

Influence of the experimental conditions on porosity and structure of adsorbents elaborated from Moroccan oil shale of Timahdit by chemical activation

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Abstract

This study records experiments undertaken to determine the suitable conditions for the use of the oil shale of Timahdit, as an adsorbent for water treatment. A simple process was proposed based on chemical activation. The preparation has been carried out by carbonization after impregnation of the precursor with phosphoric acid. The effect of different conditions of preparation on the specific surface area is discussed. These parameters are H₃PO₄/shale weight ratio, carbonization temperature, carbonization time and concentration of H₃PO₄. The properties and surface structure of the adsorbent were investigated by XPS and FT-IR. Their total surface acidity and basicity were also determined. The retention process of methylene blue (MB) by adsorbents has been studied. It was found that MHP2 and MHP7 have relatively high retention ability as compared to activated carbons.

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1. Introduction

The high costs of ingredients and treatment of water resources create the major problems in the developing countries suffers from water pollution. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Activated carbon is the most common material used for retrieving pollutants such as colouring matters from potable water or pre-treated wastewater. It is however an expensive material. To substitute activated carbon some studies have been done on natural materials [1] or agricultural waste [2–4].

For this purpose, the present work concerns the elaboration of a cost effective substitute for commercial adsorbents currently used for water treatment by activation of the oil shale rocks from Timahdit region (layer M) located in the south of Morocco. This choice was dictated firstly, by the composition of this oil shale which contains both, organic matter (a good precursor of activated carbon) and clays (known by their adsorption properties) [5]. Secondly, the previous research showed that the adsorbent elaborated from the Moroccan oil shale by thermal processing [6] or chemical activation [7] possessed good capacities to remove some organic substances, heavy metals and bacterium [8].

Activated carbons were usually prepared by heating precursors at higher temperatures followed by activation either physically or chemically. An important advantage of the chemical activation is that the process normally takes place at a lower temperature and shorter time than those used in physical activation [9]. Moreover, the carbon yield in chem-

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ical activation is usually higher than in physical activation because the chemical agents are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products [10].

Therefore, the objectives of the present research were to explore: (a) the experimental conditions for the preparation of the adsorbents prepared from the decarbonated oil shale (denoted as MH in the text) impregnated with phosphoric acid H_3PO_4 in order to seek conditions for which high surface area is attained; (b) the chemical structure (including surface groups) of the best adsorbents comparatively to the precursor; (c) to test 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.

2. Materials and methods

2.1. Precursor

The oil shale specimen used in this investigation was obtained from the Timahdit (provided 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 [11]. The layer studied in this work is the layer (M) whose mineralogical composition is illustrated in Table 1.

The raw rocks were crushed, ground and decarbonated by dissolution with concentrated hydrochloric acid (HCl 6N) until disappearance of any release of carbon dioxide. After filtration, the residue was washed with distilled water until free of chloride ions, then dried in the oven at about 110 °C. The resulting solid product (referred to as MH) was ground and sieved to 0.08–0.1 mm particle size.

2.2. Chemical activation process

Twenty grams of MH was immersed with 20 g of phosphoric acid solutions H_3PO_4 ($X = 30\text{--}100\%$) diluted in distilled water (in $\text{H}_3\text{PO}_4/\text{MH}$ weight ratios $R = 0.25, 0.33, 0.5, 1$ and 2) and dried at 100 °C for 1 h. The mixture was introduced in the furnace previously preheated to predetermine temperature (250 or 450 °C) and kept at this temperature for t hours

($t = 1\text{--}3$ h) under an air flow. After cooling to room temperature, the products were fully washed with water to extract the excess of acid and dried, the obtained samples denoted as MHP_x ($x = 1\text{--}13$).

2.3. Measurement

The specific surface areas of the solid materials were measured by the BET method [12] using nitrogen gas adsorption at 77 K by a Micromeritics Flowsorb II 2300 instrument. For adsorption measurements the samples were degassed at 160 °C for 24 h.

