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Fuel Processing Technology 57 (1998) 55–64

FUEL PROCESSING TECHNOLOGY

# Activation of olive-seed waste residue using $CO_2$ in a fluidized-bed reactor

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Received 17 November 1997; revised 13 May 1998; accepted 13 May 1998

**Abstract**

Physical activation of olive-seed waste residue was carried out under $N_2/CO_2$ atmosphere in a fluidized-bed reactor system. The effects of activation temperature, activation time and particle size on both yield and quality of the prepared products were studied. The quality was measured in terms of iodine number and adsorptive capacity towards methylene blue dye. In general, it was found that higher activation temperature, longer activation time and smaller particle size produced a higher quality activated carbon. The products were compared to a commercial grade activated carbon prepared by steam activation process. Samples of 0.71–0.85 mm particle size activated at 900°C and activation time greater than 60 min were superior to the commercial carbon. Similar results were obtained for similar samples activated at 800°C and activation times greater than 60 min. A kinetic model was applied to the data. A first order reaction kinetics was found to fit the experimental data well. The value of the rate constant for activation was found to be 0.65 $s^{-1}$.


*Keywords:* Olive seed; Carbon dioxide; Fluidized-bed reactor

## 1. Introduction

Activated carbon is used widely in adsorption processes. It is produced from natural carbonaceous materials such as coal and agricultural wastes [1,2]. Olive-seed waste residue is a by-product of the olive oil processing industry. It is an inexpensive material, which is available at large quantities and can be considered as a precursor of activated

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0378-3820/98/$19.00 
*PII* S0378-3820(98)00070-8

carbon. The activation process involves carbonization or calcination of the raw material at elevated temperatures (500–900°C) in an inert atmosphere. Many of the non-carbon elements, mainly, volatiles are removed during this process. The residue is a porous char. The porosity of the char can be increased, significantly, by physical activation process, which follows carbonization. Physical activation is the mild oxidation (gasification) of the substance with steam, carbon dioxide or air at high temperatures (800–1000°C). A simultaneous carbonization and activation can be obtained chemically by impregnation with dehydrating agents such as phosphoric acid and zinc chloride [3–5]. The adsorptive properties of activated carbon vary with the source materials and activation process [6,7].

Different types of reactors are used for activation. It was reported that fluidized-bed process was thought to yield a uniformly treated product due to the efficient heat and mass transfer which minimizes temperature variations and ensures good mixing [3,8]. It is also believed that physical activation by $CO_2$ is more easily controlled than chemical activation due to the endothermic nature of the reaction pathways [9,10]. Thus it is easier to control the porosity development by varying the experimental conditions.

The objective of this paper was to investigate the possibility of preparing acceptable activated carbon from olive-seed waste residue by physical activation with carbon dioxide in a fluidized-bed reactor. The effects of various preparation variables were studied and a comparison with a commercially available activated carbon was made.

## 2. Experimental

Olive seeds waste residue was used in this study. It consists from crushed hard seeds and soft pulp. The waste was immersed in water for a minimum of 2 h in order to remove the soft pulp. By using vigorous agitation, the soft pulp particulates float on the surface allowing easy separation by decanting. The remaining hard fragments of the seeds were dried in an oven at 105°C. Then crushed and sieved to the desired particle size. The resultant sieve cut was then soaked in chloroform overnight to extract its oils, then dried and used in the experiment.

Fig. 1 shows the experimental setup used for carbonization and activation of the materials. Briefly, it consisted of a fluidized-bed reactor inserted inside the heating element of a vertical electrically-heated furnace. The reactor was constructed from carbon-steel pipe of dimensions 4.6 cm inside diameter, 4.9 cm outside diameter and 108 cm length. The reactor was preheated to the desired temperature. A total of 100 g of solids with a particle size of 0.71–0.85 mm was used in each experiment, which corresponds to 10 cm fixed bed height. Experiments were conducted in two stages; the first stage was carbonization of the sample under an inert atmosphere using nitrogen, activation with carbon dioxide was followed. More details are found elsewhere [11].

