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Study on solar adsorption refrigeration cycle utilizing activated carbon prepared from olive stones

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Abstract - *For countries with a high potential of solar energy, producing cold using solar energy is a promising way to sustainable development since the energy used is free and not harmful for the environment. This work proposes a solar adsorption refrigerator using a compound adsorbent fabricated from activated carbon issued from olive stones. High efficiency activated carbon (AC) with different chemical characteristic was prepared. It was established that activated carbon is obtained from carbonized olive stones in presence of nitrogen in the temperature range from 700 to 800 °C and activated by $ZnCl_2$ and KOH. The characterization of the activated carbon samples and the compound adsorbent was studied by SEM (scanning electron microscope) techniques.*

Résumé - *Les pays fortement ensoleillés sont les plus nécessiteux de système de réfrigération, d'autant plus si cette dernière peut être produite de l'énergie solaire qui est une source d'énergie non polluante. Nous vous proposons dans ce travail un système de réfrigération solaire à adsorption dont l'adsorbant est à base de charbon actif issue des noyaux d'olives. Les charbons actifs préparés à base de noyaux d'olive sont activés par $ZnCl_2$ et KOH aux températures 700 et 800 °C successivement. La matière absorbante est synthétisée à partir de ce charbon actif, afin d'être utilisée dans une machine frigorifique à adsorption. Les deux produits (charbon actif et adsorbant) sont caractérisés par la technique MEB (microscopie électronique à balayage).*

Keywords: Activated carbon - Compound adsorbent – SEM – Adsorption.

1. INTRODUCTION

In Algeria, especially in the south, the rural population lives in areas often far from the electric grid, yet its need for cooling keeps growing, mainly for food and medical product preservation. A solar refrigeration unit could be used for perishable foodstuff and as a secure store for food produce during the dry season. By using the properties of some solids to adsorb some gas at low temperature and to release it at high temperature, a thermodynamic cycle can be created to produce cold. The thermal energy can be solar because it is well adapted to the intermittency of the cycle. Adsorption solar cooling units have been widely studied in late 70s and gave rise to prototypes using the performance of mainly four pairs:

- activated carbon (AC) – methanol [1-3];
- zeolite – water [4, 5];
- silicagel – water [6];
- activated carbon–ammonia [7-9].

Activated carbon obtained from olive stones and almond shells has high metal ions adsorption capacities [10]. Plum and peach stones have also been used for preparation of activated carbon [11]. The carbons from peach stones have also shown narrow pore size distribution and good properties as molecular sieves. The adsorbents prepared from plum stones had a better porosity compared to those prepared from peach stones. Some basic information about the adsorptive

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properties of activated carbon prepared from olive stones was presented by Iley and Marsh [12]. The results obtained by them made clear that olive stones, a very abundant agricultural by-product in Mediterranean countries, could be a very adequate raw material to obtain good active carbon. The preparation of these activated carbons is economical and they have, besides some special proprieties, good adsorptive proprieties and hardness, which could be of interest in future environmental protection programs. Nearly all-inexpensive carbonaceous materials can be considered as starting materials for the production of activated carbon [13]. The starting material and the method of preparation influence the quality of the resulting activated carbon [14]. The present work deals with preparation of carbon adsorbents from olive stones (OS), which are waste by product with significant amounts in the oil industry.

2. DESCRIPTION OF THE ADSORPTION CYCLE FOR REFRIGERATION

The basic adsorption cycle for refrigeration consists of four processes represented in Figure 1. In the first one A – B, the adsorbent is heated by solar energy until the pressure reaches a level that enables desorption of refrigerant (state B). During process B – C addition of heat from solar energy results in desorption of vapour refrigerant, which condenses in an ircooled condenser. At state C, when the adsorbent reaches its maximum temperature, solar irradiance starts to decrease. The collector, cut off from the condenser, drops in temperature. Cooling of the adsorbent provokes a drop of pressure in the collector (process C – D). Meanwhile, the liquid refrigerant is transferred into the evaporator. When the pressure reaches the value of the pressure at the evaporator temperature, the collector is connected to the evaporator (state D).The adsorbent continues to decrease in temperature and pumps the liquid refrigerant, which evaporates and extracts heat from the evaporator (process D – A) generating a cooling process inside the chamber. The cycle is said to be intermittent because the evaporation – cooling process happens only during the night.

