PREPARATION AND CHARACTERIZATION OF ANTIBACTERIAL ADSORBENTS MATERIALS ELABORATED FROM THE MORROCAN OIL SHALES OF TIMAHDIT

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Abstract- The preparation of the adsorbent from oil shale has been carried out by impregnation of the precursor with phosphoric acid, carbonization. The BET surface area, and surface functional groups of the best adsorbents were determined. The adsorbents with functional groups showed strong adsorption and antibacterial activity against *Escherichia coli*, which suggests it is a promising antibacterial material. The results of this study were discussed and showed that this activated oil shale can be used as adsorbent in wastewater treatment.

Keywords: Adsorbent, Oil shale, Phosphoric acid, Functional groups. Escherichia coli.

I. INTRODUCTION

Activated carbons are known to be excellent versatile adsorbents and are therefore used to remove organic and inorganic species from gaseous and liquid effluents [1-5]. Kuroda and al. have found that bacteria preferably adhered to the solids supports made of carbon material [6].

Fabrication of activated carbon has proven to be efficient but very expensive. In order to reduce cost, research was directed towards processes using natural materials [7] or agricultural waste [8-9]. For this purpose, the present work concerns elaboration of a cost effective substitute for commercial adsorbents currently used for water treatment by activation of oil shale rocks from Timahdit region (layer M) located in the south of Morocco. This choice was dictated by the composition of this oil shale which contains both, organic matter (a good precursor of activated carbon) and clays [10].

Consequently, the work described in this paper was divided into two steps. Firstly, we studied 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 and carbonised. Secondly, the antibacterial property of the best elaborated adsorbent against *Escherichia coli* (E.C) is also to be determined in this investigation.

II. MATERIALS AND METHODS

II-1. Precursor:

The 100 km^2 oil shale field of Timahdit is located in the mid-Atlas mountain at 35 km in the south of Azzrou. This deposit is a vein of schists 100 to 150 m in thickness and comprising several layers with variable content of organic matter [10]. The layer studied in this work is the layer (M) whose mineralogical composition is illustrated in table-1 :

Table 1 : Mineralogical composition of M layer of Timahdit region.

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

The raw rocks were crushed, ground and decarbonated by leaching with chlorhydric 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 a furnace at about 110°C. The resulting solid product (referred to as MH) was ground and sieved to 0.08 mm - 0.1 mm particle size.

II-2. Chemical activation process

The following experimental conditions have been used for the activation of MH by H_3PO_4. 50%.MH and 50% H_3PO_4 (30-100% diluted in distilled water) were mixed and placed in a steamer at 100°C for 1 hour. Then the products were treated in an air flow under various conditions. After, the samples were washed in a soxhlet with water for 2 days to extract the excess of acid. Finally, the samples were dried and weighed.

II-3. Antibacterial test

Antibacterial tests against E.C were conducted with sterile physiological water. The steps in the processing of the antibacterial tests are illustrated as follow.

1g of samples MH, MHP2 or CAC (Commercial Activated Carbon) as reference were introduced in syringe of 10 ml with a filter paper disc to their extremity to prevent possible flight of adsorbent. The syringe and all material used in microbial procedures were sterilized at 120°C for 20 min.

1 ml of culture of 24 h was eluding through the different syringe containing the adsorbent. In order to get a satisfactory elution, the syringe was washing with 4 ml of physiological water.

0.1 ml of every dilution were introduced and speared on the surface of the Petri dishes, after incubation for 24 h at 37°C, the bacterial number in the different dishes were counting.

II-4. Measurement

The surface chemistry of the samples was undertaken to characterize some elements by using X-ray Photoelectron Spectroscopy (VGESCALAB 22ixl XPS). The XPS apparatus used was equipped with an Mg Kα radiation source generated at 15 kV. The elements have been identified with their binding energies which are indexed in tables.

The surface areas of the solid materials were measured by the BET method [11] using nitrogen gas adsorption at 77 K by a Micromeritics Flowsorb II 2300 instrument. For adsorption measurements the samples were out gassed at 160°C for 24 hours.

