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Preparation of Adsorbent Material from Moroccan Oil Shele of Timahdit: Optimization of Parameters Processes and Adsorption Tests

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ABSTRACT

Adsorbent materials were prepared from Moroccan oil shale of Timahdit (layer Y). The objective is to optimize the procedure parameters of elaboration the adsorbents from two precursors; the raw rock Y and the decarbonated raw rock YH. The parameters examined in this study are: the activation temperature, the residence time in the furnace and the atmosphere gas. The textural and structural characteristics of the prepared adsorbents and their removal capacity of the methylene blue molecule revealed that the best adsorbents are obtained upon activation of the two precursors at 300 °C in air but with durations of different activation, 2h for Y and 2.30 for YH. Under these conditions the prepared adsorbents are characterized by significant textural and structural properties; a maximum adsorption capacity of methylene blue molecule that can reach 175 mg/g in the case (YH300 (2:30) in addition to the development of surface function.

Keywords: *Moroccan oil shale; Activation; Adsorbents; Adsorption; Methylene blue*

INTRODUCTION

Excessive use of activated carbon for decontamination of liquid effluents loaded with pollutants which are either organic or metal stable or radioactive, causing a massive exploitation of timber resources posing significant threats to the ecosystem balance. Several studies have been conducted on the investigation of new precursors cheaper and not using forest reserves such as clays [1-3] or zeolites [4-6]. Other more recent studies focused on the development of certain industrial or agricultural waste such as bagasse [7], molasses [8-9], the pomace [10-11], coffee [12] and

coconut [13-14], which enabled to manufacture activated carbon industry-standard and affordable. In this context, the present study is part of a series of studies that we conducted on the possibility of producing adsorbent materials from Moroccan oil shale [15-17]. The choice of this material for this application, elaboration of adsorbents material, was ducted by two factors; the reserve estimated at 80 billion tons in Tarfaya and 20 billion tons Timahdit and its composition rich in organic matters, constituted a source of carbon, chemically linked to the mineral matrix (carbonates, silicates and clays).

The previous were focalized great attention to the activation of a precursor obtained after décarbonatations of the raw rock of oil shal. The methods used are based on thermal activation [15-16] or chemical activation by different activates agents (sulfuric acid, phosphoric acid, potassium hydroxide, zinc chloride) [17-19]. The adsorbents obtained by these methods have good textural and structural properties and showed a good affinity vis-à-vis the organic and inorganic pollutants stable or radioactive [15-19].

In this study two objectives were fixed:

(a) Improve the process of developing adsorbents, used before in order to reduce their costs. This improvement involves consideration of two factors:

- The use of raw rock or decarbonated rock directly as a precursor.
- Optimization of thermal processing conditions, activation temperature and residence time in the oven, to reduce energy bills.

(b) Implementation of a method for the removal of organic and inorganic pollutants stable or radioactive by the use of adsorbents developed in this study. Extending this process to industrial waste will be an added advantage for any potential and actual implementation in our materials.

MATERIALS AND METHODS

2. Experimental Details

2.1-Preparation of adsorbents

2.1.1- Precursor material

The oil shale used in this study was obtained from the Timahdit located in the mid-Atlas mountain at 35 km in the south of Azzrou. This deposit is a vein of schist 100 -150m in thickness and comprising several layers with variable contents of organic matter [11]. The layer studied in this work is the layer (Y) whose mineralogical composition is summarized in Table 1.

Table 1: Mineralogical composition of Timahdit oil shale layer Y [16]

Compound	Calcite	Dolomite	Silica	Clays and other	Organic Matter
%by Weight	15,2	12,2	21,8	26,9	23,9

2.1.2-Decarbonation of the raw rock

Samples taken from the raw rock (Y) there were crushed, then ground in an electric grinder until we get a fine powder with a particle size <0.08 mm. At a mass of the powder (Y) was leached with concentrated hydrochloric acid (6N) and with stirring until no release of carbon dioxide. Reactions that result from this process are:

$$CaCO_3 + 2HCl \longrightarrow CO_2 + CaCl_2 + H_2O$$

$$CaMg(CO_3)_2 + 4HCl \longrightarrow 2CO_2 + CaCl_2 + MgCl_2 + 2H_2O$$

After filtration, the residue was judiciously washed in a Soxhlet apparatus, using water as a solvent, to remove the traces of acids and stabilize the product, then dried in oven at about 110°C.

