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## The use of insoluble matter of Moroccan oil shale for removal of dyes from aqueous solution

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### ABSTRACT

The study aims to use an adsorbent natural based of Moroccan oil shale of Timahdit area (Y layer) in a physical-chemical adsorption process for treating industrial discharges colorful. The used adsorbent is the insoluble party of the sub-critical extraction of decarbonized oil shale of Timahdit. The tests performed on the methylene blue (MB), showed a strong elimination in the first 10 minutes. The influences of various experimental parameters were studied: mass ratio of adsorbent, time and temperature of thermal treatment, contact time, pH of MB and heating temperature of solution on the parameters of material were studied. The experimental results have shown that the adsorption of methylene blue dye by the adsorbent is more than 90% at initial pH a range 6-7 at room temperature for 30 minutes. The process is simple and the adsorbent produced is a new material with interesting adsorption capacities of moderate cost which does not require an activating agent and can be used as industrial adsorbent for the decontamination of effluents containing organic pollutants.

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**Capsule Summary:** The study presents the result of the elaboration and characterization of adsorbents material from Moroccan oil shale and testing of her performance in the adsorption of organic compounds.

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### INTRODUCTION

The extensive use of dyes in dye-manufacturing industries creates significant problems due to the discharged of colored waste water. The presence of very small amounts of dyes in water is visible and affects the quality of water (Banat et al.,

1996). Most of these dyes pose cute problems for the ecological system, as they are toxic and have carcinogenic properties, which make the water contaminated with dyes inhibitory to aquatic life (Bhattacharyya et al., 2005; Crini, 2006; Weng et al., 2007). With industrialization, the discharge of industrial waste water has increased. At the

same time, there are concerns, and there is the need to find cheap and efficient methods for the industrial waste water prior to disposal in to natural waters (Gürses et al., 2006; Wang et al. 2005). The removal of dyes from wastewater has been extensively studied for decades, and many technologies have been developed, including oxidative degradation (Jadhav et al., 2011), biochemical degradation (Gardiner et al., 1978; Li et al., 2015), photo-degradation (Kalyani et al., 2009; Thiam et al., 2016), electrocoagulation (Janoš et al., 2003), electrochemical degradation (Espantaleón et al., 2003), and adsorption (Han et al., 2008; Mittal et al., 2010). The advantages and disadvantages of every removal technique have been extensively reviewed (Chiou et al., 2006; Hameed et al., 2009). Among these methods, adsorption has been found to be one of the most well-known and economic techniques for dye removal due to its easy operation, high efficiency, low cost, and recyclability (Low et al., 1990). Most recently, much attention has been paid to the development of crude biomass materials, such as peanut husk (Guechi et al., 2016), coconut husk (Vadivelan et al., 2005), potato peel (Amin et al., 2009), rice husk (Salleh et al., 2011), and pomegranate peel (Guechi et al., 2016), for the removal and separation of dyes from the wastewater. Their removal of dyes in an economic way remains an important issue for researchers and environmentalists. The adsorption is an excellently tentative election especially using in expensive and high adsorption capacity adsorbent without requiring any additional pretreatment step be for application. Adsorption is superior to other waste water treatment techniques in terms of its initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Gupta et al., 2007; Tan et al., 2008; Sachdeva et al., 2009; Al-Ghouti et al., 2009; Akgul et al., 2011; Alexandro et al., 2011). Mining and processing of the oil shale will significantly disturb the environment, as are sult of pollution by dust particles and ash derived from the oil shale (Toomik et al., 1998; Jaber et al., 1999). Valorization of these valuable by product will reduce the environmental impact and will make oil shale development economically feasible for energy production in the future (Hamadi et al., 2012).

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 (Ichcho et al., 2003; Ichcho et al., 2005; Ichcho et al., 2006). 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 in 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 decarbonization of the raw rock of oil shale. The methods used are based on thermal activation (Ichcho et al., 2003; Ichcho et al., 2005) without chemical activation by different activates agents (phosphoric acid, sulfuric acid, sodium hydroxide, potassium hydroxide, zinc chloride,...) (Ichcho et al., 2005; Ichcho et al., 2006). The adsorbent obtained by

these methods have a good structural properties and showed a good affinity against the organic and inorganic pollutants stable (Ichcho et al., 2003; Ichcho et al., 2005; Ichcho et al., 2006; Khouya et al., 2006). On the other hand, El Harti et al. optimize the procedure parameters of elaboration the adsorbents from two precursors; the raw rock Y and the decarbonized 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 (El Harti et al., 2012). Zhao et al. (Zhao et al., 2014) removed MB from solution by using oil shale ash, the experimental results showed that both the Langmuir and Freundlich models fitted the MB adsorption data well with an adsorption capacity as high as 250 mg/g. Removal of MB by OSA was relatively fast and equilibrium could be achieved in 2 h. Recently Gouza et al. (Gouza et al., 2017) study the effect of heat treatment on the surface properties of selected bituminous shale for cationic dye sorption, the result show that the active sites from shale play an important role for MB removal. As a result, this natural, widely available and low-cost resource can be a good adsorbent used for many removal applications of specific pollutants. Therefore, two principal objectives were fixed for the present research:

- (a) Studied of experimental conditions for the preparation of the adsorbents prepared from the decarbonized oil shale (denoted as YH in the text), such as time and temperature of thermal treatment, mass ratio of adsorbent.
- (b) Tested the ability of the elaborated adsorbents to retain the methylene blue (MB) which was a dye, commonly employed as indicator to evaluate adsorbents and compared their adsorption capacities with some others activated carbons, and determination of best conditions of adsorption (contact time, pH of MB and heating temperature of solution).