All samples produced by carbonization or activation processes were characterized by their adsorptive capacities. They were tested by color removal towards methylene blue dye, which is soluble in water. Iodine number tests were also conducted to characterize the produced chars. Results were compared with those of grade YA01/30 activated

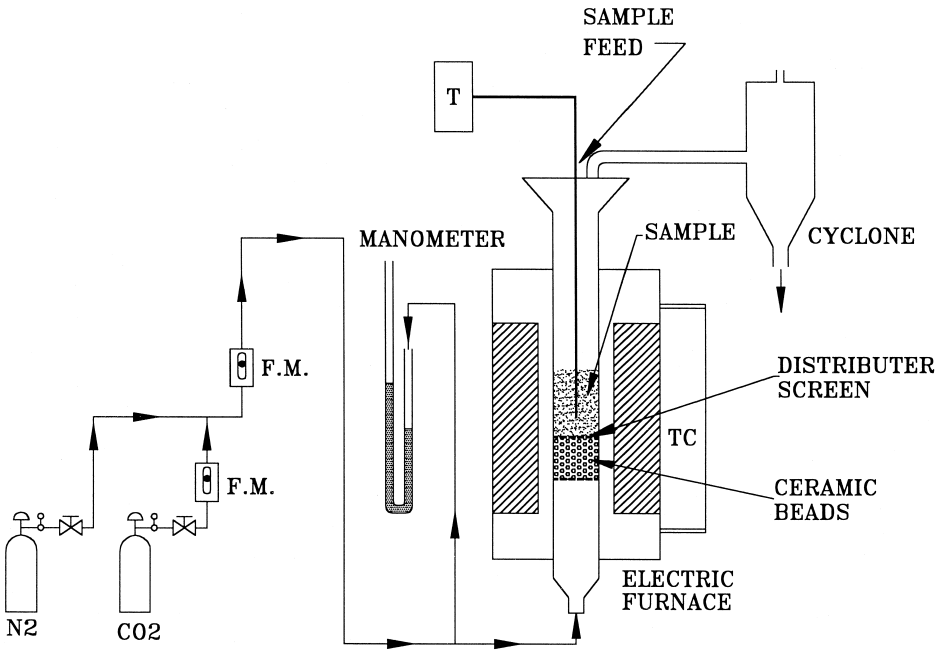


Fig. 1. Schematic diagram of the apparatus.

carbon obtained by steam activation process from Haycarb, Srilanka and used in water treatment.

## 3. Results and discussion

### *3.1. Effect of carbonization temperature and time*

Fig. 2 illustrates the effect of carbonization temperature and time on the weight loss was studied. Carbonization time was varied from 15 to 60 min. The weight loss did not change appreciably with time. The weight loss was $82 \pm 3\%$ at 700°C, $77 \pm 1\%$ at 600°C and $74 \pm 1\%$ at 500°C for the period 15–60 min. This means that after the volatile matter has been removed in the first 15 min of the carbonization experiment, no further volatilization takes place. Therefore, it was chosen to carbonize the olive residue for 30 min prior to activation. It is evident from the results that weight loss increases with increasing temperature. The adsorptive capacity and the iodine number of the char were very low and is similar to the results obtained for raw waste.

### *3.2. Effect of activation temperature*

The effect of activation temperature on burn-off is shown in Fig. 3. Burn-off increases with increasing temperature, especially those above 700°C. At temperatures below 700°C burn-off is negligible (lower than 10%).