The X-ray photoelectron spectra were recorded with a Vacuum Generator ESCALAB 22ixl spectrometer using Mg $\text{K}\alpha$ radiation source generated at 15 kV. The elements have been identified with their binding energies which are indexed in tables [13]. Data analysis (smoothing, deconvolution, curve fitting, background, etc.) was done by a micro-computer.

For FT-IR analysis, specimens were ground with KBr and pressed into disks, they were then analyzed by 205 Nicolet FT-IR spectrometer.

For the distribution of surface functionalities of adsorbents, the techniques used namely, called upon the classical Boehm's titration [14]. In this method, the various types of acid groups are classified into carboxylic acids, lactones and phenols, titrated according to their acid–base properties by inorganic bases or hydrochloric acid. Acid base titration was followed by a pH-meter Mini 80 (Tacussel, France), equipped with a combined glass electrode and a graduated burette of 0.05 ml was used.

The evaluation of the performances of the elaborated adsorbents has been made based on the adsorption of methylene blue (MB, Merck product 95% purity). Multipoint adsorption isotherms were constructed. We used the bottle point method, which consists to mixing 250 ml of MB (50 mg/l) with a mass of adsorbents (50–200 mg/l) in breakers. The temperature of the system was maintained at room temperature without adjustment of pH. When the equilibrium was reached (a preliminary kinetics study has shown that satisfactory equilibrium conditions were attained after 6 h), the adsorbate concentration was determined by UV–vis at 664 nm using a Perkin-Elmer spectrophotometer.

3. Results and discussion

3.1. Specific surface area

The best adsorbents properties were observed for particular combination of the experimental parameters: $\text{H}_3\text{PO}_4/\text{shale}$ weight ratio, temperature, acid concentration and time of activation. The results are listed in Table 2.

The effect of carbonization time ($t = 1\text{--}3$ h) on the resulting adsorbents at different temperatures and $R = 1$ on the surface area was examined. At 250 °C, the maximum S_{BET} was at-

Table 1
Mineralogical composition of M layer of Timahdit region

Constituent	Percentage in weight
Calcite	15.16
Dolomite	12.33
Silica	21.75
Clay	26.87
Organic matter	23.89

Table 2
Evolution of specific surface area as function of the experimental conditions

Sample	Temperature (°C)	H ₃ PO ₄ /shale weight ratio (<i>R</i>)	Activation time (h)	<i>X</i> (%)	<i>S</i> _{BET} (m ² /g)
M	–	–	–	–	20
MH	–	–	–	–	37
MHP1	250	1	1	80	289
MHP2	250	1	2	80	315
MHP3	250	1	3	80	119
MHP4	250	1	2	50	214
MHP5	250	1	2	30	107
MHP6	250	1	2	100	254
MHP7	450	1	1	80	294
MHP8	450	1	2	80	167
MHP9	450	1	3	80	119
MHP10	250	0.25	2	80	47
MHP11	250	0.33	2	80	69
MHP12	250	0.5	2	80	167
MHP13	250	2	2	80	117

tained for carbonization time of 2 h. For shorter time (1 h) the results suggest that carbon structure did not achieve a full development of porosity and prolongation of carbonization time beyond 2 h led to a pronounced reduction in surface area. For 450 °C, when the carbonization time increased the surface area decreased, presumably due to reactions of recombination and insertion of heteroatom such as phosphorus or oxygen in the structure with a diminution of the porosity.

The porosity of the adsorbent treated with solutions of various concentrations in H₃PO₄ was higher for the sample treated with 80% acid concentration than for those activated with less concentrated acids (30% or 50%). This is justified by the insufficient amount of acid to allow the acid to play its role of oxidation inhibitor. On the other hand, using concentrated acid (100%), showed the contrary, but this could be related to the incorporation of phosphorus in the carbonaceous skeleton as supported by the high yield obtained at this concentration [15]. Consequently, the concentration acid of 80% was selected as the optimum.