## MATERIAL AND METHODS

### Precursor material

Oil shale deposits have been identified at ten localities in Morocco (Fig. 1). The two deposits that have been explored most extensively are the Timahdit and the Tarfaya deposits; about 69000 analyses have been made of samples from 157 boreholes totaling 34632 m in length and from 800 m of mine workings (Bouchta, 1984). The Timahdit deposit, located about 250 km southeast of Rabat, underlies an area about 70 km long and 4 to 10 km wide within a northeast-trending syncline (Fig. 1). The moisture content ranges from 6 to 11 percent, and the sulfur content averages 2 percent. Total oil shale reserves are estimated at 18 billion tons within an area of 196 km<sup>2</sup>, oil yields range from 20 to 100 l/t and average 70

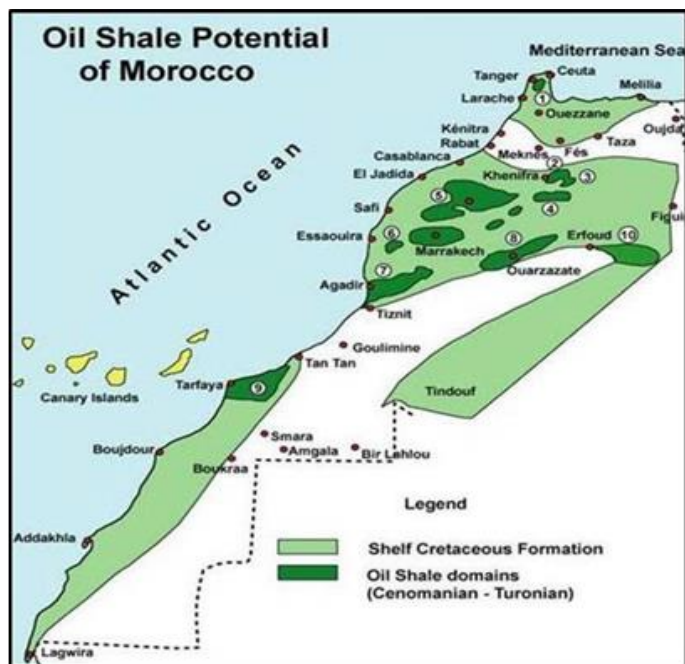
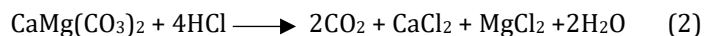
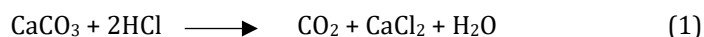


Fig. 1: Oil shale deposits in Morocco (ONHYM-Morocco)

L/t. The Tarfaya deposit is located in the south western-most part of Morocco, near the border with Western Sahara (Fig. 1). The oil shale averages 22 m in thickness and its grade averages 62 L/t. The total oil-shale resource is estimated at 86 billion tons within a 2000 km<sup>2</sup> area.

The oil shale specimen used in this investigation was obtained from the Timahdit (provide by the ONAREP: National Office of Petroleum Research and Exploitation) located in the mid-Atlas mountain at 35 km in the south of Azzrou. This deposit is a vein of schist 100–150 m in thickness and comprising several layers with variable contents of organic matter (Pechyen et al., 2010). The layer studied in this work is the layer (Y) whose mineralogical composition is illustrated in Table 1.

The raw rock (Y) were crushed, then ground in an electric grinder until we get a fine powder with a particle size <200 μm. At a mass of the powder (Y) was leached with concentrated hydrochloric acid (6N) (Yürüm et al., 1985; Rose et al., 1994) and with stirring until no release of carbon dioxide (Moore et al., 1973). Reactions that result from this process are:



After filtration, the residue was washed by distilled water to eliminate excess acid. The product obtained, referred to as YH, then dried in oven at about 110°C and stored for a possible future use.

### Preparation of adsorbent material "YHI(T)"

A mixture consisting of YH precursor and solvent is introduced into a stainless steel autoclave at 325 °C for two hours before being cooled to room temperature. After treatment in the autoclave, the residue obtained undergoes a liquid-solid extraction by chloroform, using a soxhlet apparatus to solubilize the organic extract. The insoluble fraction in chloroform, referred by YHI, is washed with soxhlet apparatus and then dried in an oven for 1 night. The adsorbent YHI was heated in furnace at different temperatures between 200 and 600 °C.

The flow chart of Fig. 2 summarizes the various steps of the process which we have adopted for the preparation of the adsorbent. The comparison between different prepared adsorbents was conduit by FT-IR spectrometer.

### Test of the performance

#### Adsorbate

The dye considered in this study is methylene blue (BM) which is a cationic dye of very high purity (99%), taken as a pollutant model without any prior purification. The solutions are prepared by dissolving the amounts of the dye in distilled water. Its characteristics are summarized in Table 2.

