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Salt-Catalyzed Activation of Olive-Seed Waste Residue Using Fluidized-Bed Reactor

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Activation of olive-seed waste residue was carried out under nitrogen atmosphere in a fluidized-bed reactor system. Initially, the starting materials were impregnated with two different salts. The salts were zinc chloride ($ZnCl_2$) and potassium chloride (KCl). The effects of some process variables on both yield and quality of the prepared products were studied. Adsorption quality was measured in terms of adsorptive capacity towards methylene blue dye and iodine number. The effects of impregnation ratio, activation temperature, time, and particle size on adsorption quality were investigated. In general, it was found that $ZnCl_2$ was more effective than KCl. Overall, higher activation temperature, longer activation time and smaller particle size produced a higher quality activated carbon. The produced materials were compared to a physically prepared activated carbon. They were comparable and found to be more superior.

Keywords chemical activation, fluidized-bed, olive-seed waste

Nearly all-inexpensive carbonaceous materials can be considered as starting materials for the production of activated carbon (Hassler, 1974; Munoz-Guillena et al., 1992). The starting material and the method of preparation influence the quality of the resulting activated carbon (Akash and O'Brien, 1996; Hippo et al., 1991; Neely and Isacoff, 1982; Rivera-Utrilla et al., 1991; Teng and Wang, 2000; Yun et al., 2001). Regardless of the end product, processes used for activation are divided into:

1. Chemical activation process; a process that depends upon the action of the inorganic chemical compounds either naturally present or added to the raw material to degrade the organic molecules during carbonization or calcination.

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2. Physical activation process; a process that depends upon selective oxidation of the carbonaceous matter with steam, air, or carbon dioxide.
3. Combined (chemical-physical) activation process; a process in which chemical activation is followed by physical (steam of CO_2) activation.

It should be noted that chemical activation is applied directly to the raw material, while for physical activation, preliminary carbonization is required. A simultaneous carbonization and activation can be obtained chemically by impregnation with dehydrating agents such as phosphoric acid and zinc chloride (Caturla et al., 1991; Edwards et al., 1993; Gierak et al., 1994; Girgis and El-Hendawy, 2002; Kirubakaran et al., 1991; Moreno-Castilla et al., 2001).

Olive-seed waste residue is a by-product of the olive oil processing industry. It is an inexpensive material that is available in large quantities and can be considered as a precursor of activated carbon (Al-Khalid et al., 1998; Baçaoui et al., 2002; Baçaoui et al., 2001; Galiatsatou et al., 2002; Lafi, 2001; Rodríguez-Valero et al., 2001). The objective of this article is to investigate the possibility of preparing acceptable activated carbon from olive-seed waste residue by chemical activation in a fluidized-bed reactor. It was reported that fluidized-bed process is thought to yield a uniformly treated product due to the efficient heat and mass transfer, which minimizes temperature variations and ensures good mixing (Edwards et al., 1993; Kirubakaran et al., 1991). The effects of various preparation variables were studied and comparisons with the results of previous study on physical activation of the same starting material were made (Al-Khalid et al., 1998).

Experimental

Olive seeds expression residue was used in this study. Initially it was immersed in water for a minimum of 2 hours in order to decompose pulp aggregates. By using vigorous agitation, the soft pulp particulates float on the surface allowing easy separation by decanting. Continuing the processes of washing, agitating and decanting, only the remaining hard fragments of the seeds were used in the experiment. Products were dried in an oven at 105°C. They were crushed and sieved to the desired particle size. The resultant sieve cut was then soaked in chloroform overnight to extract its oils. With an average of 100 g of specified particle size, it was mixed with 600-mL solution of distilled water and reagent. The reagents used are $ZnCl_2$ and KCl. The mixture was shaken for homogenization for about 7 h at 85°C. Impregnation ratios (weight of activating agent/weight of seeds) of 0.2 to 1.4 were used, heating until complete evaporation followed it. The remaining solids were then washed with distilled water and filtered. The filtrate was analyzed to determine the amount of reagent retained within the particles using atomic absorption. The particles were then dried in an oven before they were used as starting materials.

Figure 1 shows the experimental setup used for activation of the materials. Briefly, it consisted of an electrically heated furnace, mounted vertically and the fluidized-bed section was inserted through the furnace-heating unit. 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 furnace was preheated to the desired temperature. 100 g of solids with a particle size of 0.71–0.85 mm was used in all experiments, which corresponds to 10 cm fixed bed height. Experiments were conducted in single stage using nitrogen to provide inert atmospheres. More details are found elsewhere (Al-Khalid, 1995; Qasem, 1997).