In searching on the appropriate acid to precursor ratio for surface area development, a series of adsorbents were prepared at 250 °C during 2 h and *X* = 80% for *R* varying between 0.25 and 2. The surface area of adsorbent increased from 47 to 315 m²/g when the H₃PO₄/MH ratio increased from 0.25 to 1. Beyond 1, it decreased and led to a reduction in the sample porosity. These results indicate that progressive development of porosity took place as more acid was incorporated into the precursor [16], likely due to some expansion of the material. However, the beneficial effect of increasing the impregnation ratio reached a limit at which a larger excess of acid seemed to bring about collapse of pores and therefore, structural contraction. Jagtoyen and Derbyshire [15] suggested that a larger amount of acid causes some expansion, phosphate cross-links due to polymerization of acid to form polyphosphates.

Finally, we selected MHP2 and MHP7 prepared at 250, 450 °C for *X* = 80%, *R* = 1 and carbonization time of 2 and 1 h, respectively, as the best adsorbents for the characterization.

3.2. Characterization

3.2.1. XPS analysis

Fig. 1 shows a typical example of an XPS scan spectrum of the MH, MHP2 and MHP7. These had the similar structure with an increase of the content of organic carbon at an electron binding energy of 285 eV in MHP2 and MHP7. It occurred because the phosphoric acid played its important role in the catalysis of the dehydration and the protection of the organic matter against oxidation [17,18].

The results also revealed the presence of the following elements: Ca, N, O, P, Al and Si. One also notes an increase of the phosphorus content (6% in MHP7 against 3% in MHP2); it proves that, for the activation, one attends the insertion of this element in the skeleton carbon; it is coherent with the high yield obtained at 450 °C. The reduction of the nitrogen content is presumably due to the gaseous liberation that occurred along the activation process.

The surface functional groups content of the samples was determined from the XPS peak area. The results shown in Fig. 2 illustrated the curve fitting of the C 1s spectrum for MH, MHP2 and MHP7.

The measured spectrum of MH could be fitted by six peaks. The surface had a graphite carbon peak at an electron binding energy of 284.2 eV. It had the content of 28.15% which was calculated from the area under the peak. The peak of binding energy of 284.7 eV corresponded to the carbon sp³ (16.15%). We can see three small peaks corresponding to COOH (2.86%), C=O (4.01%) and C–O (7.97%) corresponded at the binding energy of 289.37, 287.7 and 286.3 eV, respectively. The peaks of binding energy of 285.3 and 283.4 eV corresponded to C–CO (12.76%) and SiO₂C₂ (28.67%), respectively.

For the curve fitting of the C 1s spectrum for the MHP2 and MHP7; these had the similar chemical structure to the MH; the C 1s peak of MHP2 was fitted by six peaks, too. At the time of activation of MH by the phosphoric acid, we could increase the percentage of the peaks COOH (4.14%), C=O