### Experimental procedure

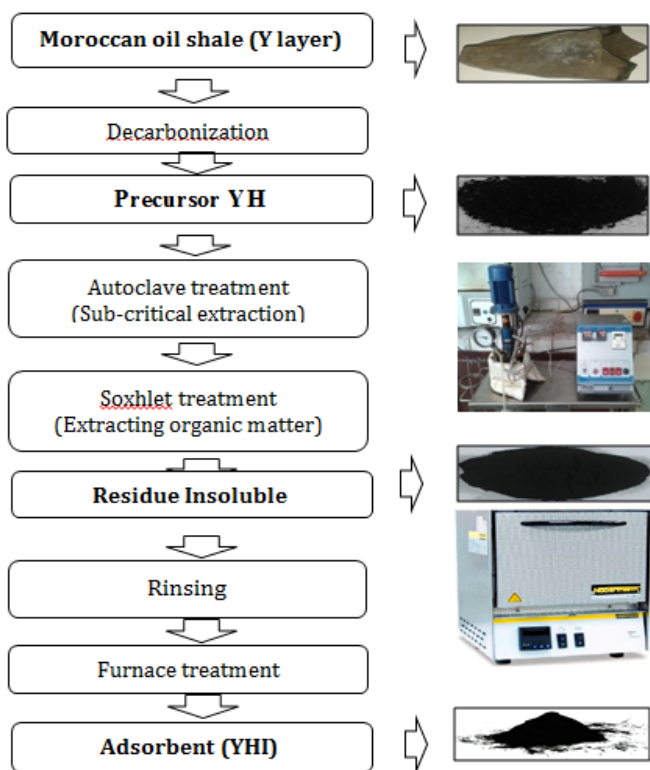
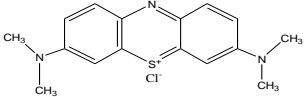


Fig. 2: Organigram for preparation of the adsorbent YHI

**Table 1:** Mineralogical composition of Timahdit oil shale (layer Y) (Ichcho et al., 2006)

Compound	Calcite	Dolomite	Silica	Clays and other	Organic Matter (OM)
% by Weight	15.2	12.2	21.8	26.9	23.9

**Table 2:** Structure and characteristics of MB

Name	MW (g.mol <sup>-1</sup> )	$\lambda_{\max}$ (nm)	Molecular formula	Chemical Structure
Methylene bleu (MB)	15.2	664	C <sub>16</sub> H <sub>18</sub> ClN <sub>3</sub> S	

MW = Molecular weight

The adsorption tests were carried out by stirring the colored synthetic solution of MB in the presence of the adsorbent (YHI) at constant temperature. The homogenization of the mixtures was carried out by a magnetic stirrer with constant agitation for 60 min. Samples were taken at regular intervals and after adsorbent separation using a centrifuge (Jenway Model 3310) for 15 min, the absorbance of the supernatant solution was measured by UV-visible spectrophotometer (JENWAY, model 7305), at the wavelength which corresponds to the maximum absorbance of the BM ( $\lambda_{\max} = 664$  nm), then the residual dye concentration is given by the Beer Lambert law, from a calibration graph. The mass of MB adsorbed per gram of adsorbent was calculated using the following formula:

$$Q_e = \left( \frac{(C_0 - C_e) \times V}{m_{\text{ads}}} \right) \times 100 \quad (3)$$

Where,  $Q_e$ : MB mass adsorbed at equilibrium per unit mass of adsorbent (mg.g<sup>-1</sup>),  $V$ : Volume of the solution of MB (L),  $C_0$ : Initial concentration of MB (mg.L<sup>-1</sup>),  $C_{eq}$ : Equilibrium concentration of MB (mg.L<sup>-1</sup>) and  $m_{\text{ads}}$ : Mass of the sample put into a liter of solution (mg).

The pH of the solution is adjusted by addition of an minor amount of hydrochloric acid (0.1 M) or sodium hydroxide (0,1M). At the end of the experiments of adsorption, the concentration of dye was given by measuring the absorbance of the solution with  $\lambda_{\max} = 664$  nm using a UV-visible spectrophotometer (type JENWAY, model 7305). All the experiments were carried out in double and the median values are presented.

## RESULTS AND DISCUSSION

### Characterization of adsorbent

Characterization of precursor YHI: Infrared Spectroscopy (FTIR) is used to reveal the effect of heat treatment on the organic structure of prepared adsorbents. The Infrared (IR) spectra were recorded between 400 and 4000 cm<sup>-1</sup> with a BURKER TENSOR 27 FT-IR spectrometer by summing 32 scans at 2 cm<sup>-1</sup> resolution. Pellets were prepared by dispersing 2 mg of oil shale (or demineralization product) into 198 mg of potassium bromide (KBr). IR Spectra were

obtained with a resolution of 2 cm<sup>-1</sup>. The infrared spectrum of the YHI adsorbent is shown in Fig. 3.

The spectrum exhibits wide and superimposed strips in the region 3600-3200 cm<sup>-1</sup>, which are due to the elongation of the -OH bonds. The band at 2923 cm<sup>-1</sup> and the band at 2846 cm<sup>-1</sup> are due respectively to the vibrations of asymmetric elongation of CH<sub>2</sub> and the symmetrical elongation of -CH<sub>3</sub> of the aliphatic acids (Delvaux et al., 1990). The band at 2380 cm<sup>-1</sup> and 2350 cm<sup>-1</sup> corresponds to the vibration frequency of the aromatic C=C- and -C-H groups (Delvaux et al., 1990). The band at 1450 cm<sup>-1</sup> corresponds to the vibration frequency of the C-H groups of methyl and methylene (Rose et al., 1993). The band at 1650 cm<sup>-1</sup> corresponds to the vibration frequency of the aromatic groups -C=C-, -C-H (Mongenot et al., 1999). The band at 1026 cm<sup>-1</sup> may be due to the vibration of the groups C-O-C or -OH (Rose et al., 1993). The bands 992 and 859 cm<sup>-1</sup> corresponds to the deformation vibrations of aromatic C-H (Rose et al., 1993).

