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Impact of chemical processes on the textural properties of the adsorbent of Moroccan oil shale for environmental applications

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Abstract

This work aims a comparative study on the structure and adsorption capability of oil shale based materials resulting carbonates removal from the rock. The oil shale from Tarfaya mine was treated using four acids: chloric acid (OSH), Phosphoric acid (OSP), sulfuric acid (OSS) and nitric acid (OSN). The obtained materials were characterized by thermo gravimetric (TG), Fourier transform infrared spectroscopy and scanning electron microscopy. The results showed that the acid used to remove carbonates obviously affects the chemical composition and the texture evolution of the residues. The removal of volatile compounds resulted in pores with enhanced rough and irregular surface. Porosity and the adsorption capability of the resulting materials were significantly increased when the rock was treated with chloride acid.

1. Introduction

Oil shale is a complex mixture of organic and inorganic components. Kerogen and bitumen comprise the organic part of oil shale[1]. Bitumen represents a small amount of the organic matter and it is soluble in ordinary solvents. Kerogen is the insoluble part of organic material and composed mainly of carbon, hydrogen and oxygen with minor amounts of nitrogen and sulfur. The major mineral constituents in the oil shale are dolomite, calcite, quartz, and feldspars. Minor amounts of pyrite and illite are usually present [2,3]. Demineralization can be obtained with physical or chemical methods. Chemical methods are based on digestion of inorganic parts by means of acid treatment. Generally, acid treatment using HCl and HF does not alter kerogen structure [4,5]. However, the nitric acid which is a strong oxidizing agent alters the kerogen by increasing nitrogen and oxygen content with the introduction of carboxylic groups into the structure of kerogen [3]. Several studies showe that treatment by the mixture of concentrated HCl and HF acids has been successfully used to remove carbonate, sulfate, clay minerals, quartz and silicates [6,7]. In this study, adsorbent are synthesized using the chemical method by differing acid and used as an adsorbent for the removal of methylene blue from aqueous solutions. The effects of the parameters of development, such as the type of acid used during development, are studied to predict the nature of the adsorption process.

2. Material and Methods

2.1. Raw material

In this study, we used the oil shale of Tarfaya (R3 layer), taken from South of Morocco. Composition of the sample is given in table 1; it consists essentially of inorganic material with more than 80% in weight. The samples were dried in an oven at 80°C during 24H. Removing carbonates from the rock by dissolution in acids was carried out using HCl, HNO_3, H_2SO_4 or H_3PO_4 [8,9].

2.2. Thermal characterization of oil shale

The organic matter in oil shale consists of both kerogen and bitumen. Kerogen comprises the major portion of the organic matter, whereas bitumen, a viscous liquid, is a mixture of organic compounds. Oil shale combustion is a complex process and involves a series of parallel reactions.

Oil shale combustion is a two step process: first is the combustion of bitumen (light organic part in oil shale) and followed by the combustion of kerogen (heavy organic part in oil shale) [10].

Table 1: Results of the composition of Tarfaya oil shale[9].

Constituent	Carbonate	Clays	Silicate	Organic matter
Wt (%)	*67.2*	*10*	*6.5*	*15.9*

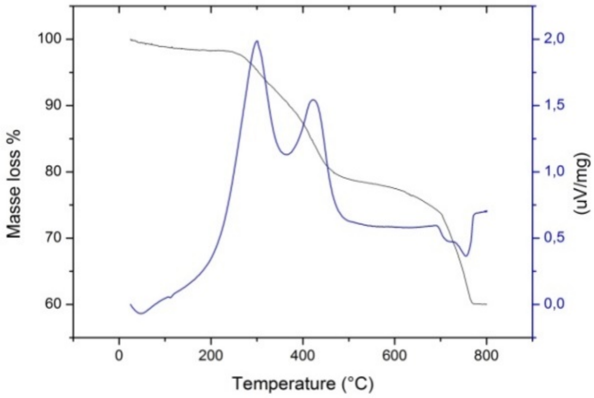

Figure 1: TG-DSC curves of the oil shale.

In the combustion of oil shale samples, using DSC and TG (figure1), it was observed that below 100 °C oil shale loses its moisture, so the H_2O components in the crystalline structure decompose. Between 250 and 500 °C[7], the organic content which is mostly kerogen and bitumen are decomposed. Above 600 °C, the mineral constituents, in the molecular structure are decomposed[11].