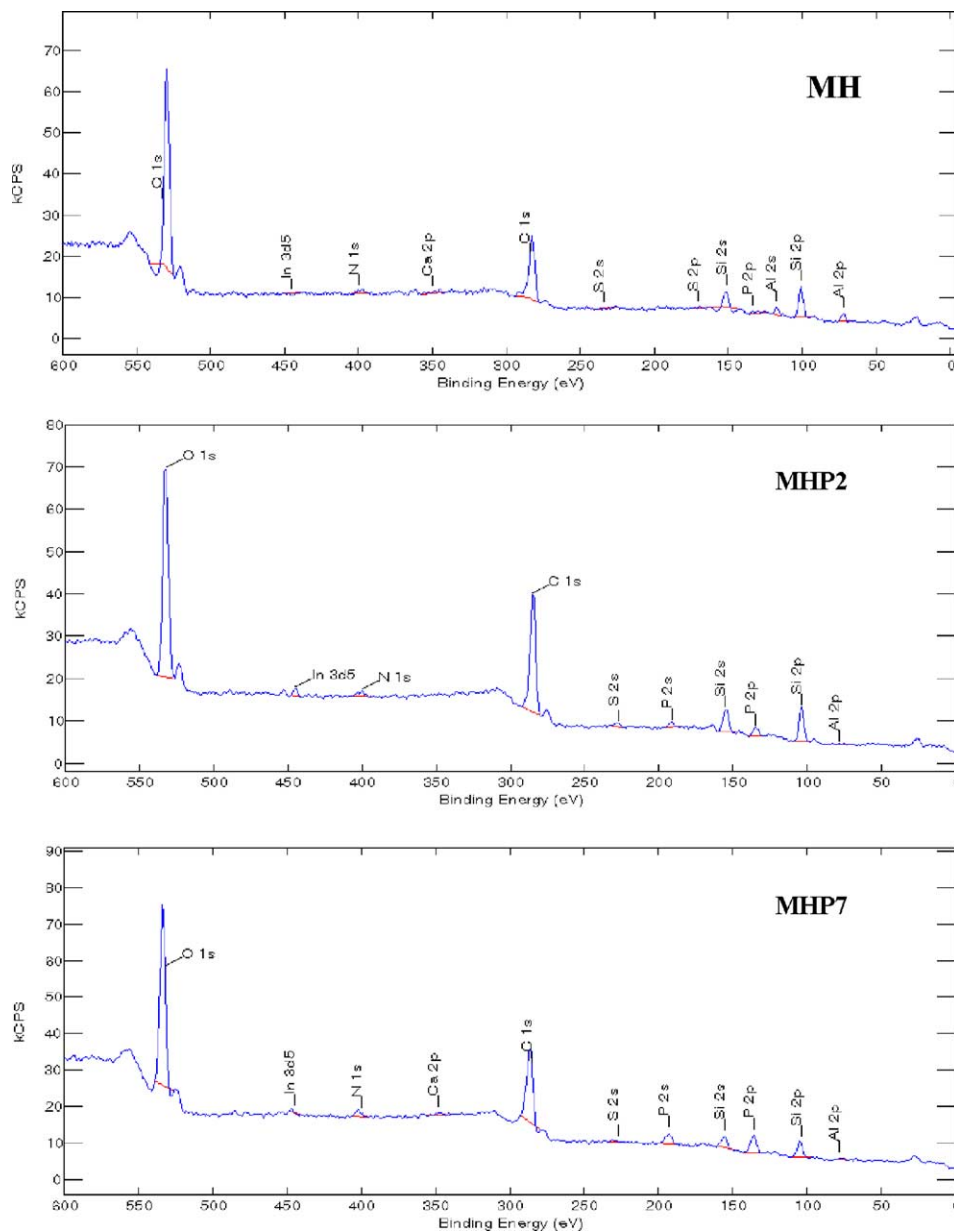


Fig. 1. XPS spectrum of samples.

(8.92%), C–C–O (18.36%) and C–O (12.12%) and we decreased the percentage of functional groups corresponded to the graphitizing carbon sp^2 (19.66%) and SiO_2C_2 (10.17%).

In addition, one note the apparition of the peak COOP in MHP7 presumably formed between the phosphoric acid and the sides of graphite aromatic layers [16–18]. It can be justified by the reduction of the carbon graphite content that passes from 28% in MH to 19% in MHP7.

3.2.2. Surface functionalities analysis

The results of the analysis are summarized in Table 3. These results show that during activation of MH, the carboxylic group decreased in MHP7 contrarily in MHP2. This is justified that MHP2 was treated at lower temper-

atures which permitted the departure of these functionalities. On the other hand, MHP7 was treated at 450 °C; the temperature that seems favourable for the departure of these functionalities groups in form of carbon monoxide and dioxide.