The resulting product, referred by YH, was ground and sieved to 0.08 - 0.1 mm particle size and stored for possible use.

2.1.3- Thermal activation of Y and YH

For thermal activation of Y and YH, the two precursors are subjected to extensive washing with water in a Soxhlet apparatus for 48 h, to extract any soluble matter and ensure their stabilization. After this operation of each precursor samples are treated in oven in air at different temperatures ranging from 200 to 450 °C, the treatment time varies between 0.5 h and 3 h. The choice of temperatures was dictated by a major change that had the structure of organic matter in this temperature range. After heat treatments are completed, the adsorbents obtained, indicated by YAx and YHAx, where x is the activation temperature. The samples were stored before use in adsorption tests.

2.2-Determination of maximum adsorption capacity

2.2.1-Adsorption kinetics of the molecule of methylene blue

To estimate the performance of the prepared adsorbents using different pollutants, a study of the adsorption kinetics of methylene blue molecule was realized. Indeed, a mass of 100 mg of each adsorbent is emerged in 400 mL of methylene blue concentration of 20 mg/L. The mixture was subjected to constant shaking and samples were taken at different time intervals. The concentration of methylene blue, in each sample, was determined by UV-visible spectroscopy.

2.2.2-Adsorption isotherms

The results of adsorption kinetics were used to select the adsorbents which have a good affinity of adsorption of MB molecule and the optimal conditions for adsorption of this molecule such as, pH, initial concentration of MB, the particle size of the adsorbent and the equilibrium time of adsorption.

In this step, the bottle method [20] we adopted to determine maximum adsorption capacity of MB molecule by different adsorbents, For this purpose, different amounts (20, 30, 50, 60, 80 mg) of each adsorbent were mixed in a 250 mL conical flask, with 200 ml of aqueous solutions containing 50 $mg.L^{-1}$ of MB molecule. To reach of thermodynamic equilibrium of the mixture, adsorbate-adsorbent is subjected to mechanical stirring constantly, for 16 hours. This method provides several equilibrium points at one time under similar experimental conditions. At the end of each series of experiments the residual concentration in MB was determined by UV-visible spectroscopy and the mass of MB adsorbed per gram of adsorbent was calculated using the following formula:

$$Q_e = V(C_0 - C_e)/m_{ads}$$

with:

Q_e : MB mass adsorbed at equilibrium per unit mass of adsorbent (mg/g)

V: volume of the solution of MB (L)

C_0: initial concentration of MB (mg/L)

C_e : Equilibrium concentration of MB (mg/L)

m_{ads}: mass of the sample put into a liter of solution (g)

2.2.3-Determination of adsorption parameters

To comprehend the mechanisms of adsorption and the adsorbent-adsorbate interactions, two adsorption models we used; Langmuir and Freundlich models [21-23].

The Langmuir equation is expressed in the case of the adsorption solution [24]:

$$1/Q_e = 1/Q_{max} + 1/ (kQ_{max}\ C_e)$$

Where:

Q_e : the adsorption capacity at equilibrium (mg/g),

Q_{max}: the maximal adsorption capacity (mg/g),

C_e: the residual concentration (mg/L)
k : the thermodynamic adsorption constant (L/mg).

The Freundlich equation is well suited to describe the system in aqueous phase. The equation used in the linear form [24] is:

$$\log Q_e = \log K_f + n \log Ce$$

Q_e: the adsorption capacity at equilibrium (mg/g).
C_e: the equilibrium concentration of solute in the aqueous phase (mg/L).
K_f and n: Constants of Freundlich model linked to the adsorption capacity and the intensity, respectively.

2.3-Characterization of adsorbents

To determine the effect of heat treatment on the structure of adsorbents and YAx YHAx compared with YH and Y, we used different techniques of textural and structural characterization.
- Infrared Spectroscopy (FTIR) is used to reveal the effect of heat treatment on the organic structure of adsorbents prepared. The apparatus used is type Nicolet 205.
- The thermogravimetric analysis (TGA): it allowed monitoring the behavior of a material when the temperatures increasing in different atmospheres. This technique is always used to detect the phenomena of decomposition and oxidations resulting of the heating of the solid precursors Y and YH. Generally, the curves are accompanied by ATG curves derived from thermogravimetric analysis (DTG). They allow the visualization of the phenomena difficult observed on normal curves ATG.