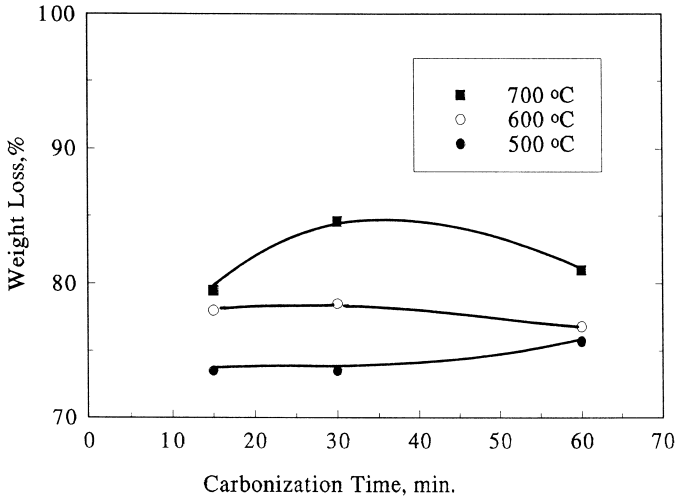


Fig. 2. Effect of carbonization temperature and time on weight loss for particle size 710–850 μm.

The effect of activation temperature on adsorptive capacity is presented in Fig. 4. Data were also compared to those of a commercially activated carbon. Materials which were activated at 900°C showed high adsorptive capacity. It was even higher than of a commercial grade activated carbon. Generally adsorptive capacities increase with increasing temperature. They had low values at activation temperatures below 700°C. The activation period was 60 min for all the runs presented in Figs. 3 and 4.

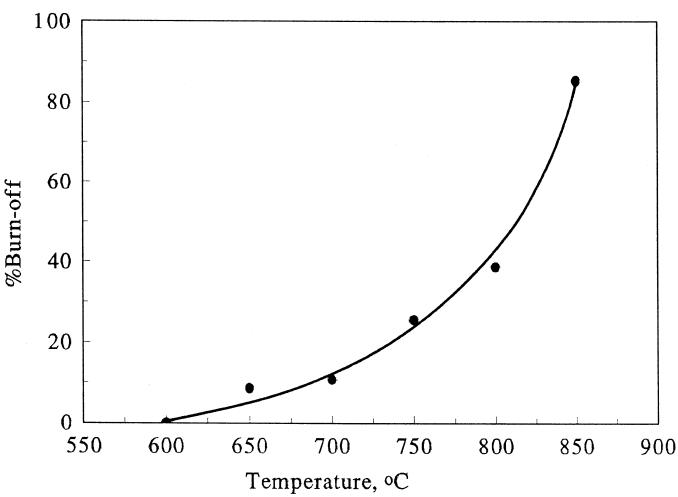


Fig. 3. Effect of activation temperature on percent burn-off for particle size 710–850 μm and activation time 60 min.

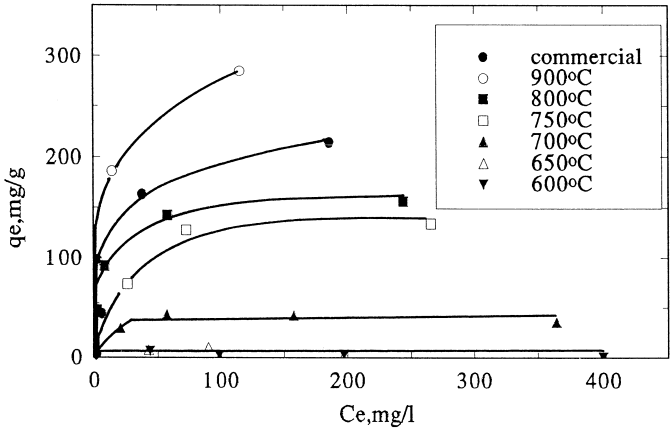


Fig. 4. Effect of activation temperature on adsorption capacity.

Iodine number tests, which can also be considered a measures of adsorption quality, were conducted. Fig. 5 illustrates the effect of activation temperature on iodine number. It increases with increasing activation temperature. At temperatures above 800°C iodine number was substantial. It was even higher than that of the commercial activated carbon. For example, iodine number of the commercial activated carbon was about 214, while that of the activated carbon prepared at 900°C was about 390; an enhancement of 82%.