All samples produced by activation processes were characterized by their adsorptive capacities. They were tested by color removal towards methylene blue dye, which is

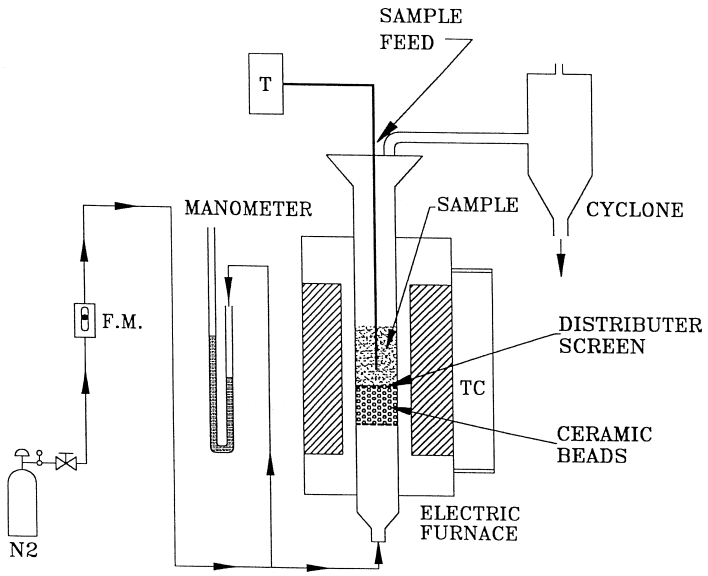

Figure 1. Schematic diagram of the apparatus.

soluble in water. Iodine number tests were also conducted to characterize the produced chars. Results were compared with those obtained using chars prepared by physical activation.

Results and Discussion

Yield of Activated Products

Yield is defined as the amount of activated carbon produced for a given amount of raw starting materials. Table 1 shows the effect of time on yield. It decreases with time for all cases when zinc-chloride and potassium chloride were used, as well as for physical activation. It is due to the effect of loss of volatiles of the materials. Overall, $ZnCl_2$ gives higher yield than KCl and physically activated materials. Also, Table 1 shows the effect of average particle diameter on yield. It increases with increasing diameter for $ZnCl_2$, KCl and physical activation. This is due to increase in exposure surface area resulting from smaller particle size, and therefore an increase in escape of volatile matter.

The effect of activation parameters such as temperature and impregnation ratio on yield are also presented in Table 1. Yield decreases with activation temperature. This can be attributed to loss of volatile materials upon increasing temperature. Yield increases sharply impregnation ratio to a value of up to 0.6 and then it begins to level off for both reagents used in this study. The effect of impregnation ratio is more effective for $ZnCl_2$ than KCl.

Adsorptive Capacity

The effect of activation time on adsorptive capacity of the prepared activated products is presented in Figure 2 for both salts: $ZnCl_2$ and KCl. It increases with activation time

Table 1
Effects of activation time, particle size, temperature, and impregnation ratio on yield using zinc and potassium chlorides as compared to physical activation

Activation time, min	Activation temperature, °C	Impregnation ratio	Average particle diameter, microns	Percentage yield using $ZnCl_2$, %	Percentage yield using KCl, %	Percentage yield using physical activation[a], %
15	800	0.4	0.775	45.4	33.4	20.2
30	800	0.4	0.775	40.1	31.5	15.4
60	800	0.4	0.775	37.3	27.6	14.1
90	800	0.4	0.775	34.8	25.3	9.8
120	800	0.4	0.775	32.1	19.7	5.4
60	400	0.4	0.775	50.1	38.1	—
60	500	0.4	0.775	48.1	31.2	—
60	600	0.4	0.775	45.1	29.5	23.1
60	650	0.4	0.775	43.2	28.1	21.0
60	700	0.4	0.775	42.0	27.1	20.5
60	750	—	—	—	—	17.1
60	800	0.4	0.775	37.3	27.6	14.1
60	800	0.2	0.775	25.1	20.7	—
60	800	0.4	0.775	37.3	27.6	—
60	800	0.6	0.775	43.1	30.2	—
60	800	0.8	0.775	41.5	29.3	—
60	800	1.0	0.775	40.6	31.6	—
60	800	1.2	0.775	41.4	32.7	—
60	800	1.4	0.775	0.7	32.2	—
60	800	0.4	0.428	27.8	22.1	10.2
60	800	0.4	0.605	31.5	25.2	11.8
60	800	0.4	0.775	37.3	27.6	14.6

[a] *Source*: Al-Khalid et al., 1998.