Table 3
Values of surface functionalities for the samples

Group	MH (mequiv./g)	MHP2 (mequiv./g)	MHP7 (mequiv./g)
GI (carboxylic)	0.39	0.38	0.02
GII (lactone)	0.07	0.26	0.38
GIII (hydroxide)	0.15	0.21	0.38
Basic functions	0.97	0.95	0.82

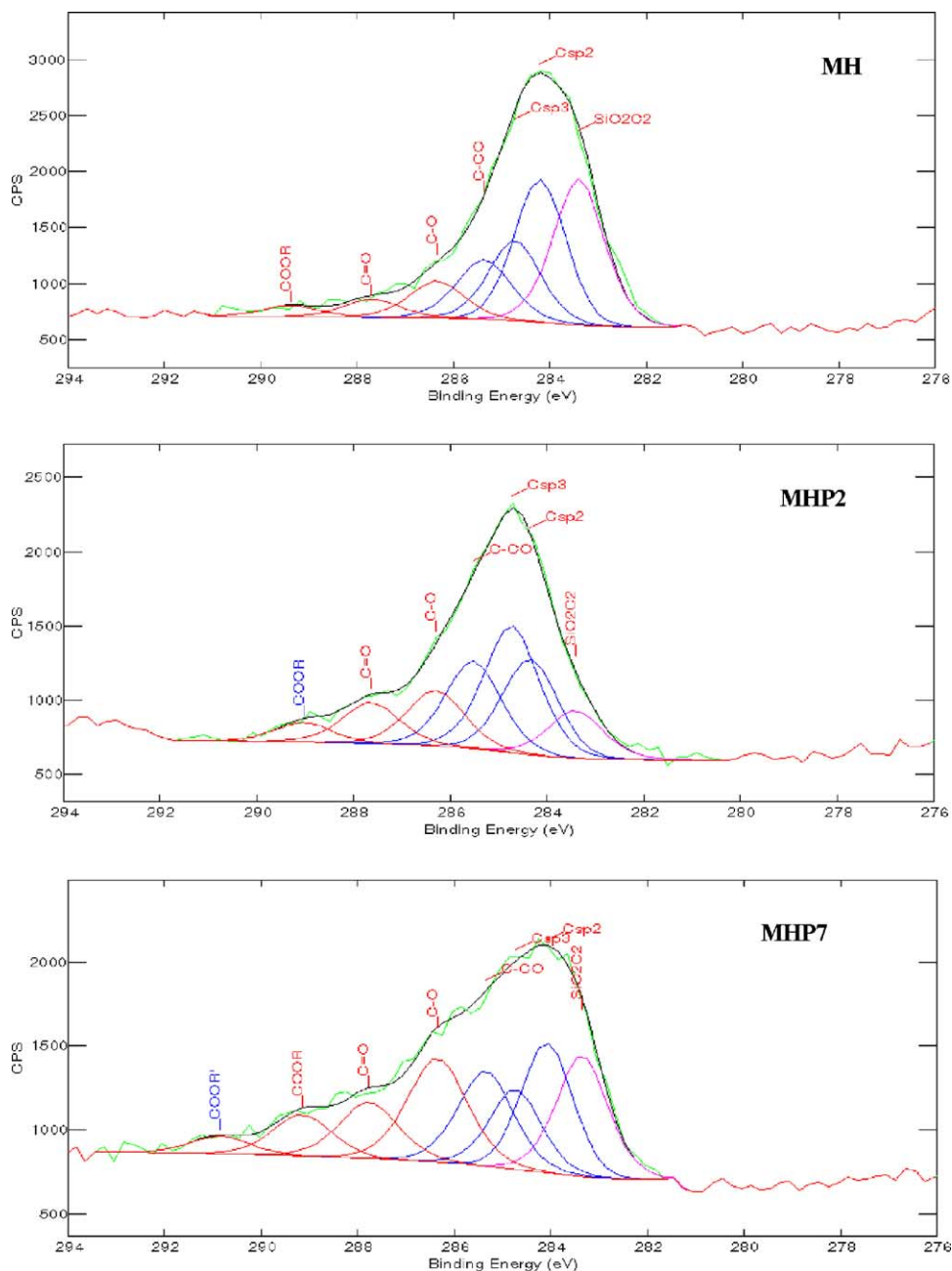


Fig. 2. Fitted C 1s XPS spectrum of samples.