- Scanning electron microscope (SEM): it allowed to studding the morphology of the prepared adsorbents in comparison with that of the raw rock. The SEM images were carried out on samples of size less than 100 µm, with a type apparatus JED JSM 840A LGS.

RESULTS AND DISCUSSION

3.1-Effect of thermal activation on the adsorption of MB

In Figures 1 and 2, we represented the results of the adsorption kinetics of MB by Y, YH, YAx and YHAx. These results show generally that activated adsorbents have good affinity adsorption of MB compared to Y and YH

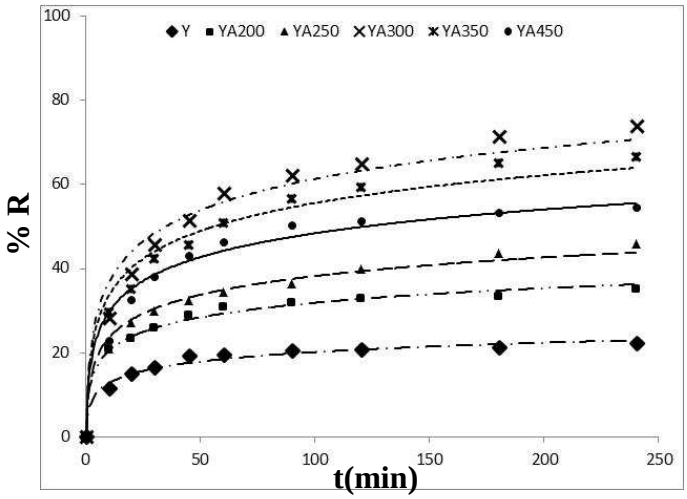

Fig 1. adsorption kinetics of MB molecule by YAx (x: activation temperature)

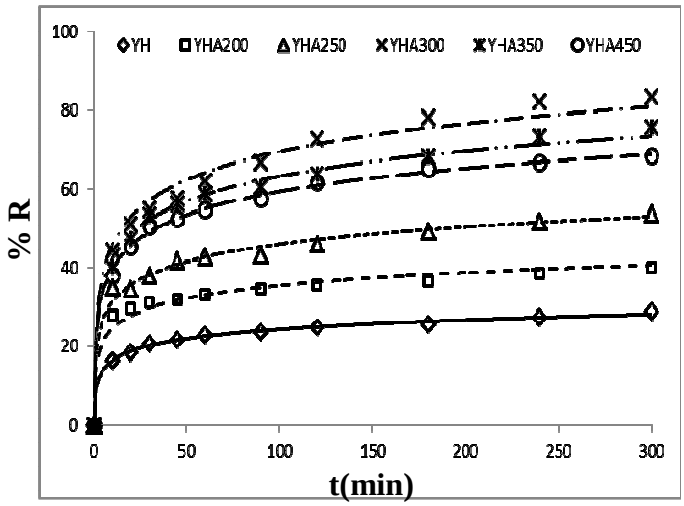

Fig 2. adsorption kinetics of MB molecule by YHAx (x : activation temperature)

This tendency reached its maximum adsorption for adsorbents YA300 and YHA300. However, we note a clear decrease in the retention of the MB molecule for superior temperatures.
To identify the different factors influencing the quality of the prepared adsorbents, we studied the effect of activation time on the textural and structural properties and the adsorption of MB. In effect, samples of Y and YH were activated at the temperature 300 °C, chosen as optimum temperature taken from the preliminary study, the activation time ranging from 0.5 to 3 h. The resulting products of this study are referenced by YA300(t) and YHA300(t), where t represents the activation time.

Figures 3 and 4 illustrate the result of the adsorption kinetics of MB molecule by YA300(t) and YHA300(t). The curves show the similar strides; rapid adsorption in the first half hour of contact between the adsorbent and the adsorbed, after this step the system tends toward equilibrium, with differing rates of adsorption. The best results are obtained by YA300(2h) and YHA300(2.5h) with rates of adsorption which are 70% and 80%, respectively.