Characterization of prepared adsorbents YHI(T): Fig. 4 shows the infrared spectrums of the adsorbents materials prepared at different temperatures YHI(T). When the activation temperature was greater than 250 °C, the peak at 1450 cm<sup>-1</sup> decreased, corresponding to C-H links of the methyl and methylene and disappearance of the peaks 2380 cm<sup>-1</sup> and 2350 cm<sup>-1</sup> characteristic the organic matter (OM) of oil shale bands. These results are in agreement with various studies (Gouza et al., 2017; Oumam et al., 2003; Ichcho et al., 2005; Lui et al., 2011).

The temperature 250 °C is therefore chosen as the optimum temperature for the physical activation of the decarbonized oil shale. It is therefore proposed to study the effect of the time of activation at this temperature on the adsorption capacity of the material YHI250.

### Adsorption

#### Influence mass ratio of adsorbent

With end to optimize the quantity of the adsorbent (YHI) added to colored solution MB of the experiments were provided by using 100 mL with the solution of MB to the various quantities of YHI were added (10-80 mg.L<sup>-1</sup>).



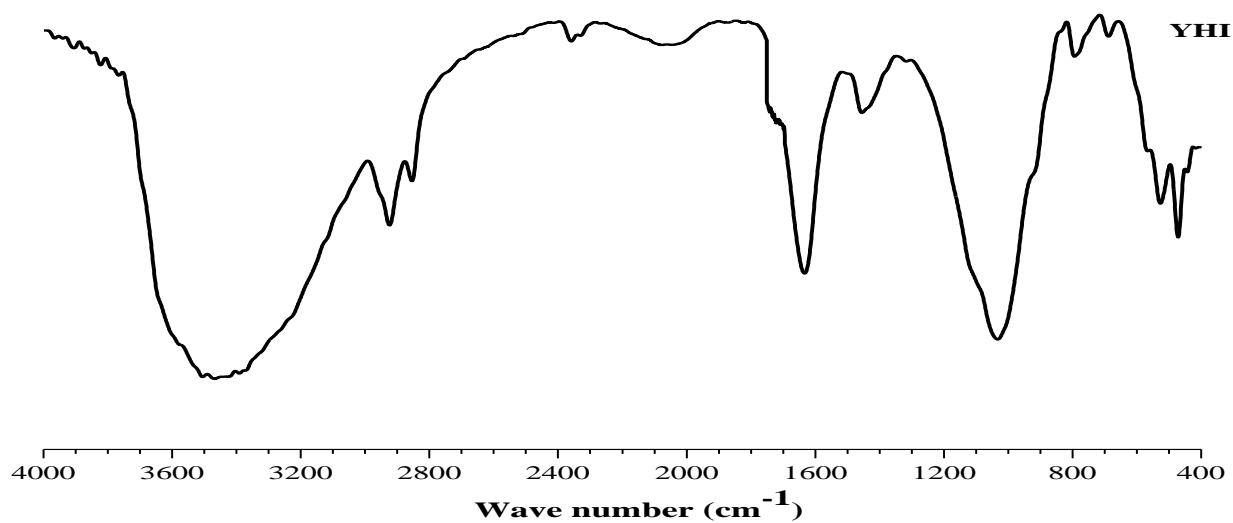


Fig. 3: Infrared spectrum of YHI adsorbent

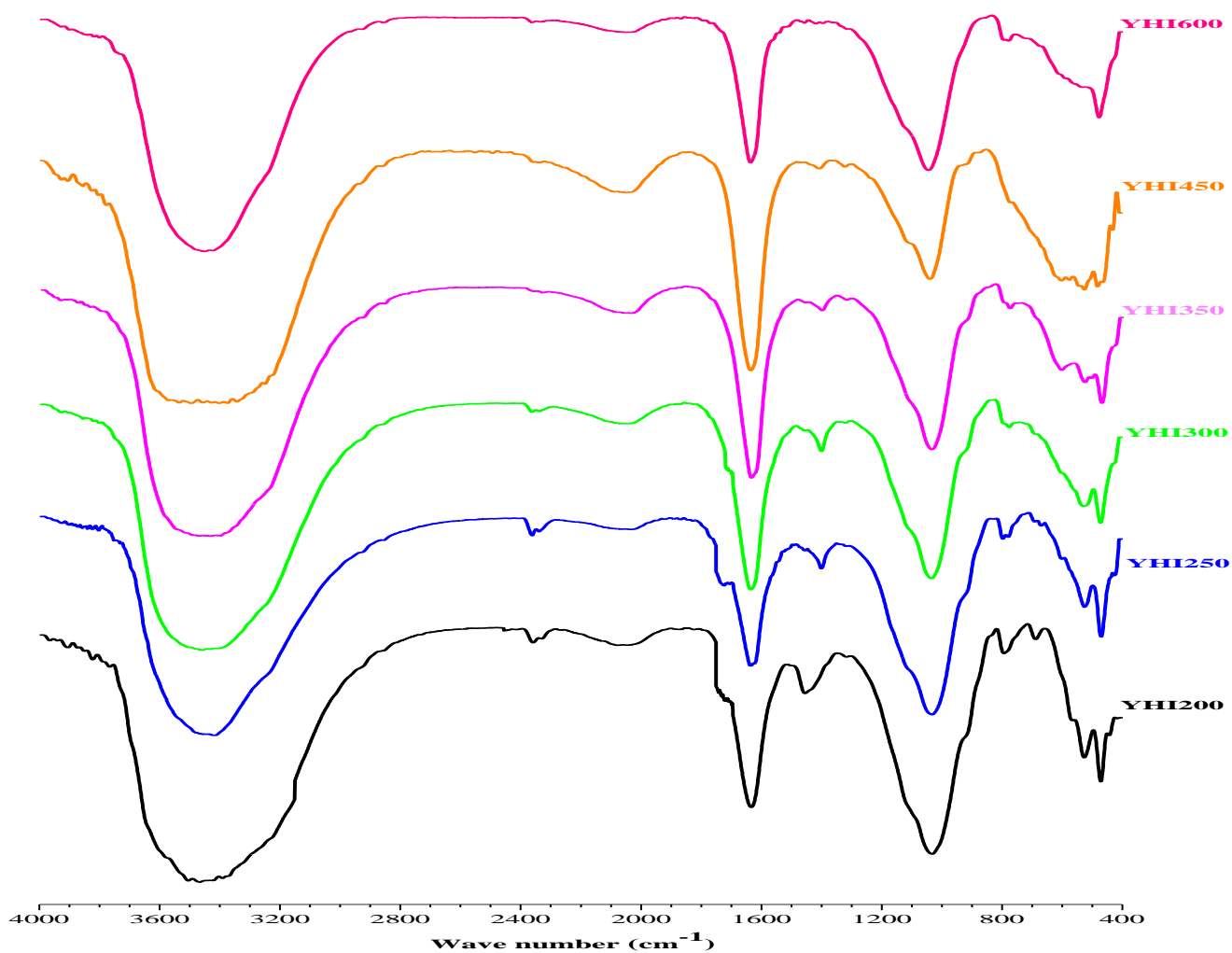


Fig. 4: The infrared spectra of the adsorbent materials YHI(T), (T=200; 250; 300; 350; 450; 600 °C).

The influence of the mass of adsorbent was studied by stirring constantly of 100 mL of MB solution ( $C_0 = 20 \text{ mg.L}^{-1}$ ), with different mass ratio of adsorbent ranging from 0.1 to 0.8  $\text{g.L}^{-1}$ , under a constant agitation for 60 min at room temperature (25 °C) and initial pH of the solution (Fig. 4). The Fig. 5 watches which the output increases with the addition of YHI up to 0.4  $\text{g.L}^{-1}$ , and reached a maximum value of 52.2% then it is decreased. The figure shows that the maximum quantity ( $Q_e$ ) of the MB increases when passing from a mass ratio of adsorbent ranging from 0.1 to 0.4  $\text{g.L}^{-1}$ . This is due to the increase in surface area and the adsorption sites attributed to the increase in adsorbent mass (Oumam et al., 2003; Ichcho et al., 2005). Thus, the adsorbent mass ratio was set at 0.4  $\text{g.L}^{-1}$  for the next experiments.

### Effect of temperature of thermal treatment of adsorbent

In the present work, we carried out the physical activation of the obtained kerogen named YHI, in a single step which consists of a heat treatment under the open air for 2 hours. The treatment temperatures chosen were 200, 250, 300, 450 and 600 °C. The samples obtained after heat treatment are named, YHI200, YHI250, YHI300, YHI350, YHI450 and YHI600. The study of the adsorption kinetics of MB is carried out at ambient temperature using a given volume of solution containing the adsorbate at initial concentration ( $C_0 = 20 \text{ mg.L}^{-1}$ ) and in the presence of mass ratio of 0.4  $\text{g.L}^{-1}$  of adsorbent. The mixture is kept under constant stirring and the sample is taken at the end of each time interval. The curve of the adsorption of the MB by the YHI samples is shown in Fig. 6.