The hydroxyl and lactones groups increased because of rearrangement and combination of organic matter during the loss of carbon monoxide and dioxide. The basic functional groups were lower for MHP2 and MHP7 compared to MH due to the thermal treatment.

3.2.3. FT-IR analysis

The possible assignments of the observed peaks in the FT-IR spectra of MHP2 and MHP7 compared to MH are provided in Fig. 3.

The IR spectra of MHP2 and MHP7 show the disappearance of the bands at 3697 and 3620 cm^{-1} corresponding to the hydroxyl groups. We also note the disappearance of the bands located at 530 and 430 cm^{-1} is the characteristic of alkane.

When the activation temperature rose to $250\text{ }^{\circ}\text{C}$, the peak intensity at 1398 cm^{-1} increased corresponding to C–H links of the methyl and methylene groups. When the activation temperature was greater than $250\text{ }^{\circ}\text{C}$, the peak at 1715 cm^{-1} decreased, which means the amount of carbonyl group decreased.

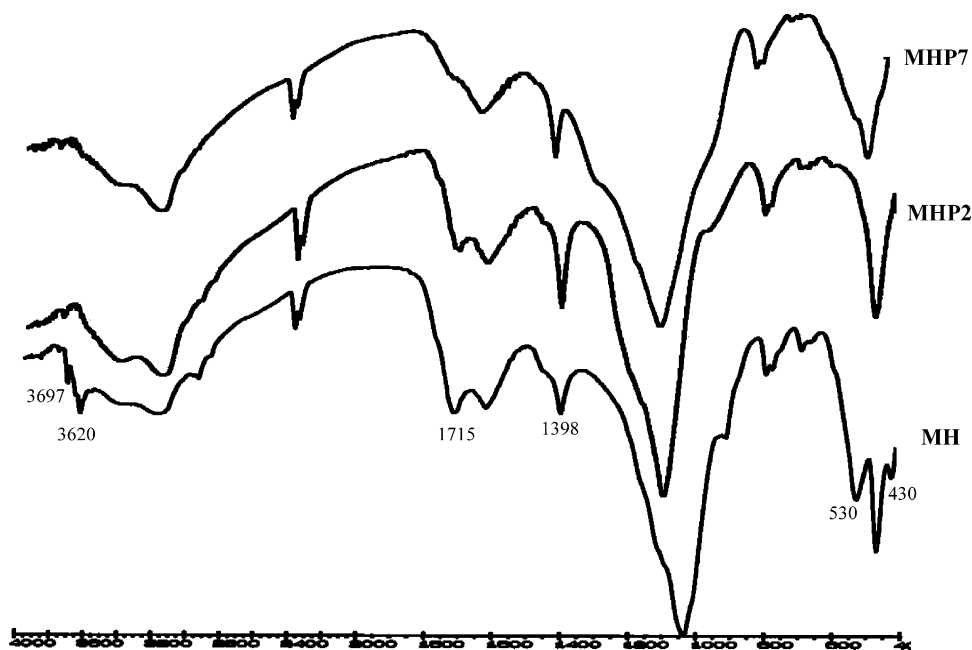


Fig. 3. FT-IR spectra of samples.

