

International Scientific Organization http://iscientific.org/ Chemistry International www.bosaljournals.com/chemint/



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

Az-iddin Chham¹, El Hassane Khouya^{1,2}, Mina Oumam¹, Abdelkerim Abourriche³, Said Gmouh¹, Mohamed larzek¹, Ssaid Mansouri¹, Nawal Elhammoudi¹, Naima Hanafi¹ and Hassan Hannache^{1,4}

¹LIMAT-Thermostructural Materials and Polymers Team, Faculty of science Ben M'sik, University Hassan II of Casablanca, Boulevard Cdt Driss Harti, BP.7955, Ben M'sik, Casablanca, Morocco
²Teaching and Training Regional Center - Souss Massa, Avenue My Abdallah, BP. N° 106 Inzegane, Morocco
³Laboratoire Matériaux, Procédés, Environnement et Qualité, École Nationale des Sciences Appliquées, B.P. 63, 46000Safi, Morocco
⁴Materials Science and Nanoengineering Department, Mohamed VI Polytechnic University, Lot 660 – Hay Moulay Rachid, 43150 Benguerir, Morocco
*Corresponding author's E. mail: e.khouya@crmefsm.ac.ma

ARTICLE INFO

Article type: Research article Article history: Received January 2017 Accepted November 2017 January 2018 Issue Keywords: Adsorption Moroccan oil shale Wastewaters Colored discharges Methylene blue (MB)

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.

© 2018 International Scientific Organization: All rights reserved.

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.

Cite This Article As: A. Chham, E. Khouya, M. Oumam, A. K. Abourriche, S. Gmouh, M. larzek, S. Mansouri, N. Elhammoudi, N. Hanafi and H. Hannache. The use of insoluble matter of Moroccan oil shale for removal of dyes from aqueous solution. Chemistry International 4(1) (2018) 67-76.

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 km², oil yields range from 20 to 100 l/t and average 70

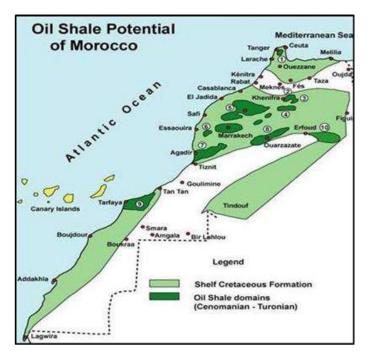


Fig. 1: Oil shale deposits in Morocco (ONHYM-Morocco)

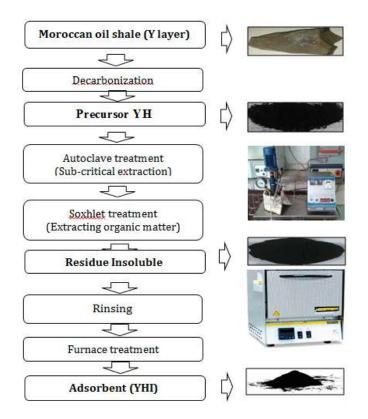


Fig. 2: Organigram for preparation of the adsorbent YHI

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 km² 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 $<200 \ \mu$ m. 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:

$CaCO_3 + 2HCl \longrightarrow CO_2 + CaCl_2 + H_2O$	(1)
$CaMg(CO_3)_2 + 4HCl \longrightarrow 2CO_2 + CaCl_2 + MgCl_2 + 2H_2O$	(2)

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

Chham et al / Chemistry International 4(1) (2018) 67-76

Compound	Calcite	Dolomite	Silica	Clays andother	OrganicMatter (OM)
% by Weight	15.2	12.2	21.8	26.9	23.9
Fable 2: Structure and c	characteristics of MI	В			
Fable 2: Structure and c Name	characteristics of M MW (g.mol ⁻¹)	B λ _{max} (nm)	Molecular fo	ormula	Chemical Structure

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:

$$Qe = \left(\frac{(CO-Ce) \times V}{mads}\right) \times 100$$
(3)

