

Purification of water by activated carbon prepared from olive stones

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Received 6 February 2007; accepted 13 February 2007

Abstract

High efficiency activated carbon with different chemical characteristics, appropriate for the purification of waste and potable water with different pollutions (metal ions) 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 ZnCl₂ and KOH. The pore structure of the activated carbon was characterized by CO₂ adsorption at 273 K and by N₂ adsorption at 77 K. B.E.T and Dubinin equations were used to deduce the effective surface area. Micro and mesoporosity have been measured by immersion calorimetry. The prepared activated carbon has very large surface area as well as highly developed microporosity. Experimental conditions for the preparation of the active carbon, highly microporous but with well developed mesoporosity, are discussed. Activated carbon prepared from olive stones can be used for Pb²⁺ ions removal from potable water in the presence of other metal ions and found that NaCl will interfere in adsorption. The sample activated by KOH has the highest adsorption capacity followed by ZnCl₂. The high concentration of active sites on the surface of the carbon from olive stones activated by KOH might have facilitated the adsorption of metal ions.

Keywords: Activated carbon; Potable water; Purification; Metal ions

1. Introduction

Activated carbon is extensively used as efficient and versatile adsorbents for purification of water, air and many chemicals and natural products.

The application of high-surface active carbons in gas separation, medicine and catalysis is also well known.

The continuously increasing list of environmental concerns and the interest in utilization of various wastes have awoken the interest for development of new processes for production of

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Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

carbon adsorbents based on agricultural and forest wastes. Activated carbon produced from coconut shells and pine wood wastes has shown good mechanical strength and high adsorption capacities towards various gases. Olive stones and almond shells are also suitable raw materials for activated carbon with high adsorption capacities, sufficient mechanical strength, and low ash contents. The narrow range of the pore size distribution in these carbons makes them suitable for selective gas adsorption [1]. Activated carbon obtained from olive stones and almond shells has high metal ions adsorption capacities [2]. Plum and peach stones have also been used for preparation of activated carbon [3]. 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 properties of activated carbon prepared from olive stones was presented by Iley and Marsh [4]. 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 properties, good adsorptive properties 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 [5]. The starting material and the method of preparation influence the quality of the resulting activated carbon [6].

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. The effect of the treatment conditions and the choice of precursors on the properties of the activated carbon are studied.

The adsorption capacities for metal ions are of particular interest.

2. Experimental

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 1 h before the furnace was allowed to cool down to room temperature (Fig. 1).

Adsorption isotherms were determined using conventional McBain silica spring balances. Nitrogen was adsorbed at 77 K and carbon dioxide at 273 K. Adsorption data was complimented by calorimetric immersion.

The adsorption capacities for lead ion was determined by adding 0.2 g from the samples of activated carbon to 10 cm³ aqueous solutions (1 × 10⁻⁵ M) of the nitrates of the above metals at 298 K and pH 6. Equilibrium concentration of the ion in the solutions was reached after 6 h of contact.

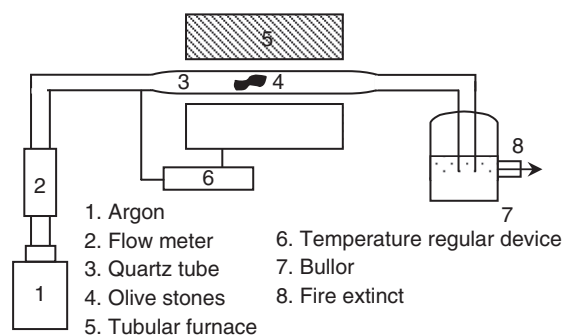


Fig. 1. Schematic diagram of the apparatus.

Table 1
Effects of the impregnation rates on the yield using ZnCl₂ and KOH

Rates (mmol/g OS)	Percentage yield using ZnCl ₂ , % (700°C)	Percentage yield using KOH, % (800°C)
0	37	37
3.67	28.8	32.8
7.35	27.1	24
14.7	26.9	9
22.05	26.1	4.9

3. Results and discussion

3.1. Yield of activated products

The effect of activation parameters such as temperature and the impregnation rates on yield are presented in Table 1. The yield decreases with activation temperature. This can be attributed to the loss of volatile materials when the temperature increases (Table 2). The effect of impregnation rates is more effective for KOH than ZnCl₂.

3.2. Samples characterization

According to Fig. 2, the surface area S_{N_2} increases with the increase of the impregnation rate, however a decrease is noticed for very high rates. This is probably due to a partial collapse of porosity with high impregnation rates.