### *3.3. Effect of activation time*

The burn-off results of activation at 800°C as a function of time are presented in Fig. 6. As expected, burn-off increases with increasing time, and it is evident that during activation, the reaction proceeds with an almost linear weight loss. Adsorption capacities

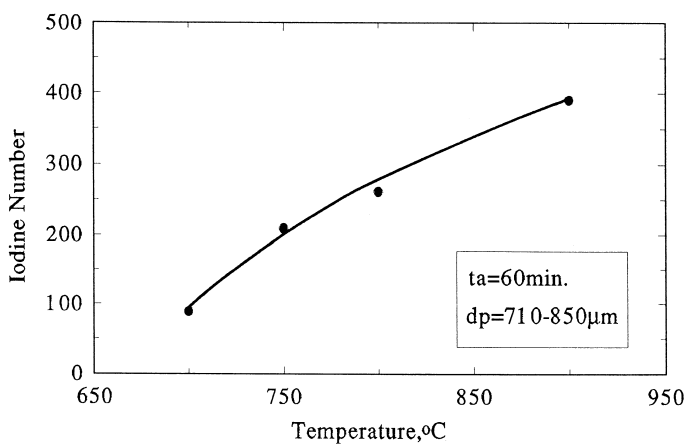


Fig. 5. Effect of activation temperature on iodine number.

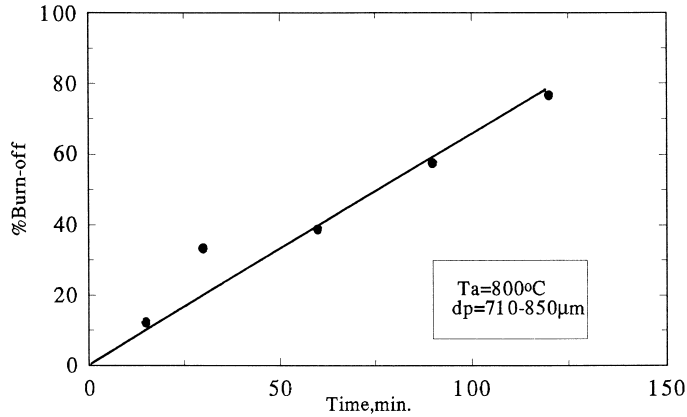


Fig. 6. Effect of activation time on percent burn-off of char.

for prepared samples were also determined. They are presented in Fig. 7. An increase in adsorption capacity was obtained with increasing the time of activation.

Iodine number increases with increasing time, as presented in Fig. 8. Samples obtained at and above 60 min of activation time, showed substantial increase in iodine number. It was even higher than that of the commercial product. This result agrees with the result on adsorptive capacities towards methylene blue dye.

### *3.4. Effect of particle size*

The effect of particle size on overall weight losses were studied. The activation temperature and time were 800°C and 60 min respectively. Fig. 9 shows that the trend is

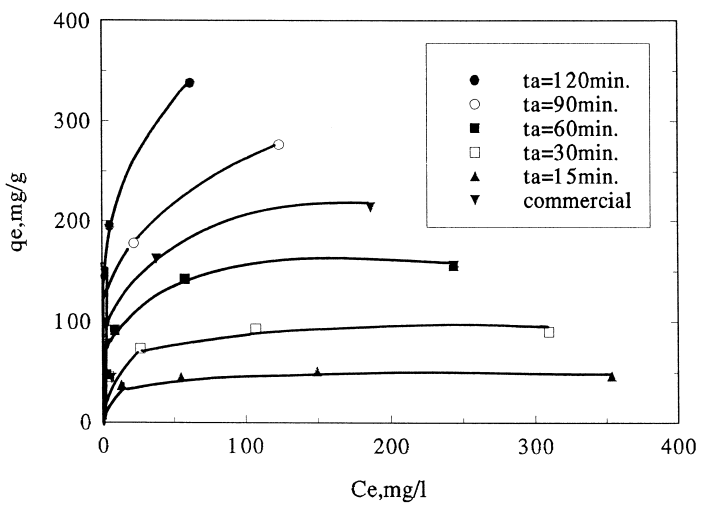


Fig. 7. Effect of activation time on adsorptive capacity for $d_p$ = 710–850 μm and temperature 800°C.