A thorough examination of the adsorption histogram (Fig. 6) makes it possible to subdivide them into three classes according to the adsorption yield. The first contains those obtained by activation at temperatures below 250 °C, characterized by low adsorption of MB (At 200 °C the adsorption yield is average to 50%). This inefficiency of the prepared samples seems to result from the absence of the internal porosity that these temperatures (below 250 °C.) remain insufficient to create them and therefore we assume the presence of surface retention of the MB by the adsorbent YHI200. As result, the carbonization temperature is one of the most influencing factors for the development of porosity during activation process, these results in accordance with reference (Ranganathan et al., 2000; Mohan et al., 2005; Nabais et al., 2008).

The second class corresponds to the temperatures between 300 °C and 600 °C, whose adsorption process is slow compared with the other temperatures. This slowing seems to be due to the phenomena of material transfer between the aqueous phase and the solid phase during the intra-granular diffusion of the MB into pores which appear to be inaccessible by this molecule or reclosed by the oxidation of the organic matter of the kerogen, conducting beyond 600 °C to ashes completely devoid of organic matter, these results are in agreement with various studies (Lui et al., 2011). Between these two classes, the curve corresponds to the product obtained by activation of YHI at a temperature of

250 °C., which has the best adsorption capacity of the MB which exceeds 70%. This increase in the adsorbed amount is certainly due to the development of the porosity of the YHI250 adsorbent created by the gasification reactions which can take place between the carbon matrix and the departure of the volatiles matters which block the pores. These results are in agreement with the studies of Gouza et al. (Gouza et al., 2017), which was studying the effect of the thermal treatment of Moroccan oil shale from Tangier Region (OST) on its sorption capacity, they was demonstrated that the active sites from shale play an important role for MB removal. In other hand, the adsorption efficiency of the YHI250 material can also be related to the existence of surface functions. We noting the presence of C=O band around 1734  $\text{cm}^{-1}$  on the spectrum of YHI250 (Fig. 4) and it's disappearance on the spectra of the samples YHI350, YHI400 and YHI600.