Where, Q_e : MB mass adsorbed at equilibrium per unit mass of adsorbent (mg.g⁻¹), V : Volume of the solution of MB (L), C₀: Initial concentration of MB (mg.L⁻¹), C_{eq} : Equilibrium concentration of MB (mg.L⁻¹) and m_{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 λ_{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⁻¹ with a BURKER TENSOR 27 FT-IR spectrometer by summing 32 scans at 2 cm⁻¹ 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⁻¹. 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⁻¹, which are due to the elongation of the -OH bonds. The band at 2923 cm⁻¹ and the band at 2846 cm⁻¹ are due respectively to the vibrations of asymmetric elongation of CH₂ and the symmetrical elongation of -CH₃ of the aliphatic acids (Delvaux et al., 1990). The band at 2380 cm⁻¹ and 2350 cm⁻¹ corresponds to the vibration frequency of the aromatic C=C- and -C-H groups (Delvaux et al., 1990). The band at 1450 cm⁻¹ corresponds to the vibration frequency of the C-H groups of methyl and methylene (Rose et al., 1993). The band at 1650 cm⁻¹ corresponds to the vibration frequency of the aromatic groups -C=C-, -C-H (Mongenot et al., 1999). The band at 1026 cm⁻¹ may be due to the vibration of the groups C-O-C or -OH (Rose et al., 1993). The bands 992 and 859 cm⁻¹ 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⁻¹decreased, corresponding to C-H links of the methyl and methylene and disappearance of the peaks 2380 cm⁻¹and 2350 cm⁻¹characteristic 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⁻¹).

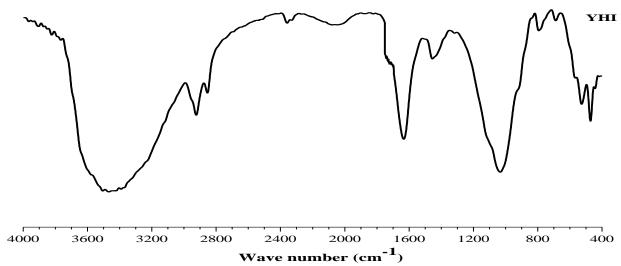


Fig. 3: Infrared spectrum of YHI adsorbent

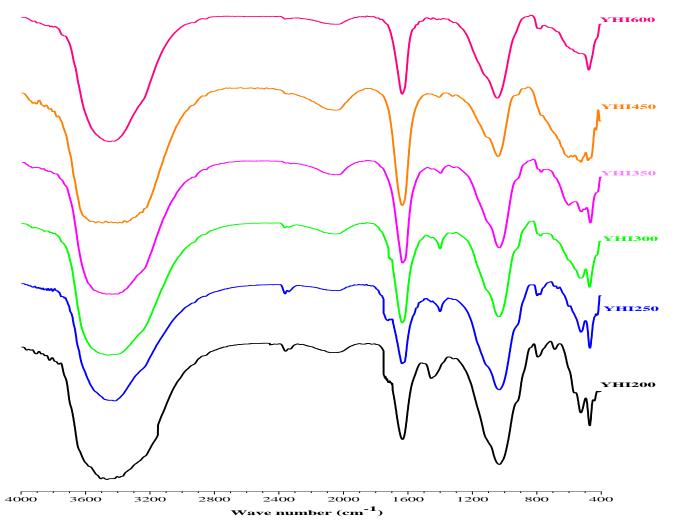


Fig. 4: The infrared spectrums of the adsorbent materials YHI(T), (T=200; 250; 300; 350; 450; 600 °C).

The influence of the mass of adsorbent was studied by stirring constantly of 100 mL of MB solution ($C_0 = 20$ mg.L⁻¹), with different mass ratio of adsorbent ranging from 0.1 to 0.8 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 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 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 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 ($C_0 = 20$ mg.L⁻¹) and in the presence of mass ratio of 0.4 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 BM 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 BM (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 studding 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 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 mg.L⁻¹) and in the presence of a given mass of the adsorbent (m= 40 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 ($C_0 = 20$ 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.