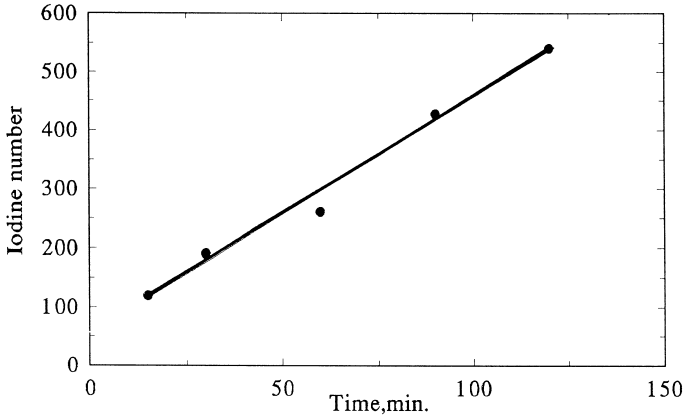


Fig. 8. Effect of activation time on iodine number for $d_p$ = 710–850 μm and temperature 800°C.

slightly decreasing for overall burn-off as particle size increases. Adsorption isotherms for these samples were obtained. They are presented in Fig. 10, and compared to the commercial product. The results show improvement of activation quality with decreasing particle size. The products with an average diameter of 0.587 and 0.415 mm show adsorptive capacity higher than that of the commercial product.

The effect of particle size on iodine number of the produced activated carbon is shown in Fig. 11. Iodine number decreases with increasing particle size. These results are consistent with the results obtained from adsorption isotherms.

### *3.5. Activation kinetics*

The activation process is a complicated process. It involves burn-off of the disorganized carbon followed by non-uniform burning-out of the crystallites which leads to the

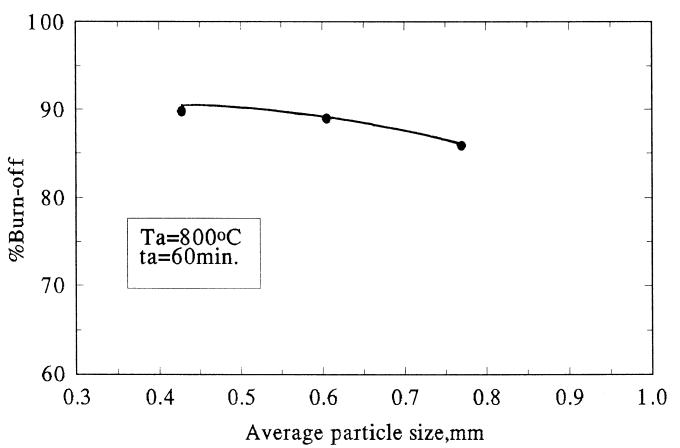


Fig. 9. Effect of particle size on percent burn-off for activation stage.

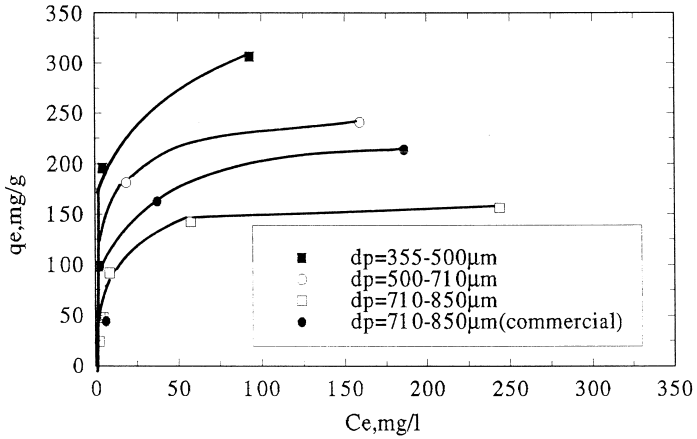


Fig. 10. Effect of particle size on adsorptive capacity at $T_a = 800°C$ and $t_a = 60$ min.

formation of new pores. In the subsequent phases, the widening of existing pores becomes more significant due to complete burn-out of walls between adjacent micropores. The overall reaction could be presented by:

$$\text{Char} \xrightarrow{k} \text{Activated Carbon}$$

The lumped analysis method was used in order to determine the reaction rate constant *k*. This method of lumped analysis was used by others [12–14]. The method is simple and gives an overall reaction rate constant which could be used for the process design.