### Effect of thermal treatment time

We studied the influence of the heat treatment time on yield efficiency; first we determined the evolution of the material development efficiency for different activation times. The samples are treated at 250 °C for the period between 30 and 180 minutes and then weighed to determine the carbonization yield. The latter becomes stable and is 72% after 2 hours of thermal treatment as shown by the following graph (Fig. 7).

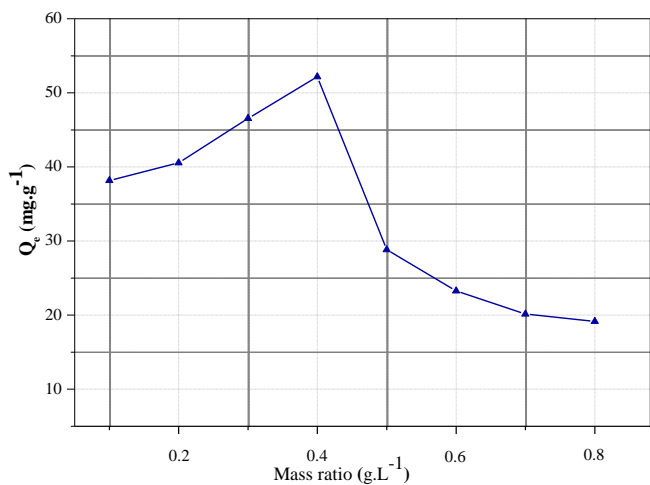
### Effect of time of contact on MB adsorption

The study of the adsorption kinetics of MB is carried out at room temperature using a given volume of solution containing the adsorbate at initial concentration ( $C_0 = 20 \text{ mg.L}^{-1}$ ) and in the presence of a given mass of the adsorbent ( $m = 40 \text{ mg}$ ). The mixture is kept under constant stirring and the sample is taken at the end of each time interval. The kinetic curve of the adsorption of the MB by the adsorbent YHI250 is shown in Fig. 8. The results of the graph (Fig. 8) shows that the phenomenon of adsorption is instantaneous and that the saturation of the various samples took place after almost 15 minutes of contact between the adsorbent and the adsorbate, whose adsorption-desorption equilibrium is reached at about 30 minutes of contact. This may be related to the stabilization of the organic matter of the YH sample which at this temperature has not yet occurred.

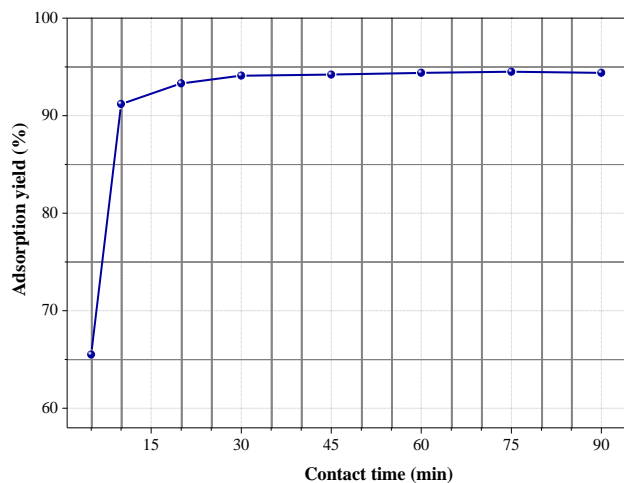
### Effect of temperature on MB adsorption

The experiments were carried out by adding 40 mg of the adsorbent YHI250 to a solution of methylene blue ( $C_0 = 20 \text{ mg.L}^{-1}$ ) at temperatures varying between 25 and 50 °C (Fig. 9). The figure shows that an increase in the temperature from 25 °C to 50 °C is accompanied by a reduction in the adsorption yield of the dye (MB) which decreases from 95.5% to 72.5%.

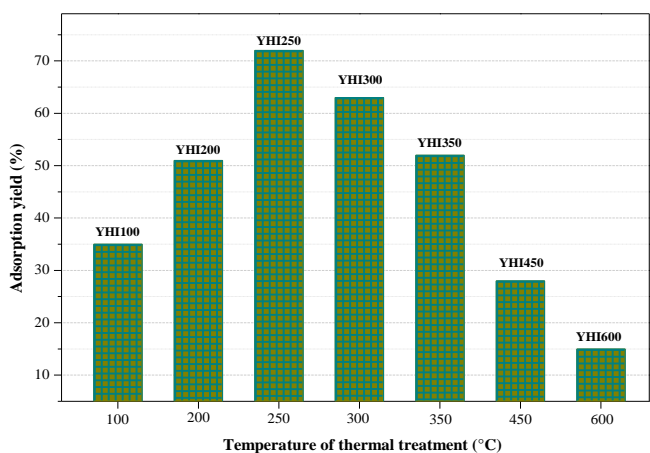
This phenomenon suggests that the reaction is exothermic, the increase of temperature of which disadvantages the adsorption mechanism. So far, at higher temperature higher dye was adsorbed.