III. Results and discussion

III-1. Specific surface area

The best adsorbents properties were observed for particular combination of the experimental parameters: temperature, acid concentration and time of activation. The product obtained in these conditions was referred to MHPx (x= 1-9). The results are listed in Table 2 and compared to those for MH.

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

Sample	Température (°C)	Activation time (h)	X %	$S_{BET}(m^2/g)$
M	-	-	-	20
MH	-	-	-	37
MHP1	250	1	80	289
MHP2	250	2	80	315
MHP3	250	3	80	119
MHP4	250	2	50	214
MHP5	250	2	30	107
MHP6	250	2	100	254
MHP7	450	1	80	294
MHP8	450	2	80	167
MHP9	450	3	80	119

The highest specific surface area is obtained for the adsorbent treated at 250°C. At 250°C, one favours the oxidation of the organic matter and the release of gases which create porosity. At 450°C, one expects reactions of recombination and insertion of heteroatom such as phosphorus or oxygen in the structure with a diminution of the porosity. Consequently, we selected 250°C as the optimal temperature. For the temperature of 250°C, the adsorbents display rather similar specific surface areas with a small decrease as a function of time beyond 2 hours of processing. So we selected 2 hours as carbonization time.

The porosity of the adsorbent treated with solutions of various concentrations in H_3PO_4 is higher for the sample treated with 80% acid concentration than for those activated with acids less concentrated (30 to 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, for the highly concentrated acid (100%), one notices exactly the contrary, but this could be related to the incorporation of phosphorus in the carbonaceous skeleton as supported by the high yield for this concentration [12]. Consequently, the concentration of 80% of acid was selected as the optimum concentration. Finally, we selected MHP2 as the best adsorbent for the characterization and the antibacterial tests.

III-2. Structure of the samples.

Figure 1 shows a typical example of an XPS scan spectrum of the MH and MHP2 samples. These had similar structure with an increase of the content in MHP2 organic carbon at an electron binding energy of 285 eV. It comes because the phosphoric acid played its important role in the catalysis of the dehydratation and the protection of the organic matter against the oxidization.

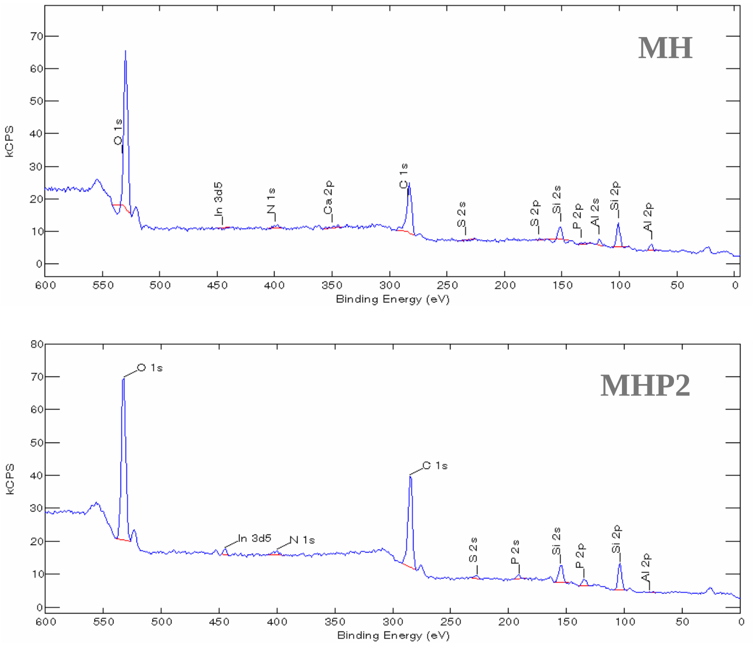

Figure 1: XPS spectrum of MH and MHP2

III-3. Surface chemical composition

The surface functional groups content of the samples was determined from the XPS peak area after substraction of a linear background. The results shown in figure 2 illustrated the curve fitting of the C1s spectrum for MH and MHP2 samples.