2.3. Morphology characterization of oil shale

The SEM image of the raw oil shale solid exhibits compact surface structure (figure 2).

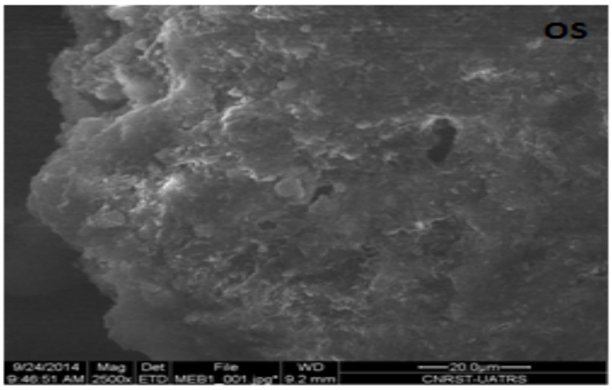

Figure 2: SEM photographs of the raw oil shale.

2.4. Decarbonation

The carbonate-free oil shale samples were obtained by dissolution of carbonates using four acids (diluted in 20%) chloric acid (OSH), phosphoric acid (OSP), sulfuric acid (OSS) and nitric acid (OSN). 20 g of R3 powdered rock (particle size less than 0.08 mm) were mixed separately with 100 ml of each acid in 500 ml Teflon beakers and stirred for 24 h at room temperature. The CO_2 produced was trapped by bubbling in a solution of barium hydroxide. After filtration, the solid residues were washed carefully with distilled water, dried at 70 °C and stocked in sealed plastic bags.

2.5. Characterization of oil shale decarbonated.

The samples for the following analytical tests were prepared to ASTM standards. Duplicate experiments were performed to ensure reproducibility.

Thermogravimetric (TG) analysis was conducted using a SETSYS EVOLUTION TGA-DTA thermal analyzer system. The finely ground sample (<75 µm) was heated from ambient temperature to 1000°C, with a heating rate of 5°C / min.

Functional groups and structure of different samples were studied by a Fourier Transform Infrared Spectrometer (FTIR). The IR spectrum of the resulting materials has been recorded on a BRUKER Tensor 27 transform to Fourier spectrophotometer.

The morphology of the materials was observed with a scanning electron microscopy (SEM-EDX, XL30 and Philips Nether land).

3. Results and discussion

3.1. TG analysis

Figure 3 shows the total mass loss (TG) and differential mass loss (DTG) curves of carbonate-free oil shale samples with the used acids. Through comparative analysis of the pyrolytic behavior curves, it can be concluded that the main decomposition of kerogen is occurring in the temperature range of about 250 to 550°C [10]. The mechanism for the hydrocarbon evolution contains multiple parallel and series reactions [7,11].