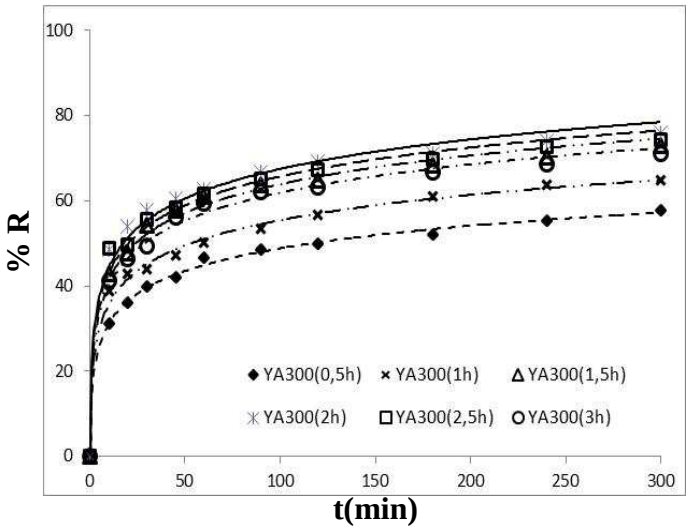

Fig 3. adsorption kinetics of MB molecule by YA300t (t: the activation time)

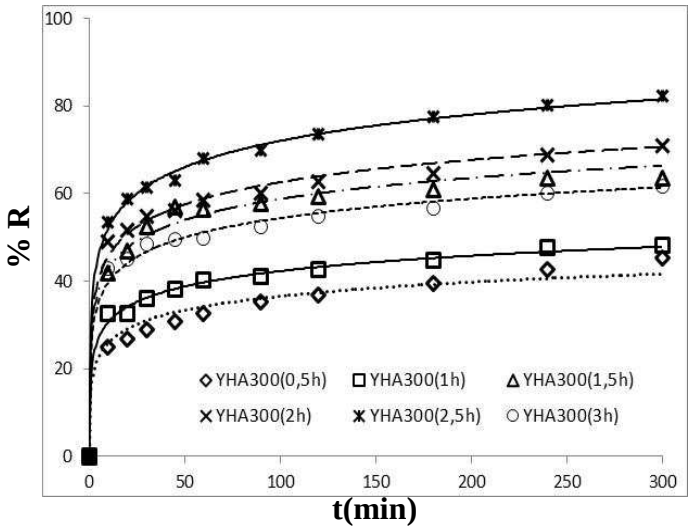

Fig 4. adsorption kinetics of MB molecule by YHA300t (t: the activation time)