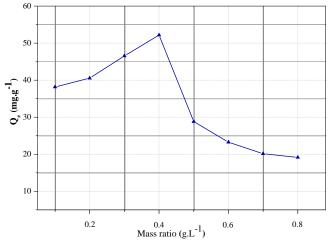


Fig. 5: Effect of mass ratio on MB mass adsorbed on the maximum quantity of the MB ($C_0 = 20 \text{ mg.L}^{-1}$; pH = 6.4; V= 100 mL; T= 25±2 °C).

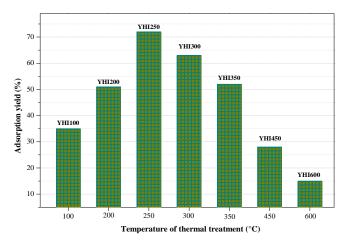


Fig. 6: Effect of temperature of thermal treatment on adsorption yield of MB on YHI ($C_0 = 20 \text{ mg.L}^{-1}$; m= 40 mg; pH= 6.4; V= 100 mL; T= 25±2 °C).

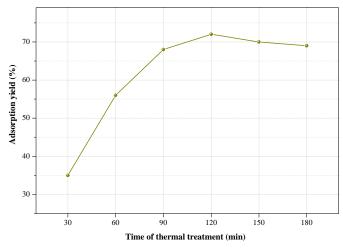


Fig. 7: Effect of time of thermal treatment on adsorption yield of MB on YHI250 (C_0 = 20 mg.L⁻¹; m= 40 mg; pH= 6.4; V = 100 mL; T= 25±2 °C).

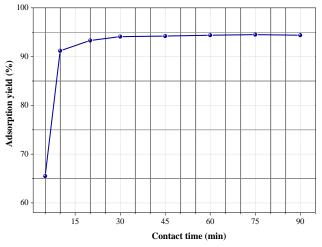


Fig. 8: Effect of contact time on adsorption yield of MB on YHI250 (C_0 = 20 mg.L⁻¹; pH= 6.4; V= 100 mL; m= 40 mg; T= 25±2 °C)

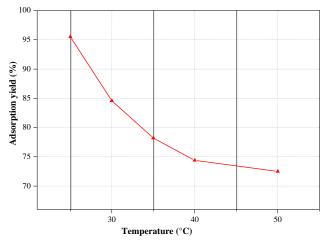


Fig. 9: Effect of temperature of MB on adsorption yield of MB on YHI250 ($C_0 = 20 \text{ mg.L}^{-1}$; t = 30 min; V= 100 mL; m= 40 mg; pH= 6.4).

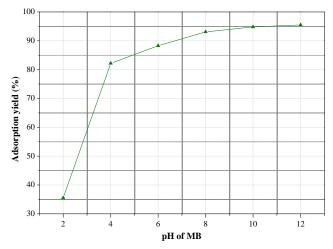


Fig. 10: Effect of pH on adsorption yield of MB on YHI250 (C_0 = 20 mg.L⁻¹; t = 30 min; V= 100 mL; m = 40 mg; T= 25±2 °C).

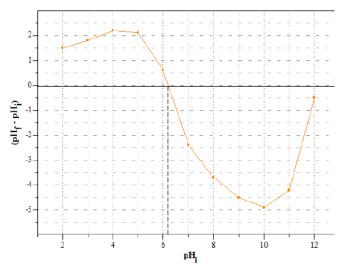


Fig. 11: Effect of pH and point of zero charge (pH_{pzc})on adsorption yield of MB on YHI250

Effect of pH and point of zero charge (pH_{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 pH = 4, the percentage increase is still observed but at a lower rate, reaching 94.5% at pH = 12.

The point of zero charge (pH_{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 pH>pH_{pzc}, due to presence of functional groups such as OH-, COO- groups. Anionic dye adsorption is favored at pH<pH_{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 pH_f. The PZC corresponds to the intersection of the curve carrying $\Delta pH = (pH_f - pH_i)$ as a function of pH_iwith 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 pH = 2 due to the repulsion of the cationic molecules BM, which leads to the reduction of adsorption of the dve, 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 carbonatefree 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 °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.