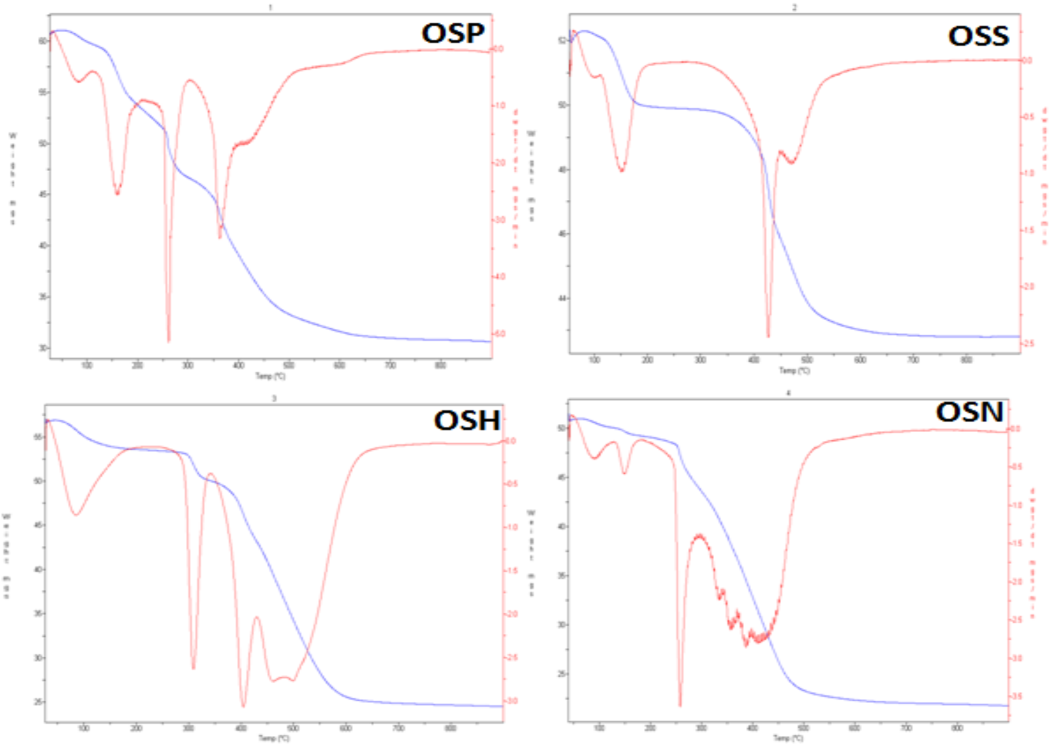

Figure 3: TG and DTG curves of OSH, OSS, OSP and OSN samples.

This result consistent with the observations of Aboulkas and El Harfi [6] and the results of Burnham and Pelet [4]. Indeed, El Harfi observed that the indigenous mineral matters have an inhibition effect on the thermal decomposition of kerogen isolated from Tarfaya (Moroccan) oil shale. Burnham and Pelet studied the effect of mineral compounds in the rock such quartz, calcite and dolomite on the activation energy and their effect on the thermic decomposition of the rock [12].

3.2. SEM analysis

The observation of SEM micrographs of several materials obtained following the various acids used to prepare free-carbonate samples from oil shale, shows that the hydrochloric acid has a significant influence on the microstructure. The maximum porosity developed has been observed in the OSH material which presents a microporous structure, followed by OSN.

By comparing the SEM images (figure 4) of the various samples, we can draw conclusions on the morphological evolution during demineralization. The material exhibits a compact surface structure in OSP and OSS while the cracks and breakages are clearly observed in the textures of OSH and OSN, that may be attributed to the release of great amount of Carbon dioxide formed during the acidic attacks of the carbonates in the rock with this two strong acids. However, most pores in the oil shale are not yet fully open.

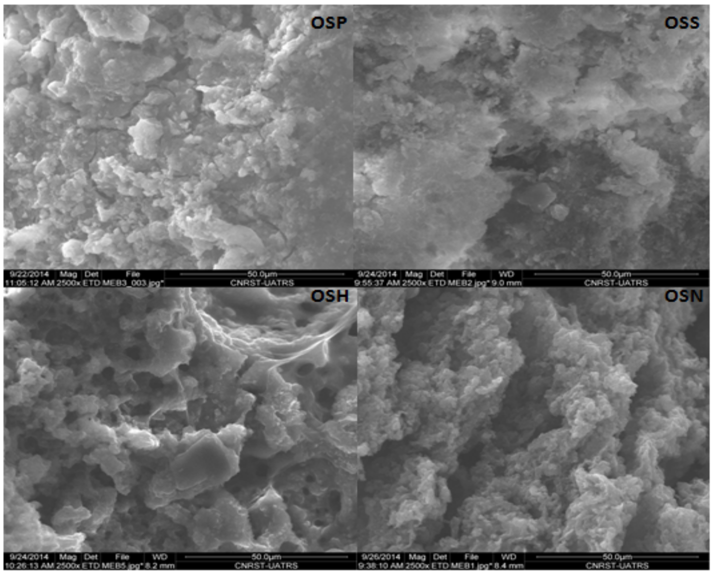

Figure 4: SEM images of the OSH, OSS, OP and OSN samples.

3.3. FTIR analysis

The FTIR spectrum of the carbonate-free oil shale samples OSH, OSP, OSN and OSS, contain fewer peaks comparing to the crude sample OS (figure 5). The missing peaks correspond to those of carbonate minerals originally present in the oil shale. The decrease of peak around 1427–1431 cm-1 is related to the release of NH^{4+} in ammonium illite and the peaks at 1460 cm-1[13,14]. A sharp peak appeared at about 720 cm-1 is attributed to the skeletal vibration of straight chains with more than four CH_2 groups, this is consistent with the conclusion from ^{13}C NMR reported by Tong[14].