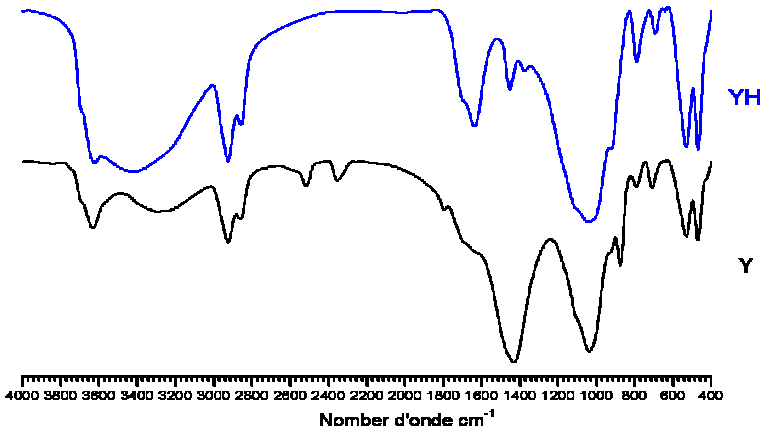

Fig 5. Infra-red spectrum (FTIR) of the precursors Y and YH

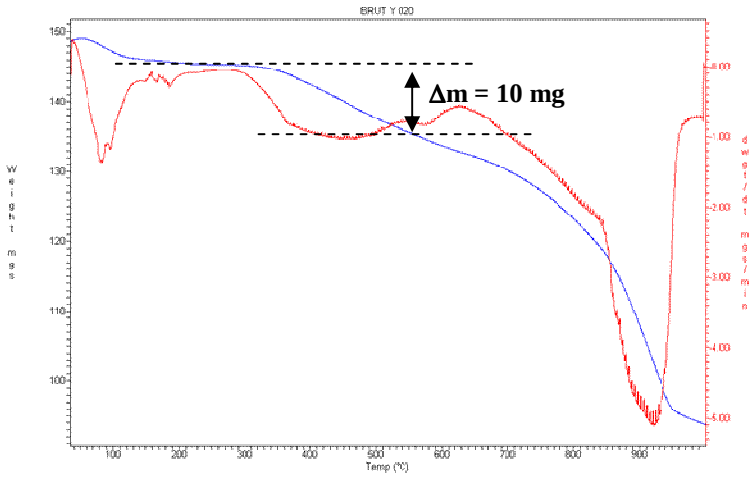

Fig 7. Thermo-grams (ATG) of the precursor YH

The difference registered on the activation time can be explained by the amount of organic matter existing in each precursor [16]. This hypothesis is strongly supported by the results of the characterization performed on the powder Y and YH. Infrared spectra spectrum of the two precursors (Figure 5) reveal that the intensities of the bands 2920 cm^{-1}, 1650 cm^{-1} and 1050 cm^{-1} corresponding respectively to vibrations frequency of the groups -C=C-, -CH and C=O , most of the observed intensities are stronger in the case of the precursor YH compared to Y.

Thermogravimetric analysis TGA (Figures 6 and 7) also shows that the mass loss recorded during the heating of the same quantity of precursors at the same temperature level, is more important in the case of YH compared to Y.

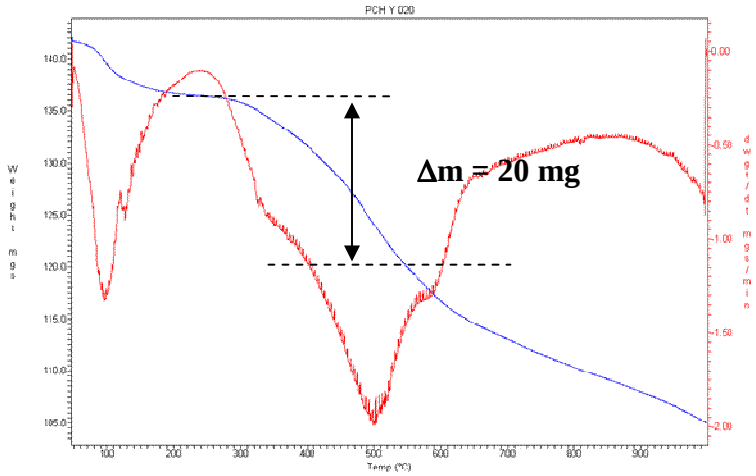

Fig 7. Thermo-grams (ATG) of the precursor YH

4.1-Parameters of adsorption of MB

Figure 8 contains the equilibrium isotherms of adsorbents YA300(2h) and YHA300(2.5 h), reflecting the evolution of the quantity Q_e of BM molecule adsorbed at equilibrium as a function of the equilibrium concentration Ce.

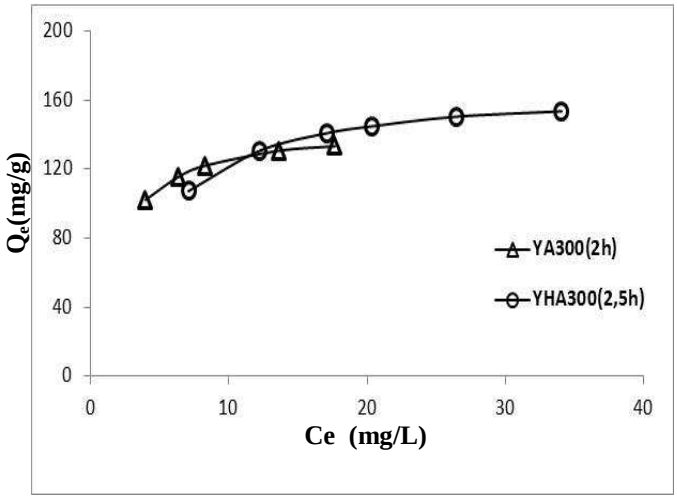

Fig 8. Adsorption isotherms of MB molecule by YA300(2h) et YHA300(2,5h)

The equilibrium isotherms of adsorbents YA300(2h) and YHA300(2.5 h) are linear-type H according to the classification of Giles et al. [25-26]. Those types of curves are observed when couples adsorbent/adsorbate exhibit a high affinity towards each other and the adsorption phenomena are instantaneous.

The linear regression lines in Figure 8, using Langmuir and Freundlich models, allowed us to determine the adsorption parameter k and the maximum adsorption capacity (Q_{max}) of BM molecule for the Langmuir model and the constants of Freundlich model (n and k_f) linked to the adsorption capacity and the intensity of adsorption (table 2).

