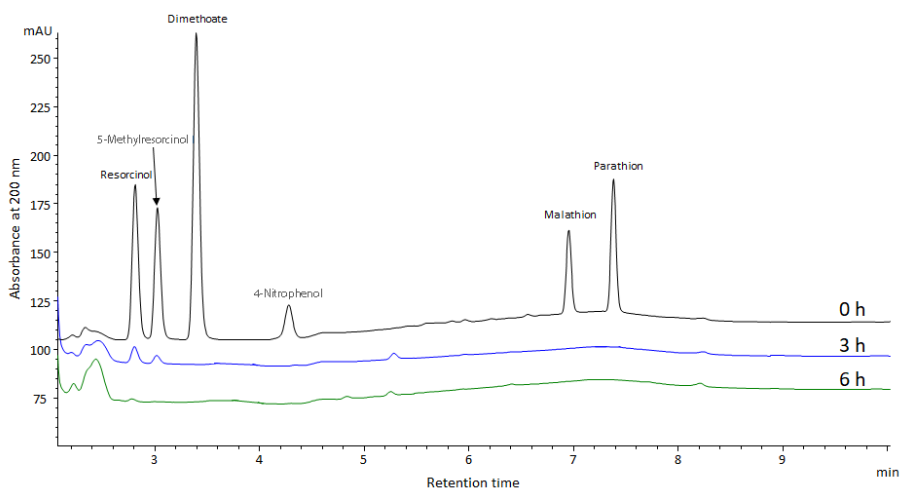

Fig. 5. HPLC chromatograms obtained before (0 h) and after (3 and 6 h) water purification with the semi-coke sorbent. The initial concentration of phenolic compounds was 10 μM and that of pesticides 100 μM, the dosage of sorbent was 10 mg/mL, stirring speed 300 rpm, room temperature.

The results demonstrated that the required time for the adsorption depends on the target compound. Table 3 summarizes the results of adsorption effectiveness of the semi-coke sorbent for the studied compounds after 6 hours. The experimental data confirmed that the concentration of all pollutants decreased substantially after purification with the semi-coke sorbent within a short period of time.

4. Conclusions

The goal of the present work was to study the possibility of oil shale semi-coke for the production of porous carbon material, thereby offering a new and sustainable use for oil shale. Mainly, the formation of pores was investigated as this is the crucial parameter determining the effectiveness of the obtained material. For this purpose, enriched oil shale samples with different kerogen contents ($\approx$ 60, 80, 90 wt%) were prepared and then pyrolyzed in nitrogen gas flow at temperatures from 600 to 900 °C. The 80 wt% kerogen-enriched oil shale sample pyrolyzed at 700 °C displayed the highest surface area and porosity and was therefore chosen as the model semi-coke sorbent for the adsorption experiments. According to the results of this study, the kerogen semi-coke can be considered as a promising adsorbent for the removal of pollutants, such as phenols and pesticides, from aqueous samples. The experimental data showed that the concentration of all pollutants decreased substantially after being in contact with the semi-coke sorbent. More precisely, the pesticides dimethoate, malathion and parathion were completely adsorbed on the semi-coke sorbent already within 1 hour. However, in the case of the phenolic compounds resorcinol, 5-methylresorcinol and 4-nitrophenol, the adsorption increased with exposure time. After 6 hours, the adsorption percentages of resorcinol, 5-methylresorcinol and 4-nitrophenol were 97.2, 99.6 and 100%, respectively. There is naturally a range of different environmental contaminants and concentrations that could be also studied, but the present results suggest that further examination of the possibilities for such materials is warranted. In this pioneering study, only laboratory-made kerogen semi-cokes were tested in the adsorption experiments as it is believed that this semi-coke material has the same characteristics as the carbons of industrial semi-coke materials. However, real industrial samples are planned to be tested in the future studies to further prove this insight. The results of the present study provide a strong argument for the use of the investigated material as a sorbent to mitigate the current environmental risk of dumping of the particular waste product.

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