ACKNOWLEDGEMENT

The authors are grateful to Center of Analyses and Research (CARB) of faculty of Ben M'sik (Morocco) for FT-IR analysis.

REFERENCES

Akgul, M., Karabakan, A., 2011. Promoted dye adsorption performance over desilicated natural zeolite. Microporous and Mesoporous Materials 145(1), 157– 164.

- Alexandro, M.M.V., Andre, L.C., Marcos, H.K., Tais, L.S., Vitor, C. A., 2011. Adsorption of methylene blue on activated carbon produced from flamboyant pods. Chemical Engineering Journal 168(2), 722–730.
- Al-Ghouti, M.A., Khraisheh, M.A.M., Ahmad, M.N.M., Allen, S., 2009. Adsorption behavior of methylene blue onto Jordanian diatomite: a kinetic study. Journal Hazardous Materials 165: 589–598.
- Amin, N.K., 2009. Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: adsorption equilibrium and kinetics. Journal of Hazardous Materials 165(1/3): 52– 62.
- Banat, I.M., Nigam, P., Singh, D., Marchant, R., 1996. Microbial decolorization of textile-dye-containing effluents: a review. Bioresource Technology 58(3), 217–227.
- Bhattacharyya, K.G., Sharma, A., 2005. Kinetics and thermodynamics of methylene blue adsorption on Neem (*Azadirachta indica*) leaf powder. Dyes Pigments 65(1), 51–59.
- Bouchta, R., 1984. Valorization studies of the Moroccan oil shales: Office National de Researches et Exploitations Pétrolènes B.P. 774, Agdal, Rabat, Maroc 28.
- Chakraborty, S., Chowdhury, S., Saha, P.D., 2011. Adsorption of Crystal Violet from aqueous solution on to NaOHmodified rice husk. Carbohydrate Polymers 86(4), 1533– 1541.
- Chiou, M.S., Chuang, G.S., 2006. Competitive adsorption of dye in acid solutions on chemically metanil yellow and RB15 cross-linked chitosan beads. Chemosphere 62(5), 731– 740.
- Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal, a review. Bioresource Technology 97(9), 1061– 1085.
- Delvaux, D., Martins, H., Leplat, P., Paulet, J., 1990. Comparative Rock-Eval pyrolysis as an improved tool for sedimentary organic matter analysis. Organic Geochemistry 16 (4/6), 1221–1229.
- El Haddad, M., Slimani, R., Mamouni, R., El Antri, S., Lazar,S., 2013. Removal of two textile dyes from aqueous solutions onto calcined bones. Journal of the Association of Arab Universities for Basic and Applied Sciences 14(1), 51–59.
- El Harti, M., Legrouri, K., Khouya, E., Hannache, H., Hanafi, N., Solhy, A., Hammouti, B., Preparation of Adsorbent Material from Moroccan Oil Shele of Timahdit: Optimization of Parameters Processes and Adsorption Tests. 2012. Der PharmaChemica 4(5), 2130–2139.
- Espantaleón, A.G., Nieto, J.A., Fernández, M., Marsal, A., 2003. Use of activated clays in the removal of dyes and surfactants from tannery waste waters, Applied Clay Science 24(1/2), 105–110.
- Gardiner, D.K., Borne, B.J., 1978. Textile waste waters: treatment and environmental effects, Journal of the Society of Dyers and Colourists 94(8): 339–348.
- Gouza, A., Fanidi, K., Saoiabi, S., Laghzizil, A., A. Saoiabi, 2017. Effect of heat treatment on the surface properties of

selected bituminous shale for cationic dye sorption. Desalination and Water Treatment 66, 274–280.