In order to establish kinetic data for the activation olive-seed residue, experiments were conducted at 800°C for particle size 710–850 μm at various times. The continuous reaction model with zero, first, and second order reaction rates has been applied to the

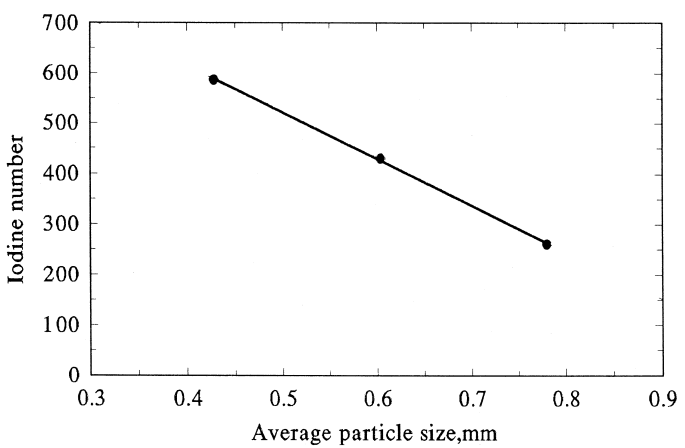


Fig. 11. Effect of particle size on iodine number for activation at 800°C and 60 min.

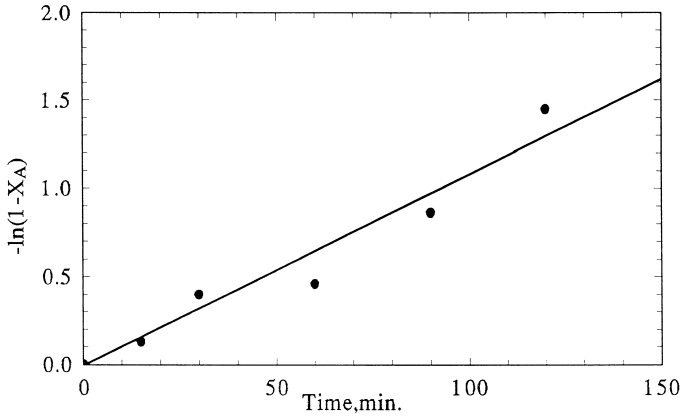


Fig. 12. Plot of $-\ln(1-X_A)$ vs. time for activation of olive-seed residue of $d_p = 710–850$ μm at 800°C.

experimental data. The first order reaction kinetics were found to fit the data best. Fig. 12 shows a plot of $-\ln(1-X_A)$ vs. time, $t$, where $X_A$ is the fractional burn-off. A straight line that passes through the origin with a slope (which represents $k$) equals to 0.65 $s^{-1}$ was obtained.

## 4. Conclusions

An approach has been taken to produce activated carbon successfully from olive-seed waste residue. Based on adsorptive capacities toward methylene blue dye and iodine numbers, it was shown that an acceptable activated carbon can be produced from such materials. The prepared activated carbon from olive-seed waste residue compares well to a commercially available activated carbon prepared by steam activation. The best conditions for activation were using particle size of 0.71–0.85 mm at 800°C and an activation time of 90 min. The first order reaction kinetics were found to fit the data best with a rate constant of 0.65 $s^{-1}$.

## 5. Nomenclature

| | |
|---|---|
| $C_e$ | Equilibrium dye concentration in the solution (kg/$m^3$) |
| $d_p$ | Solid particle diameter (m) |
| $k$ | First order rate constant ($s^{-1}$) |
| $q_e$ | Equilibrium dye concentration on the solid (kg dye/kg solid) |
| $t_a$ | Activation time (min) |
| $t_c$ | Carbonization time (min) |
| $T_a$ | Activation temperature (°C) |
| $T_c$ | Carbonization temperature (°C) |
| $X_A$ | Fractional burn-off |

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