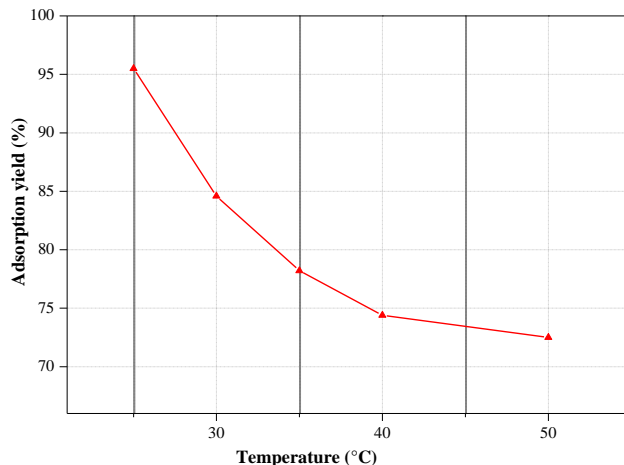
**Fig. 5:** Effect of mass ratio on MB mass adsorbed on the maximum quantity of the MB ( $C_0 = 20 \text{ mg.L}^{-1}$ ;  $\text{pH} = 6.4$ ;  $V = 100 \text{ mL}$ ;  $T = 25 \pm 2 \text{ }^\circ\text{C}$ ).



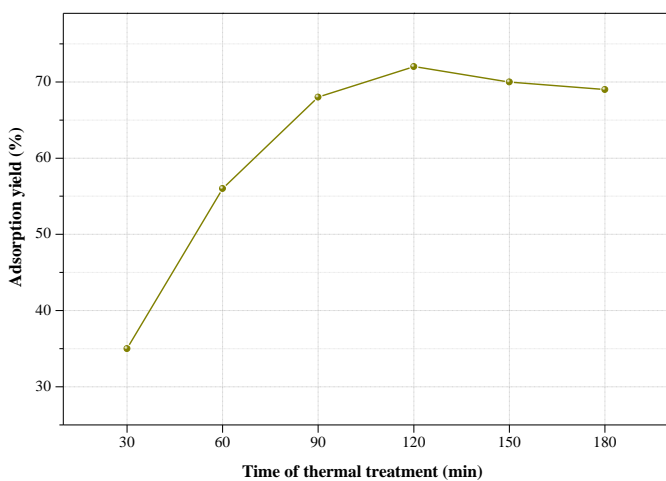
**Fig. 8:** Effect of contact time on adsorption yield of MB on YHI250 ( $C_0 = 20 \text{ mg.L}^{-1}$ ;  $\text{pH} = 6.4$ ;  $V = 100 \text{ mL}$ ;  $m = 40 \text{ mg}$ ;  $T = 25 \pm 2 \text{ }^\circ\text{C}$ ).



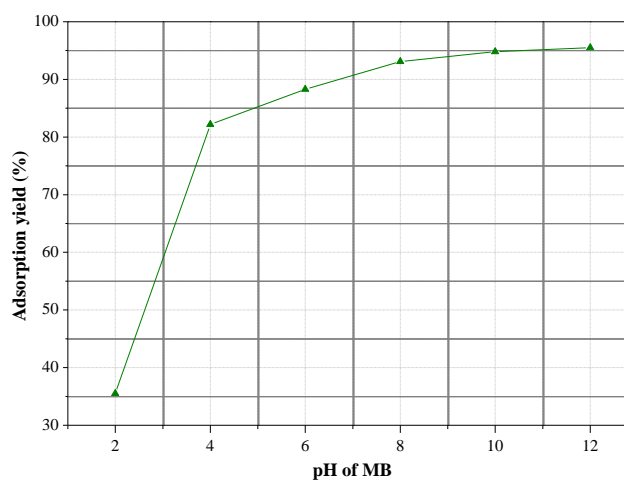
**Fig. 6:** Effect of temperature of thermal treatment on adsorption yield of MB on YHI ( $C_0 = 20 \text{ mg.L}^{-1}$ ;  $m = 40 \text{ mg}$ ;  $\text{pH} = 6.4$ ;  $V = 100 \text{ mL}$ ;  $T = 25 \pm 2 \text{ }^\circ\text{C}$ ).



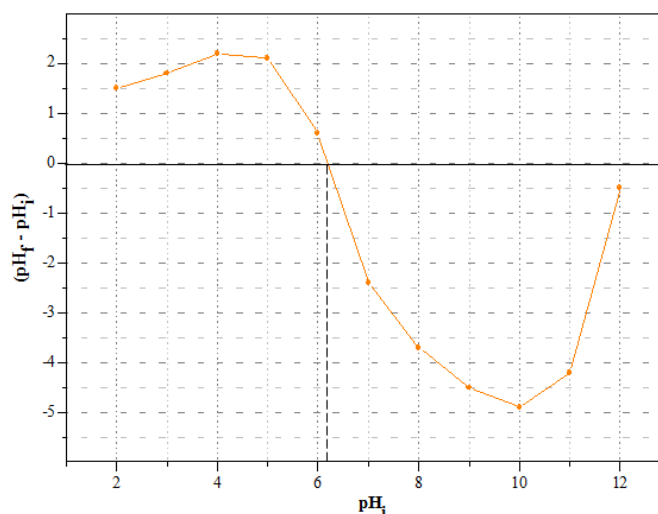
**Fig. 9:** Effect of temperature of MB on adsorption yield of MB on YHI250 ( $C_0 = 20 \text{ mg.L}^{-1}$ ;  $t = 30 \text{ min}$ ;  $V = 100 \text{ mL}$ ;  $m = 40 \text{ mg}$ ;  $\text{pH} = 6.4$ ).