- Guechi, E.K., Hamdaoui, O., 2016. Sorption of malachite green from aqueous solution by potato peel: kinetics and equilibrium modeling using non-linear analysis method, Arabian Journal of Chemistry 9, 416–424.
- Gupta, V.K., Jain, R., Varshney, S., 2007. Electrochemical removal of hazardous dye React fix Red 3 BFN from industrial effluents, Journal of Colloid and Interface Science 312(2), 292–296.
- Gürses, A., Dogar, Ç., Yalçin, M., Açikyildiz, M., Bayrak, R., Karaca, S., 2006. The adsorption kinetics of the cationic dye, methylene blue, onto clay, Journal Hazardous Materials B 131, 217–228.
- Hamadi, A., Nabih, K., 2012. Alkali activation of oil shale ash based ceramics, E-Journal of Chemistry 9(3), 1373–1388.
- Hameed, B. H., 2009. Spent tea leaves: a new nonconventional and low-cost adsorbent for removal of basic dye from aqueous solutions, Journal Hazardous Materials 161(2), 753–759.
- Han, R.P., Han, P., Cai, Z.H., Zhao, Z.H., Tang, M.S., 2008. Kinetics and isotherms of neutral red adsorption on peanut husk. Journal of Environmental Sciences 20(9), 1035–1041.
- Ichcho, S., Ezzine, M., Khouya, E., Abourriche, A., Hannache, H., Naislain, R., Pailler, R., 2003. Removal of methylene blue from aqueous by adsorption over an adsorbent elaborated from Moroccan oil shale. Journal Physical Chemical News 12, 88-89.
- Ichcho, S., Khouya, E., Fakhi, S., Ezzine, M., Hannache, H., Pallier, R., Naslain, R., 2005. Influence of the experimental conditions on porosity and structure of adsorbents elaborated from Moroccan oil shale of Timahdit by chemical activation. Journal of Hazardous Materials A118, 45–51.
- Ichcho, S., Khouya, E., Ezzine, M., Hannache, H., Pallier, R., Naslain, R., 2005. Phosphoric acid activation of Morrocan oil shale of Timahdit: Influence of the experimental conditions on yield and surface area of adsorbents. Journal de Physique IV France 123, 81-85.
- Ichcho, S., Khouya, E., Fakhi, S., Ezzine, M., Hannache, H., Pallier, R., Naslain, R., 2006. Activation chimique et évaluation des performances des schistes bitumineux de Timahdit. Journal Physical Chemical News 28, 135-141.
- Jaber, J.O., Probert, S.D., 1999. Environmental-impact assessment for the proposed oil-shale integrated trigeneration plant. Applied Energy 62(3), 169–209.
- Jadhav, S.B., Phugare, S.S., Patil, P.S., Jadhav, J.P., 2011. Biochemical degradation pathway of textile dye Remazol red and subsequent toxicological evaluation by cytotoxicity, genotoxicity and oxidative stress studies. International Biodeterioration and Biodegradation 65(6), 733–743.
- Janoš, P., Buchtová, H., Rýznarová, M., 2003. Sorption of dyes from aqueous solutions onto fly ash. Water Research 37(20), 4938–4944.