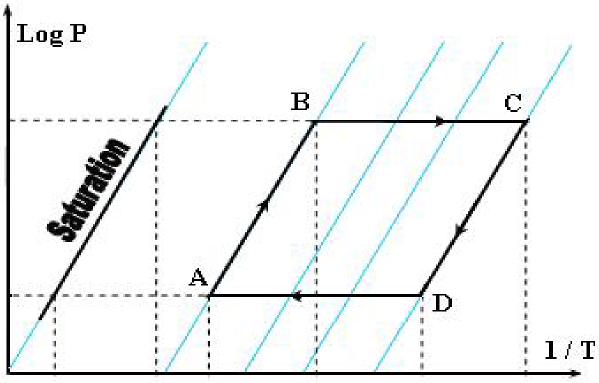
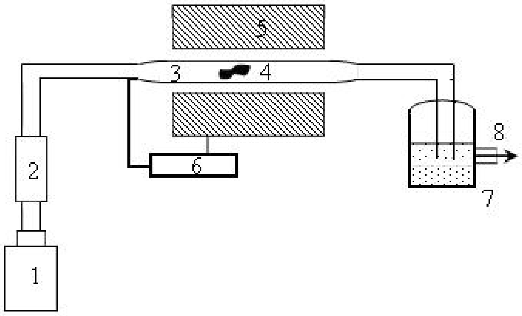


Fig. 1: The ideal cycle in the Clapeyron diagram

3. EXPERIMENTAL

3.1 Preparation of activated carbon from olive stones

Olive stones freed from their fruit were obtained from the olive oil industry. They were crushed in a 10 % solution of sulfuric acid and refluxed in distilled water to zero acid removal. A part of the crushed olives with particle size of 0.5 - 1 mm diameter was impregnated with different rates of $ZnCl_2$ and carbonized under continuous nitrogen flow at 700 °C. The second part was impregnated with different rates of KOH and carbonized under continuous nitrogen flow at 800 °C using a heating rate of 5 $°C.min^{-1}$. After the carbonization temperature was reached the sample was kept for one hour before the furnace was allowed to cool down to room temperature (Fig. 2).



1. Argon
2. Flow meter
3. Quartz tube
4. Olive stones
5. Tubular furnace
6. Temperature regular device
7. Boiler
8. Exterior

Fig. 2: Schematic diagram of the apparatus

3.2 Compound adsorbent preparation

A novel type of modified polyetheretherketone, PEEK WC (8, 10 and 15 wt. %) and 2 % of AC were dissolved in DMF or DMA, at room temperature. The solution was magnetically stirred for at least 1 day to allow a complete dissolution of the polymer. The polymer solution (*phase 1*) was add to the feed tank of the module in the compound adsorbent preparation (Fig. 3). Then, it flowed by means of gravity through the mono-pore film of polyethylene (PE). The droplets formed at PE hole border moved through the dodecane or isooctane (*phase 2*), which induce a spherical shape to the latter. These immediately coagulated by phase inversion when in contact with the non-solvent phase, water/alcohol at different concentration (*phase 3*). The compound adsorbent obtained was re-immersed and stabilised in the water bath for 24 h, and then recovered using a filter paper. The compound adsorbent were then dried over night at room temperature and set in an oven under vacuum for 24 h to remove completely the last traces of the solvent.

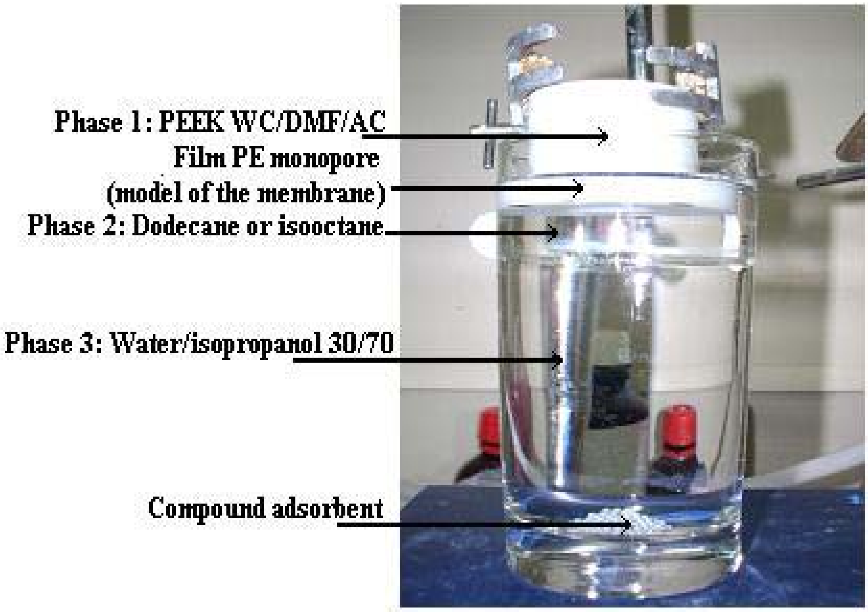


Fig. 3: Picture of the PEEK WC compound absorbent preparation

4. RESULTS AND DISCUSSION

4.1 Sem analysis of the activated carbons

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the olive stone derived activated carbon. Figure 4 shows the SEM photographs of the olive stone before and after the impregnation at the optimum operating condition with 1000× magnification. It can be seen from the micrographs that the external surface of the chemically activated carbon is full of cavities, exhibiting a heterogeneous structure in terms of both size and shape. The reason for the formation of the cavities on the $ZnCl_2$ activated carbon is not clear. According to this micrograph, it seems that the cavities resulted from the evaporation of $ZnCl_2$ during carbonization, leaving the space previously occupied by the $ZnCl_2$. It can also be said that some salt particles are scattered on the surface of the activated carbon, probably due to the presence of remaining zinc chloride or other metal compounds on the activated carbon. Some particles were even trapped into the pores and could possibly block the entry of pores to some extent.