This closing will be confirmed by the immersion calorimetry.

Table 2
Effects of temperature on yield

Temperature (°C)	Percentage yield (%)
0	39.3
600	37.4
700	37.1
800	37

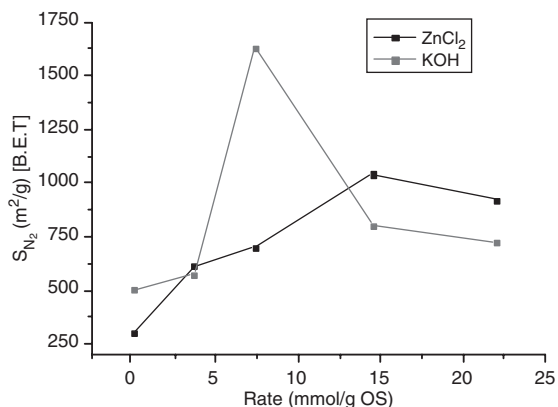


Fig. 2. Surface areas of samples activated with ZnCl₂ (700°C) and KOH (800°C) [BET].

Fig. 3 shows the effect of impregnation rate on the surface area of activated carbons. The surface area increases with the increase of the impregnation rate and reach a maximum value at 14.7. In addition, results show that ZnCl₂ has a positive effect on the development of porous texture at a relatively low pyrolysis temperature. On the other hand, KOH gives high specific area at higher temperature (Table 3).

Results presented in Table 4 show that ZnCl₂ has a positive purpose in developing porous texture at relatively low pyrolysis temperature. On the other hand additive KOH gives high microporous volumes at higher temperature.

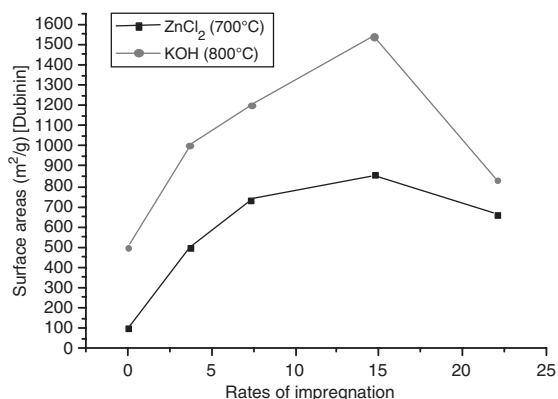


Fig. 3. Surface areas of samples activated with ZnCl₂ (700°C) and KOH (800°C) [Dubinin].

Table 3
Areas S (m^2/g) and micropores volume W_0 (mL/g) of carbonized samples

Impregnated rates (mmol/g OS)	W_0 (mL/g)		S (m^2/g)	
	ZnCl ₂ (700°C)	KOH (800°C)	ZnCl ₂ (700°C)	KOH (800°C)
0	0.039	0.196	100	500
3.67	0.196	0.392	501	1002
7.35	0.288	0.472	735	1203
14.7	0.335	0.604	856	1541
22.05	0.259	0.326	661	831

Initial increase in W_0 is due to volatile matter, whereas its reduction at high impregnated rates is due to a partial collapse of porosity. The mechanism of carbonization of the olive stones in the presence of KOH is probably similar to the mechanism of carbonization of other carbonaceous materials (lignite, residues of oil, coals). It is summarized in

- A dispersion of KOH in material at low temperature lead in forming complex surfaces;
- A later activation by the excess of additive.

On the other hand, the mechanism of carbonization of the olive stones in the presence of ZnCl₂ is not well known. However Smisek and Cerny [7] think that this additive degrades materials. This is due to the degradation of the cellulose compound and the dehydration of material during carbonization; it results an aromatization of the carbonaceous skeleton. The fundamental difference resides in the activation which is a decisive stage in the creation of the pores.

BET equation has been used to determine the surface area of activated carbon from nitrogen adsorption isotherms measured at 77 K. It is agreed that N₂ adsorption at 77 K does not measure the total surface area of activated carbon for two reasons.

First, due to the activated diffusion limitations, N₂ molecules at 77 K do not have enough kinetic energy to penetrate into the micropores. Thus, long periods are required to reach the equilibrium. Secondly, the micropores undergo some decrease in their size at low temperatures. On the other hand, in some cases, the CO₂ areas greatly exceed those determined from N₂ adsorption at 77 K. This is due to the minimum dimension of CO₂ molecules which are smaller than N₂ molecules. In addition, the kinetic energy of CO₂ molecules at the used adsorption temperatures exceeds the N₂ molecules at 77 K. Consequently, the rate of diffusion of CO₂ into the activated carbon micropores will be significantly higher than the N₂ one.