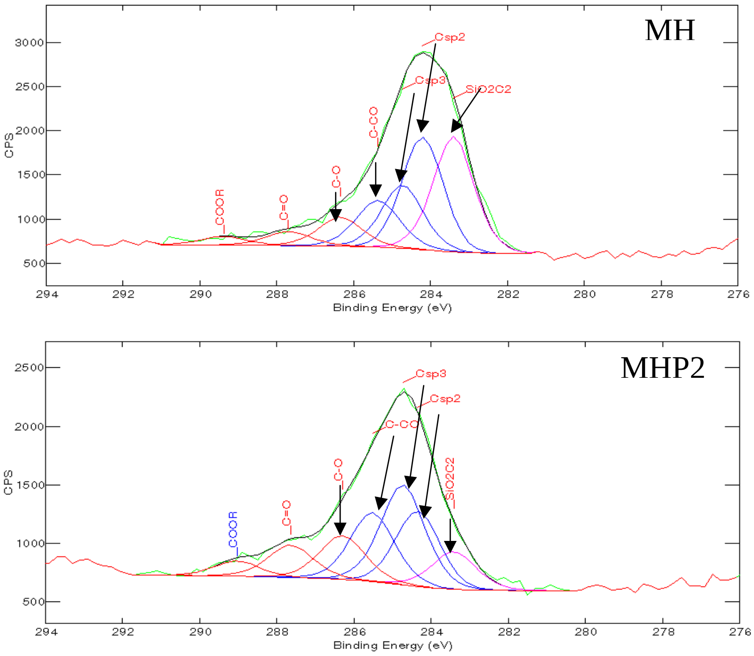

Figure 2: Fitted C1s XPS spectrum of MH and MHP2

The measured spectrum of MH could be fitted by six peaks. The surface had a graphitizing 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 284.7eV corresponded to the carbon Sp^3 (16.15%). We can see tree small peaks corresponding to COOH (2.86%), C=O (4.01%) and C-O (7.97%) corresponded at binding energy of 289.37, 287.7 and 286.3eV respectively. The peaks of binding energy 285.3 and 283.4 eV corresponded to C-CO (12.76%) and SiO_2C_2 (28.67%) respectively.

For the curve fitting of the C1s spectrum for the MHP2 sample. It had similar chemical structure to the MH, the C1s 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 (8.92%), C-Co (18.36%) and C-O (12.12%) and we decrease the percentage of functional groups corresponded to the graphitizing carbon sp^2 (19.66%) and SiO_2C_2 (10.17%).

III-4. Antibacterial activity

The results of antibacterial activity are given in table 3.

Table 3 : Results of the antibacterial tests against E.C.

Bacterial solution	Bacterial number CFU/ml	%
Culture solution	$54\ 10^7$	-
MH solution	$23\ 10^6$	4.25
MHP2 solution	0	100
CAC solution	7510^4	72

The exam of the results shows the efficiency of the MHP2. For a initial culture solution counting 5410^7 CFU/ml, we did not detect any bacterium in Petri dish. Comparatively with MH and CAC, one notes a reduction of number of CFU/ml in the CAC>MH sense.

This efficiency is probably the results of interactions between the microorganism and the support. It would be favoured by the heterogeneity of the material surface.

Conclusion

It has been demonstrated in the present work that adsorbents with medium surface area can be produced by chemical activation with H_3PO_4 from oil shale's of Timahdit. The activation process produces adsorbents having a surface area higher than $300m^2/g$.

The effect of different parameters during activation was investigated. Surface area was strongly depending on the combined effects of preparation conditions, this behaviour might be due to some expansion of the material, as more acid is incorporated into the precursor, until a limit is reached at which the carbon structure collapses.

Under the experimental conditions investigated, have been found to be appropriate for preparing adsorbents of medium surface area from precursor MH impregnated with phosphoric acid with potential antibacterial activity against *Escheichia coli*.

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