However, the impregnation by KOH shows clearly that it contributes to the development of the intern micro porous cavities having for result a higher specific surface, important factor for adsorption.

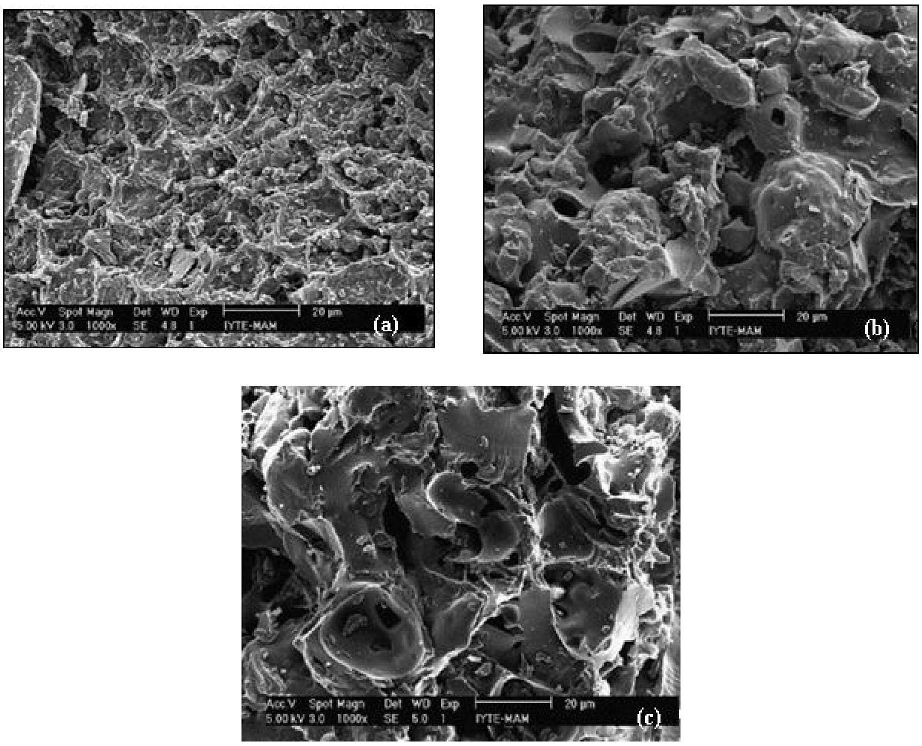


Fig. 4: SEMs of (a) no impregned olive stones, _ (b) olive stones impregned by $ZnCl_2$ (7.35 mmol/g), _ (c) olive stones impregned by KOH (7.35 mmol/g)

4.2 Sem analysis of the compound adsorbent

The SEM pictures of the compound adsorbent, obtained with PEEK WC/DMF 10 wt. %, Activated carbon 2 % are shown in Figure 5. These compounds adsorbents were prepared by using a pore diameter of 550 µm and water/isopropanol (30/70) as non-solvent (*phase 3*). The formation of an O1/O2 emulsion, made by well defined round droplets of PEEK WC/AC/DMF in iso-octane, was accomplished. The droplets in contact with the phase 3, immediately coagulated and formed the final compound adsorbent keeping the spherical shape with a roughness surface (Fig. 5-A). The higher affinity of iso-octane with the polymer/AC solution caused a starting of demixing before coagulating at the non-solvent phase 3 with the formation of a roughness and porous surface. Nevertheless, the capsule cross-section (Fig. 5-B and 5-C) shows a central cavity and an asymmetric structure, finger type support layer with a porous skin at the shell side.

The SEM pictures of the Compound adsorbent, obtained with dodecane, are shown in Figure 6. These compounds were produced by using the same aforementioned. The compounds adsorbents have again a spherical shape but a smooth surface (Fig. 6-A). Moreover, the capsule crossection, as shown in Fig. 6-B and 6-C, present a central cavity and an asymmetric (finger type) structure but with a dense skin layer at the shell side. These results are in good agreement with various studies on the effect on the morphology of asymmetric membranes of the coagulation medium and conditions. The higher alcohols, i.e. iso-propanol, give membranes with a much thicker dense top layer [14]. These studies indicate that the top layer thickness of the membrane, in general, increases with increasing molar volume of the external nonsolvent species due to their lower diffusion rate which leads to delayed liquid – liquid phase demixing.