ISSN: 2410-9649

- Kalyani, K.S.P., Balasubramanian, N., Srinivasakannan, C., 2009. Decolorization and COD reduction of paper industrial effluent using electro-coagulation. Chemical Engineering Journal 151(1/3), 97–104.
- Khouya, E.; Ichcho, S.; Legrouri, K.; Hannache, H.; Fakhi, S.; Nourredine, A.; Ezzine, M.; Pailler, R.; Naslain, R., 2006. Ann. Chim. Sci. Mat. 31(5): 583-596.
- Li, B., Hao, Y., Shao, X., 2015. Synthesis of hierarchically porous metal oxides and Au/TiO₂ nanohybrids for photo degradation of organic dye and catalytic reduction of 4-nitrophenol. Journal of Catalysis 329, 368–378.
- Low, K., Lee, C., 1990. The removal of cationic dyes using coconut husk as an adsorbent. Pertanika 13(2), 221–228.
- Lui,R., Zhang, B., Mei, D., Zhang, H., Lui, J., 2011. Adsorption of methyl violet from aqueous solution by halloysite nanotubes. Desalination 268, 111–116.
- Mittal, A., Mittal, J., Malviya, A., Kaur, D., Gupta, V.K., 2010. Adsorption of hazardous dye crystal violet from wastewater by waste materials. Journal of Colloid and Interface Science 343(2), 463–473.
- Mohan, D., Singh, K.P., Singh, V.K., 2005. Removal of hexavalent chromium from aqueous solution using lowcost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. Industrial and Engineering Chemistry Research 44(4), 1027–1042.
- Mongenot, T., Derenne, S., Largeau, C., Tribovillard, N.P., Lallier-Vergès, E., Dessort, D., Connan, J., 1999. Organic Geochemistry 30(1), 39–56
- Moore, S.W., Ried, F.D., 1973. Extraction of radium from natural waters using manganese-impregnated acrylic fibers. Journal of Geophysical Research 78(36), 8880– 8886
- Nabais, J.V., Carrott, P., Carrott, M.M.L.R., Luz, V.; Ortiz, A.L., 2008. Influence of preparation conditions in the textural and chemical properties of activated carbons from a novel biomass precursor: the coffee endocarp, Bioresource Technology 99(15), 7224–7231.
- Oumam, M., Abourriche, Ak., Adil, A.; Hannache, H., Pailler, R., Naslain, R., Birot, M., Pillot, J.-P., 2003. Annales de Chimie Science des Matériaux 28, 59–74
- Pechyen, C., Aht-Ong, D., Sricharoenchaikul, V., Atong, D., 2010. Materials Science Forum 658, 113–116.
- Radovic, L.R., Silva, I.F., Ume, J.I., Menendez, J. A., Leon, C.A.Y., Leon, A.W., Scaroni, A.W., 1997. An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons. Carbon 35, 1339–1348.
- Ranganathan, K., 2000. Chromium removal by activated carbons prepared from Casurina Equisetifolia leaves. Bioresource Technology 73(2), 99–103.
- Rose, H. R., Smith, D.R., Quezada, R.A., Hanna, J. V., Wilson, M. A., 1993. Role of minerals and additives during kerogen pyrolysis, Fuel Process Technology 33(2), 149–157.
- Rose, H.R., Smith, D.R., Vassallo, A.M., 1994. An investigation of thermal transformations of the products of oil shale

demineralization using infrared emission spectroscopy. Journal Energy & Fuels 7, 319–325.

- Sachdeva, S., Kumar, A., 2009. Preparation of nanoporous composite carbon membrane for separation of Rhodamine B dye. Journal of Membrane Science 329(1/2), 2–10.
- Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A., Idris, A., 2011. Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. Desalination 280(1/3), 1–13.
- Savova, D., Petrov, N., Yardim, M.F., Ekinci, E., Budinova, T., Razvigorova, M., Minkova, V., 2003. The influence of the texture and surface properties of carbon adsorbents obtained from biomass products on the adsorption of manganese ions from aqueous solution. Carbon 41(10), 1897–1903.
- Tan, I.A.W., Ahmad, A.L., Hameed, B.H., 2008. Adsorption of basic dye on high-surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. Journal of Hazardous Materials 154(1/3), 337–346.
- Thiam, A., Brillas, E., Garrido, J.A., Rodríguez, R.M., I. Sirés, 2016. Routes for the electrochemical degradation of the artificial food azo-colour Ponceau 4R by advanced oxidation processes. Applied Catalysis B: Environmental 180, 227–236.
- Toomik, A., Liblik, V., 1998. Oil shale mining and processing impact on landscapes in north-east Estonia: Landscape and Urban Planning 41(3/4), 285–292.
- Vadivelan, V., Kumar, K.V., 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. Journal of Colloid and Interface Science 286(1), 90–100.
- Wang, S., Zhu, Z.H., Coomes, A., Haghseresht, F., Lu, G.Q., 2005. The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. Journal of Colloid and Interface Science 284(2), 440–446.
- Weng, C.H., Pan, Y.F., 2007. Adsorption of a cationic dye (methylene blue) onto spent activated clay, Journal Hazardous Materials 144, 355–362.
- Zhao, Z., Yuan, J., Fu, M.; Su, L.; Li, Z., 2014. Removal of methylene blue from aqueous solution by using oil ash. Oil Shale 31(2), 161–173.

Visit us at: http://bosaljournals.com/chemint/ Submissions are accepted at: editorci@bosaljournals.com