Table 4
Areas S (m^2/g) and micropores volume of carbonized samples

Temperature (°C)	Olives stones (OS)		7.35 mmol ZnCl ₂ /g OS		7.35 mmol KOH/g OS	
	W_0 (mL/g)	S (m^2/g)	W_0 (mL/g)	S (m^2/g)	W_0 (mL/g)	S (m^2/g)
600	0.036	92	0.214	545	0.241	614
700	0.039	100	0.288	735	0.360	918
800	0.196	500	0.268	683	0.472	1203

Table 5
Enthalpy of immersion in benzene ($\phi = 0.41$ nm)

Rate (mmol/g OS)	W_0 (mL/g)		$-\Delta H_{\text{theo}}$ (J/g)		$-\Delta H_{\text{exp}}$ (J/g)		$(W/W_0) \cdot 10^2$ (%)	
	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH
0	0.039	0.196	34.3	146.7	1	2	2.9	1.35
3.67	0.196	0.392	114.5	226.2	79	65	69	28.7
7.35	0.288	0.472	170.5	271.9	83	97	48.7	35.6
14.7	0.335	0.604	194.8	346.1	90	106	46.2	30.6
22.05	0.259	0.326	152.9	191.4	78	73	51	38.2

In this study, we have proposed to add the characterization by the determination of the distribution of microporosity by calorimetry immersion of the samples; successively for non-impregnated and impregnated with various rates of ZnCl₂ pyrolyzed at 700°C and KOH at 800°C with 1 h of stage under inert gas current. The ratio W/W_0 represents the micropores volume fraction reaches by each used liquid of molecular diameter (ϕ).

3.3. Maxwell's distribution of the micropores

We proposed to determine the distribution of microporosity by immersion calorimetry method. The function of Maxwell distribution can be written in the following form:

$$\frac{dW}{d\phi} = -2W_0C(\phi - L_m)\exp[-C(\phi - L_m)^2] \quad (1)$$

Table 6
Enthalpy of immersion in cyclo C₆H₁₂ ($\phi = 0.54$ nm)

Rates (mmol/g OS)	W_0 (mL/g)		$-\Delta H_{\text{theo}}$ (J/g)		$-\Delta H_{\text{exp}}$ (J/g)		$(W/W_0) \cdot 10^2$ (%)	
	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH
0	0.039	0.196	28.2	121.6	0	0	0	0
3.67	0.196	0.392	94.6	179.4	62	10	65.5	5.6
7.35	0.288	0.472	135.2	215.5	61	65	45.1	30.1
14.7	0.335	0.604	154.5	274.4	73	69	47.2	25.1
22.05	0.259	0.326	121.2	151.7	52	49	42.9	32.3

$$W = \int_{\phi}^{\infty} dW = W_0 \exp[-C(\phi - L_m)^2] \quad (2)$$

where C is a constant determined graphically from the Eq. (1) (standardized) and W_0 is the micropores volume which corresponds to the interval $[L_m, \infty]$. L_m is the maximum opening of the pores, in our case $L_m = 0.28$ nm.

Values presented in Tables 5–8 and the histogram of Fig. 4(a), show that a strong proportion of the micropores has a diameter ranging between 0.54 and 0.63 nm for the sample impregnated by 7.37 mmol/g of ZnCl₂ per gram of olive stones. However, for an impregnation rate of 14.7 mmol/g, represented in Fig. 4(b), the micropores have a diameter between 0.41 and 0.8 nm. The Fig. 4(c) which represents an impregnation rate of 22.05 mmol/g of ZnCl₂ shows that a strong proportion of micropores has a diameter

Table 7
Enthalpy of immersion in CCl_4 ($\phi = 0.63$ nm)

Rates (mmol/g OS)	W_0 (mL/g)		$-\Delta H_{\text{theo}}$ (J/g)		$-\Delta H_{\text{exp}}$ (J/g)		$(W/W_0) \cdot 10^2$ (%)	
	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH
0	0.039	0.196	34.5	148.7	0	0	0	0
3.67	0.196	0.392	115.7	218	65	11	56.2	5.04
7.35	0.288	0.472	164.2	261.9	64	52	38.9	9.2
14.7	0.335	0.604	187.7	333.4	72	62	38.3	18.6
22.05	0.259	0.326	138.7	184.4	54	13	38.9	7.05

ranging between 0.41 and 0.63 nm. There is a contracting of the pores thus formation of very fine pores.