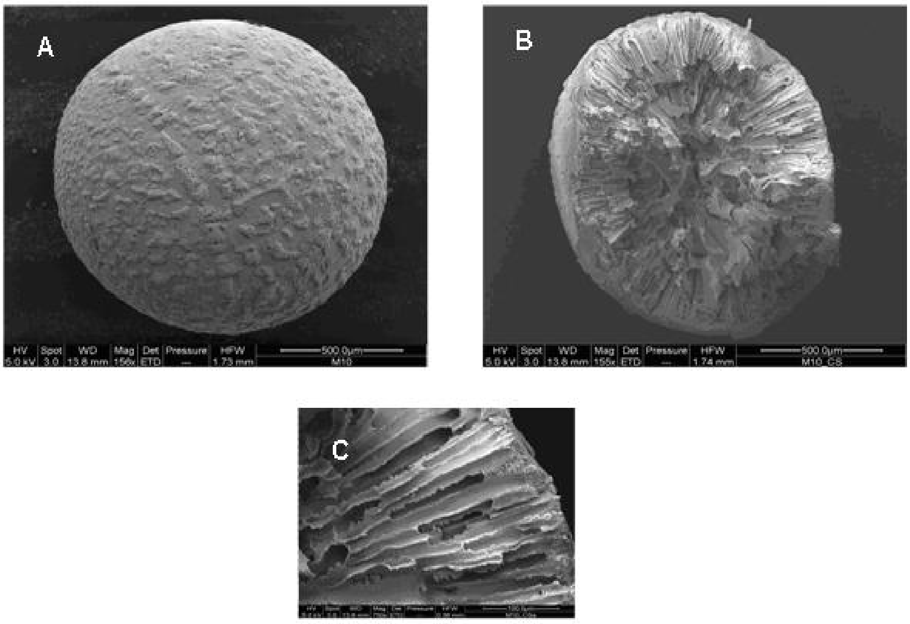


Fig. 5: SEM pictures of the A) surface and B, C) cross-section of the compound adsorbent prepared using a film with the pore size of 550 µm and PEEK WC/DMF 10 wt.%, AC 2% Phase 1, iso-octane, Phase 2, and water:iso-propanol, Phase 3

5. CONCLUSION

The fabrication of PEEK WC/AC Compound adsorbent with different morphologies was successfully developed exploiting the advantages of two well established technologies, such as membrane emulsification and phase inversion. We recommended using our fabricated compound adsorbent in a real solar adsorption refrigeration machine in order to evaluate the real comportment of the process with the new adsorbent.

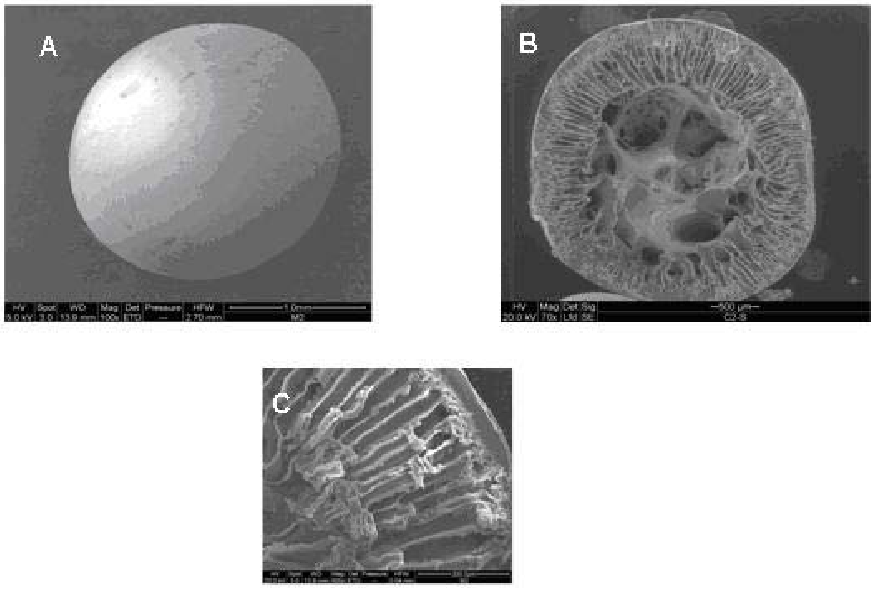


Fig. 6: SEM pictures of the A) Surface and B, C) Cross-section of the compound adsorbent prepared using a film with the pore size of 550 µm and PEEK WC/DMF 10 wt.%, AC 2 % Phase 1, dodecane, Phase 2, and water:iso-propanol, Phase 3

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