3.2.4. Adsorption tests

The MB adsorption isotherms of adsorbents fit well the Langmuir model ($1/q = 1/Q_0 + 1/bQ_0C$) where Q_0 is the saturated adsorption, b the constant related to the adsorption energy and C the MB concentration at equilibrium, suggesting that the adsorption almost reached saturation. The parameters of the Langmuir equation were listed in Table 4.

The adsorption of MB followed the Langmuir model for the present systems indicated the formation of monolayer coverage of adsorbate (MB) at the outer surfaces of the adsorbents. Likewise, it may be stated that the dye retention by both adsorbents was ruled by physisorption as well as a cationic exchange process.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L [19] which is defined by: $R_L = 1/1 + bC_0$, where b is the Langmuir constant and C_0 the initial MB concentration (mg/l). R_L value between 0 and 1 indicated favourable adsorption.

For comparison, the adsorption capacities of other activated carbons reported in the literature were given in Table 5 along with that for the adsorbent of the present study. The comparative adsorption capacity showed that the adsorption efficiency of our adsorbent is relatively higher than activated carbons. The gas adsorption tests indicated that the adsor-

bents have a low surface area compared to activated carbons. Nonetheless, the adsorbents also displayed a relatively high capacity for adsorbing MB from water, such behaviour suggested that a potential ion exchange or acid/base reaction may be accruing, rather than a purely physical adsorption process. This difference in the retention ability was doubtless due to the difference in the mineralogical constitution and surface functionalities of adsorbents and activated carbons.

Further work is now under progress to develop this process for practical usage and to clarify the detailed mechanisms involved.

3.2.5. Cost estimation

The raw material used in the present study, oil shale, is very abundant ore in Morocco (93 billion/t).

After considering the cost of transport, chemicals, electrical energy (250 °C), etc., the final adsorbent will be very low cost compared with activated carbon (treated at high temperature). The comparative cost and adsorption capacity of MHP2 and MHP7 with activated carbons showed that the adsorption efficiency of our adsorbents is higher than activated carbons. This indicated the favourable use of oil shale as precursor for the elaboration of low cost adsorbent.

Table 4
Parameters of the Langmuir equation for the samples

Sample	Q_0 (mg/g)	R_L	b
M	23	0.09	0.100
MH	46	0.06	0.139
MHP2	370	0.13	0.066
MHP7	345	0.29	0.024

Table 5
Comparison of Langmuir constant Q_0

Adsorbent	Q_0 (mg/g)	Reference
CAC	313	[2]
SCB	258	[2]
EZKA	435	[3]
CAGO	403	[20]
MHP2	370	Present work

4. Conclusion

We could develop new adsorbents by chemical activation of the bituminous shale's of Timahdit region (layer M). The process of activation by H_3PO_4 drove to adsorbents with a relatively developed specific surface ($\sim 300\text{ m}^2/\text{g}$).

The quality of the products obtained depended strongly on the combined effect of the preparation conditions such as the time, the temperature of treatment, the weight ratio and the phosphoric acid concentration. The best adsorbents that reach a specific surface order to $300\text{ m}^2/\text{g}$ are those obtained at 250 and 450 °C during 2 and 1 h, respectively, with a concentration in H_3PO_4 and H_3PO_4/MH weigh ratio equal to 80% and 1%, respectively.

The characterization of MHP2 and the MHP7 allowed us to bring up the role of dehydrating and catalyst of the phosphoric acid as well as the different transformations that the precursor MH had undergone. A high adsorption capacity toward MB was observed: about 300 mg/g, it has been compared with that of activated carbons and found to be competitive with this material.

The process is simple and the adsorbents can be used at the industrial level. Additional research is warranted to evaluate the adsorption potential of this adsorbent with respect to various real industrial wastewaters.