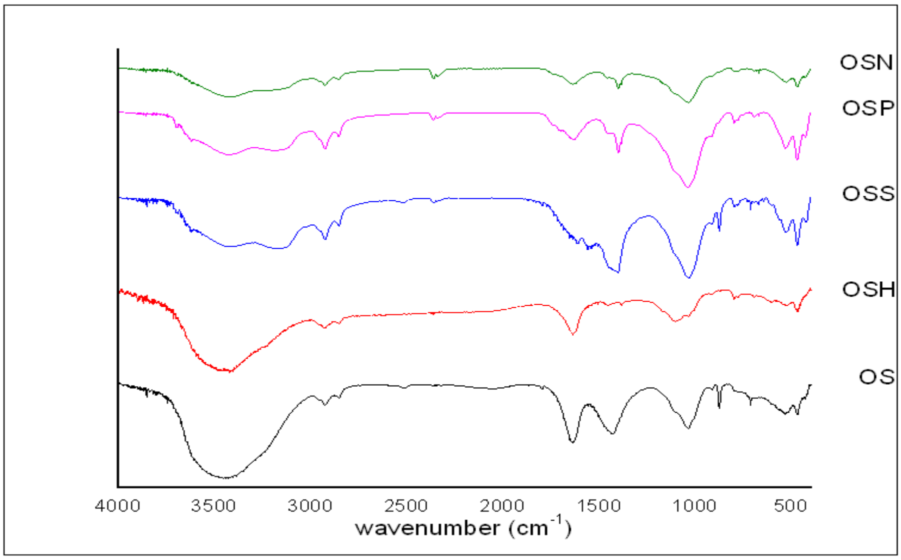

Figure 5: FTIR spectrum of the oil shale and solid residues trait at different acid.

3.4. Evolution of the residue rate

The residue rate in relation to the oil shale OS initially used is defined as follows:

$$R(\%) = 100 \times \frac{M}{m}$$

With
M: Final mass of residue after contact with the acid (g).
m: Mass of crude sample of oil shale initially mixture with the acid (g).

Figure 6 gives the evolution of residue rates obtained for different acids used in this study. The residue rate is about 62% for sulfuric acid and it less for the other acids. The hydrochloric acid, which is very strong acid removes an important amount of the mineral matter in relation to the other acids used in this work and gives a residue rate about 47%.

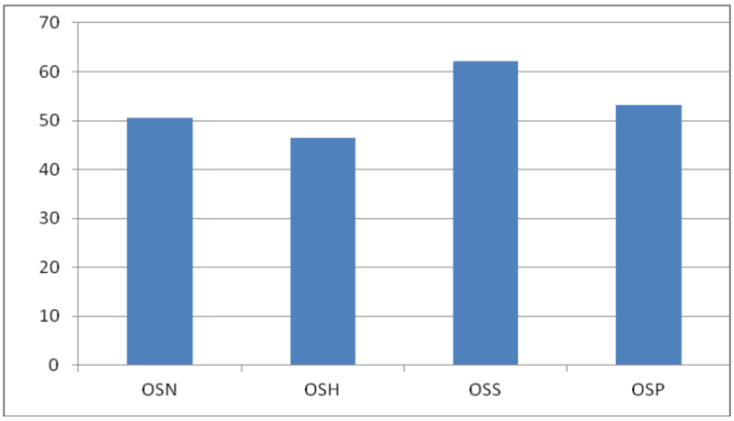

Figure 6: Evolution of residue rates with the acids used.

3.5. Batch adsorption

To perform the adsorption experiments, a stock solution of methylene blue in concentration of 1000 mg/l, was prepared by dissolving MB in deionized water. The desired dye concentrations were prepared from the stock solution by diluting for each adsorption experiment. The concentration of the dye in each sample was analyzed with UV–Vis spectrophotometer (UNICO, China), measuring the absorbance at λ max=664 nm. Amount of materials (OSH, OSS, OSP, and OSN) was placed in a 100 ml Erlenmeyer flask containing 50 ml of dye solution. The following equation is used to calculate adsorption amount in mg/g[15].

$$Qe = \frac{Co - Ce}{m \times 100} \times V$$

Where:

- Qe is the amount of the MB adsorbed on one gram of the adsorbent (mg/g),
- C_O is concentration of the dye (mg/L) at initial time,
- Ce is the equilibrium concentrations of BM (mg/L),
- V is the volume of BM solution (L),
- m is weight of adsorbent (g).