Table 2. adsorption parameters of Y, YH, YA300(2h) and YHA300(2.5h)

	Langmuir		Freundlich	
	Q_{max} (en mg/g)	k	K_f	n
Y	68	0,16	22,64	0,274
YA300(2h)	147	0,58	82,27	0,175
YH	84	0,12	21,11	0,341
YHA300(2,5h)	175	0,23	66,67	0,247

Under both models, the correlation coefficients are near to unity, indicating that the adsorption of MB molecule finished on two major steps:

- A surface adsorption, a phenomenon resulting Langmuir by building a mono-molecular layer of adsorbate on the adsorbent area.
- The intra-granular distribution that promotes the adsorption of adsorbate molecules within the pores and in the grain boundaries of the adsorbent. This resulted in a low adsorption capacity depending on the model of Freundlich.

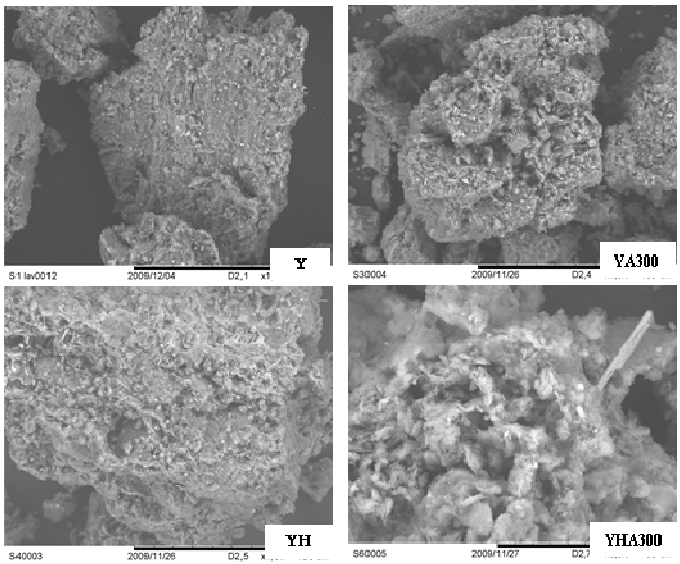

Fig 9. SEM photographs of precursor Y and YH and adsorbents YA300 (2h) and YHA300 (2.5 h)

Examination of the values listed in Table 2 reveals a significant increase in the maximum adsorption capacity upon activation of the precursor at 300°C. However, it should be noted that this value differs from one sample to another 147mg/g for YA300 (2h) and 175 mg/g for YHA300(2.5h). This difference may be explained by the rate of organic matter existing in each

precursor and the beneficial effect of thermal activation in an oxidizing atmosphere (air). This type of activation favors one hand the formation of a carbon skeleton with high organic carbon and secondly the development of porosity by the release of small molecules (CO and CO_2) formed by controlled oxidation of organic matter existing in the precursor. This finding can be demonstrated by examining the morphology of these products. Indeed, photographs taken by scanning electron microscope (SEM) and YH and Y precursors and adsorbents YA300 (2h) and YHA300 (2.5 h) (Figure 9) show that these last two structures are more developed and well distributed in all samples

The values found are larger than those found in the study conducted by Ichccho et al. [16-18] in the case of activation without the use of activating agent. However, the chemical activation is still required to have a marked improvement in the adsorption capacity and the textural and structural properties of the prepared adsorbents.

CONCLUSION

The adsorbent materials prepared from oil shale are an attractive alternative for wastewater treatment. The production processes depend on several parameters, the activation temperature, residence time in the oven and the atmosphere gas without forgetting the base precursor. The study conducted in this work has identified the most influential parameters and requires strict control of the activation process. The estimated effects of these parameters based on adsorption tests and textural and structural characteristics concluded that the activation temperature and duration of activation are the most affecting factors to the maximum adsorption capacity.

The results are very conclusive, under optimal conditions, the activation temperature equal to 300 ° C and the activation time is 2h for Y and 2.30h for YH. Testing elimination of the methylene blue molecule revealed that the adsorbent YH300 (2.30h) to a maximum adsorption capacity of up to 300 mg / g. The adsorbents prepared from oil shale can be used in the decontamination of effluents containing organic pollutants. Besides the large adsorption capacity of these adsorbents, they have the advantage of being accessible in very mild conditions.

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