Histograms of Fig. 4(d–g) show that for a KOH rate of 3.67 mmol/g, the pores are very small. Indeed, these pores are accessible only partially to the smallest molecule (benzene). However, for a KOH rate of 7.35 mmol/g, the pores are relatively small but slightly larger than those impregnated by 3.67 mmol/g. For a rate of 14.7 mmol/g, there are small pores but even larger than the previous ones. Finally for a rate of 22.05 mmol/g the pores are narrower than those of the rate of 14.7 mmol/g.

We can say that the olive stones treated by ZnCl₂ or by KOH are characterized by micropores. In addition, the treatment by KOH involves the formation of a proportion of mesopores.

3.4. Effect of interference

Activated carbon may be used for purification of drinking and waste waters, in which the content of metal ions often exceeds the admissible sanitary standards. Table 9 shows the adsorption capacities of the samples of activated carbon from olive stones.

The sample activated by KOH has the highest adsorption capacity, followed by the sample activated by ZnCl₂ (Table 9). The high concentration of active sites on the surface of the carbon from olive stones activated by KOH may facilitate the adsorption of metal ions. In spite of the largest surface area of the carbon activated by ZnCl₂ (856 m²/g, Table 3) its adsorption capacity is not the highest because of the predominant presence of micropores with small diameters which are difficult to penetrate for the hydrated metal ions.

Table 8
Enthalpy of immersion in α -pinene ($\phi = 0.80$ nm)

Rates (mmol/g OS)	W_0 (mL/g)		$-\Delta H_{\text{theo}}$ (J/g)		$-\Delta H_{\text{exp}}$ (J/g)		$(W/W_0) \cdot 10^2$ (%)	
	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH	ZnCl ₂	KOH
0	0.039	0.196	32.5	140	0	0	0	0
3.67	0.196	0.392	109	205.4	55	7	50.4	3.4
7.35	0.288	0.472	154.7	246.8	54	23	34.9	9.3
14.7	0.335	0.604	177	314.2	65	48	36.7	15.3
22.05	0.259	0.326	138.8	173.7	53	9	38.2	5.2