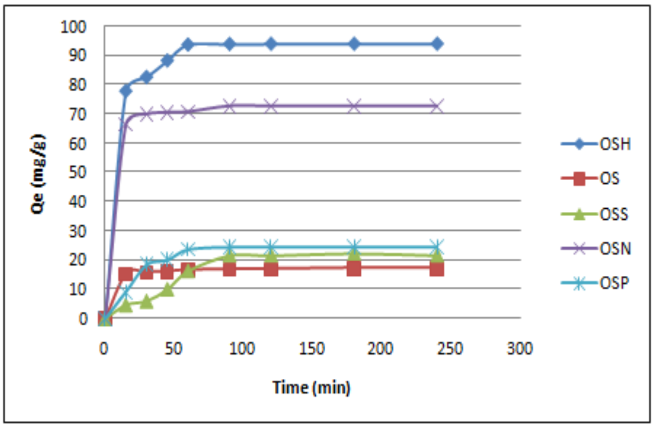

Figure 7: The evolution of the adsorption capacity as a function of time for the different supports.

Figure 7 this curves show that the elimination of MB with OSH and OSN can be decomposed into three phases, a first fast phase followed by a second phase with an average speed to reach finally the level of saturation. This phenomenon is explained by an adsorption process on the sites easily accessible, followed by diffusion toward sites of adsorption less accessible before reaching a balance of adsorption where all the sites become occupied. The comparison of the four supports allows concluding that the OSH presents a texture with adsorbent sites and developed porosity. This result is consistent with the observations of SEM micrographs

3.6. Influence of pH on the adsorption of methylene blue on the active charcoal

The pH is a key parameter to take into account in the process of adsorption of dyes since it acts on the state of ionization of the surface of the adsorbent. Samples were prepared in the same operating conditions cited before and at the time of the balance. The pH is adjusted to the desired value by the sulfuric acid or soda.

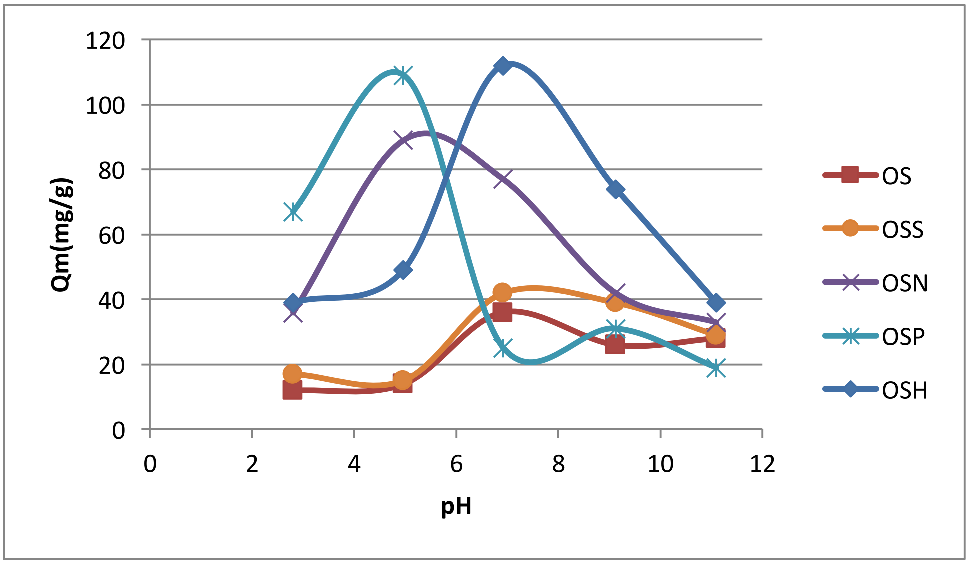

Figure 8: Solution pH influence for the different supports

Figure 8 shows the influence of the pH of the solution on the adsorption for the different media. The adsorption increases with the increase in the pH, the maximum adsorption (112mg/g) was reached in pH to approximately 6.92For the Media (OSH). This result indicates the important effect of the solution pH on the adsorption of methylene blue.

Conclusion

SEM analysis, TG analysis and IR spectra of oil shale and its derived products obtained using different acids to remove minerals, show that the acid used during decarbonation affects the texture of the material and has influence on porous structure development. During oil shale pyrolysis, accompanying with complex physical and chemical reactions in oil shale, pore structure also undergoes a complex process. The demineralization of oil shale with hydrochloric acid has shown a significant influence on the microstructure and on its adsorption capability of the BM dye.

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