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References

- [1] M. Bagane, S. Guiza, Elimination d'un colorant des effluents de l'industrie textile par adsorption, *J. Ann. Chim. Sci. Mater.* 25 (2000) 615–625.
- [2] J.B. Castro, P.R. Bonelli, E.G. Cerrella, A.L. Cukierman, Phosphoric acid activation of agricultural residues and bagasse from sugar cane: influence of the experimental conditions on adsorption characteristics of activated carbons, *J. Ind. Eng. Chem. Res.* 39 (2000) 4166–4172.
- [3] K. Legrouiri, M. Ezzine, H. Hannache, R. Donoyel, R. Pallier, R. Naslain, Removal of organic and inorganic pollutants by activated carbon elaborated from molasses, *J. Ann. Chim. Sci. Mater.* 26 (2001) 383–389.
- [4] K. Anoop Krishnan, T.S. Anirudhan, Uptake of heavy metals in batch systems by sulfurized steam activated carbon prepared from sugarcane bagasse pith, *J. Ind. Eng. Chem. Res.* 41 (2002) 5085–5093.
- [5] O. Bekri, M. Ziyad, Proceedings of the Eastern Oil Shale Symposium, Lexington, Kentucky, USA, November, 1991.
- [6] S. Ichcho, M. Ezzine, E. Khouya, A. Abourriche, H. Hannache, R. Pailler, R. Naslain, Removal of methylene blue from aqueous solution by adsorption over an adsorbent elaborated from Moroccan oil shale, *J. Phys. Chem. News* 12 (2003) 88–89.
- [7] M. Oumam, A. Abourriche, A. Adil, H. Hannache, R. Pailler, R. Naslain, M. Birot, J.P. Pillot, Elaboration et caractérisation d'un nouveau matériau adsorbant à partir des schistes bitumineux du Maroc, *J. Ann. Chim. Sci. Mater.* 28 (2003) 59–74.
- [8] M. Oumam, A. Abourriche, H. Hannache, A. Abourriche, A. Benamara, M. Charrouf, R. Pailler, R. Naslain, Bioactives properties of extracts from Moroccan oil shale, *J. Sci. Pharm.* 70 (2002) 271–276.
- [9] D. Lozano-Castello, M.A. Lillo-Rodenas, D. Cazorla-Amoros, A. Linares-Solaro, Preparation of activated carbons from Spanish anthracite. I. Activation by KOH, *J. Carbon* 39 (2001) 741–749.
- [10] M. Jagtoyen, F. Derbyshire, Some considerations of the origins of porosity in carbons from chemically activated wood, *J. Carbon* 31 (7) (1993) 1185–1192.
- [11] M. Tahiri, C.M. Sliepcevich, R.G. Mallinson, vol. 32, ACS, Division of Petroleum Chemistry, 1987, p. 71.
- [12] S. Brunauer, P.H. Emmet, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309.
- [13] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bombau, in: J. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, Prairie, MN, 1992.
- [14] H.P. Boehm, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.), Advances in Catalysis, vol. 16, Academic Press, New York, 1966, pp. 179–274.
- [15] M. Jagtoyen, F. Derbyshire, Activated carbons from yellow poplar and white oak by H_3PO_4 activation, *J. Carbon* 36 (7/8) (1998) 1085–1097.
- [16] M. Oumam, Doctoral Thesis, University Hassan II-Mohammedia, Casablanca, 2000.
- [17] J. Laine, A. Calafat, M. Labady, Preparation and characterization of activated carbons from coconut shell impregnated with phosphoric acid, *J. Carbon* 27 (2) (1989) 191–195.
- [18] M.S. Solum, R.J. Pugmire, M. Jagtoyen, F. Derbyshire, Evolution of carbon structure in chemically activated wood, *J. Carbon* 33 (9) (1995) 1247–1254.
- [19] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, *J. Waste Manage.* 21 (2001) 381–387.
- [20] A. Baçaoui, A. Yaakoubi, A. Dahbi, C. Bennouna, J. Ayele, M. Mazet, Characterization and utilisation of a new activated carbon obtained from Moroccan olive wastes, *J. Water SRT-Aqua* 47 (1998) 68–75.