**Fig. 7:** Effect of time of thermal treatment on adsorption yield of MB on YHI250 ( $C_0 = 20 \text{ mg.L}^{-1}$ ;  $m = 40 \text{ mg}$ ;  $\text{pH} = 6.4$ ;  $V = 100 \text{ mL}$ ;  $T = 25 \pm 2 \text{ }^\circ\text{C}$ ).



**Fig. 10:** Effect of pH on adsorption yield of MB on YHI250 ( $C_0 = 20 \text{ mg.L}^{-1}$ ;  $t = 30 \text{ min}$ ;  $V = 100 \text{ mL}$ ;  $m = 40 \text{ mg}$ ;  $T = 25 \pm 2 \text{ }^\circ\text{C}$ ).



**Fig. 11:** Effect of pH and point of zero charge ( $\text{pH}_{\text{pzc}}$ ) on adsorption yield of MB on YHI250

### Effect of pH and point of zero charge ( $\text{pH}_{\text{pzc}}$ ) studies on MB adsorption

The influence of pH on the removal rate of MB on YHI250 (Fig. 10) was studied using a Jenway model 3310 pH-meter. The experiments were carried out by mixing 40 mg of the YHI250 adsorbent with MB solutions ( $C_0 = 20 \text{ mg.L}^{-1}$ ). The pH of the solutions was adjusted to precise values of: 2; 4; 6; 8; 10 and 12 by addition of a few drops of hydrochloric acid (0.1 M) or sodium hydroxide (0,1M).

The curve of Fig. 9 shows a large increase in the adsorption efficiency of the dye (MB), when the pH of the solution increases from 2 to 4, from 35.5% to 82.2 %. Beyond  $\text{pH} = 4$ , the percentage increase is still observed but at a lower rate, reaching 94.5% at  $\text{pH} = 12$ .

The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) is an important factor that determines the linear range of pH sensitivity and then indicates the type of surface active centers and the adsorption ability of the surface (Gouza et al., 2017). Many researchers studied the point of zero charge of adsorbents that prepared from agricultural solid wastes in order to better understand of adsorption mechanism. Cationic dye adsorption is favored at  $\text{pH} > \text{pH}_{\text{pzc}}$ , due to presence of functional groups such as  $\text{OH}^-$ ,  $\text{COO}^-$  groups. Anionic dye adsorption is favored at  $\text{pH} < \text{pH}_{\text{pzc}}$  where the surface becomes positively charged (Savova et al., 2003; Chakraborty et al., 2011).

To better illustrate these results, we have determined the point of zero charge which corresponds to the pH value for which the net charge of the adsorbent surface is zero, since the adsorption depends not only on the Van der Waals forces of but also on the electrostatic attractions. The PZC was determined by a simple electrochemical method (El Haddad et al., 2013), by adding 50 ml of sodium chloride (0.05 M) to a series of beakers, the pH of each was adjusted to precise values from 2 to 12 by

addition of hydrochloric acid (0.1 M) or sodium hydroxide (0,1M), then 40 mg of adsorbent was added to each beaker. The suspensions were kept under constant agitation at ambient temperature for 48 h, in order to determine the final  $\text{pH}_f$ . The PZC corresponds to the intersection of the curve carrying  $\Delta\text{pH} = (\text{pH}_f - \text{pH}_i)$  as a function of  $\text{pH}_i$  with the abscissa axis (Fig. 11). The PZC of the YHI250 adsorbent is 6.2, which means that the adsorbent surface is positively charged at pH below 6.2, and negatively at a pH above 6.2. The more the pH increases towards PZC, the more negative ion density on the surface of the adsorbent YHI250 increases the adsorption of the cationic MB. This is confirmed by the low binding of the MB molecules to a strongly acidic medium at  $\text{pH} = 2$  due to the repulsion of the cationic molecules BM, which leads to the reduction of adsorption of the dye, and a maximum adsorption of the MB to YHI250 has been reached above the PZC since the negative charges are much more than the positive ones, leading to better adsorption of the cationic MB by the electrostatic attraction phenomenon.

### CONCLUSIONS

This work describes the elaboration of new adsorbent material from Moroccan oil shale. The manufacturing of this material was carried out by thermal treatment of carbonate-free oil shale from Timahdit deposit (Y layer). The quality of the products obtained depended strongly on the combined effect of the preparation conditions such as mass ratio of adsorbent, time and temperature of thermal treatment, contact time, pH of MB and heating temperature of solution. The results show that the optimum conditions with provide the best adsorption proprieties are 40 mg of adsorbent, 30 minutes of contact time, 60 minutes of thermal time at  $250^\circ\text{C}$  of thermal treatment, pH of MB of 6.2, with a best yield adsorption of MB (95.5%). The characterization of the adsorbent was performed by Fourier transforms infrared spectrometer (FTIR). Finally, the prepared adsorbent can be used in the decontamination of effluents containing organic pollutants. The simplicity of the process used and the efficiency of the adsorbents obtained make it possible to envisage their possible use in the industry. Additional research is warranted to evaluate the adsorption potential of this adsorbent with respect to various real industrial wastewaters.

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