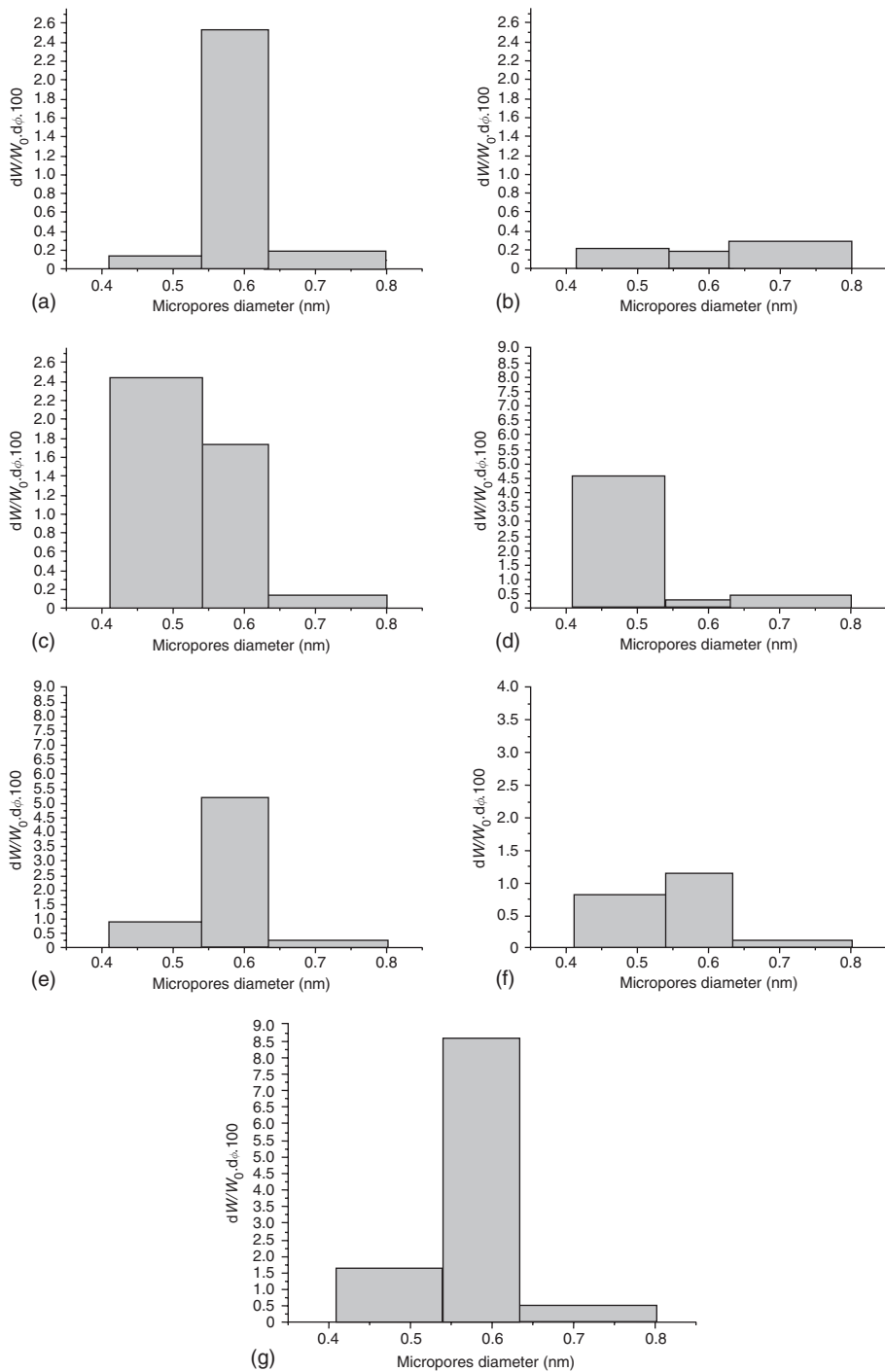


Fig. 4. Standardized Maxwellian distribution of olive stones impregnated by (a) 7.35 mmol of ZnCl₂; (b) 14.7 mmol of ZnCl₂; (c) 22.05 mmol of ZnCl₂; (d) 3.67 mmol of KOH; (e) 7.35 mmol of KOH; (f) 14.7 mmol of KOH and (g) 22.05 mmol of KOH.

Table 9

Variation of adsorption of lead ions with time for samples activated by KOH and ZnCl₂

<i>t</i> (h)	<i>A</i> (%)	
	<i>N</i> _{KOH}	<i>N</i> _{ZnCl₂}
2	52	26
4	90	26
6	100	34
24	100	48
48	100	48

Selection of activated carbon as adsorbent for removal of metal ions from water requires knowledge of both the properties of the activated carbon and the ions, which have to be adsorbed. The results depend on various factors with the most significant are ionic radius, ionic potential q/r (q – ionic charge; r – ionic radius), chemical properties, and the hydration. Activated carbon obtained by steam pyrolysis of olive stones is suitable for removing lead ions from water. However, the presence of several ions in the solution decreases the adsorption of lead (Table 10). In spite of the selective adsorption of the metal ions by the activated carbon, the preferentially adsorbed ions do not hinder the adsorption of other ions.

It is also noticed that the addition of NaCl concentrated at 0.15 M, strongly reduce the adsorption of lead. However, for low concentrations, the salt does not have any influence. It is deduced that activated carbon prepared from olive stones can be used to treat desalinated seawater.

Table 10

Variation of adsorption of lead ions with activated olive stones impregnated by 14.7 mmol of KOH

M	Co	Mg	Zn	Sr	Cu	Ba	NaCl
<i>A</i> (%)	52	100	44	44	16	100	4

4. Conclusion

The aim of this work was the preparation of activated carbon from olive stones, treated consecutively by ZnCl₂ and KOH, to purify water. The first step towards the design of an efficient and economical treatment was to study the influence of the temperature of carbonization. We found an optimum of 700°C for the samples treated by ZnCl₂ volumes of the micropores. On the other hand, the samples treated by KOH volumes of the micropores are proportional to temperature and reach a maximum at 800°C. The second step was to study the influence of the rates of additives on the development of the porous texture. We noticed that the surface area of the porous texture increases with the rates of additives up to the value of 14.7 mmol/g. The samples treated by KOH lead to a texture more developed than those treated by ZnCl₂ with a relatively lower temperature. The results obtained by immersion calorimetry technique show that the porous texture of the samples impregnated by ZnCl₂ and pyrolyzed at 700°C are very fine. In addition, the KOH causes the enlargement of the pores. Distribution size of the micropores could be determined by the same technique. The activated carbon prepared in our laboratory from olive stones proved to be very effective in the treatment of polluted water. Indeed, the activated carbon treated by KOH is an excellent decontaminant of polluted water by lead even in presence of other cations.

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