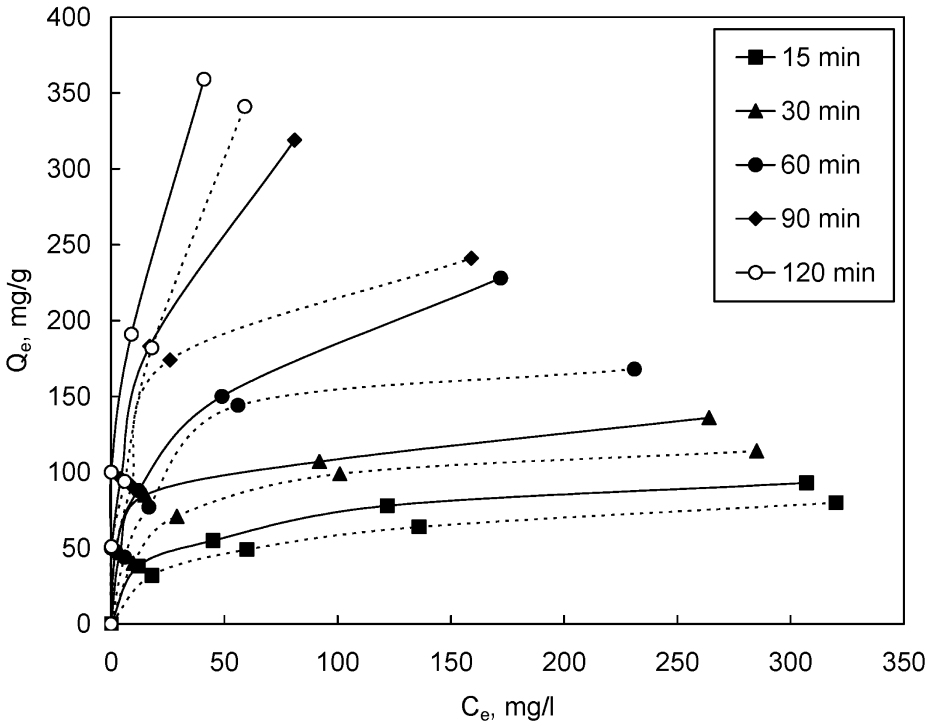

Figure 2. Effect of activation time on adsorptive capacity of methylene blue dye on activated product.

for both reagents. However, $ZnCl_2$ shows higher adsorptive capacities than activation with KCl.

Figure 3 shows the effect of particle size on adsorptive capacity. It increases with decreasing average particle diameter, due to the increase in the exposed surface area of particles to be activated. The effect of activation temperature on adsorptive capacity is presented in Figure 4. As expected, it increases with temperature.

Figure 5 presents the effect of impregnation ratio on adsorptive capacity of the activated products. It was found that adsorptive capacity increases with impregnation ratio due to increase in the amount of reagent adsorbed by the raw materials, which lead to a better-activated product. Again, the adsorptive capacity when $ZnCl_2$ was used was higher than that obtained using KCl.

Iodine Number

Iodine number increases with activation time as shown in Figure 6. Materials treated with $ZnCl_2$ show better activation than those treated with KCl. Chemical activation iodine number was higher than physical activation. The effect of particle size on iodine number is presented in Figure 7. It decreases with increasing average particle diameter, and was better for $ZnCl_2$ than KCl. A particle average diameter range of 355 to 500 μm was best.

Iodine number increases with activation temperature. The result is shown in Figure 8 by which it was higher for $ZnCl_2$ than KCl. The effect of impregnation ratio on iodine number is presented in Figure 9. It increases with impregnation ratio due to higher

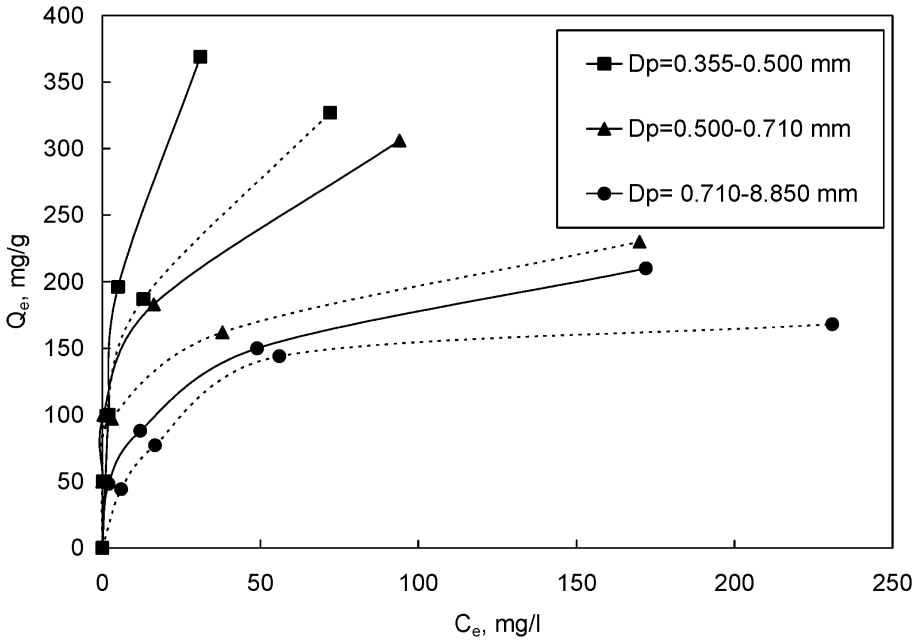

Figure 3. Effect of particle size on adsorptive capacity of methylene blue dye on activated product.

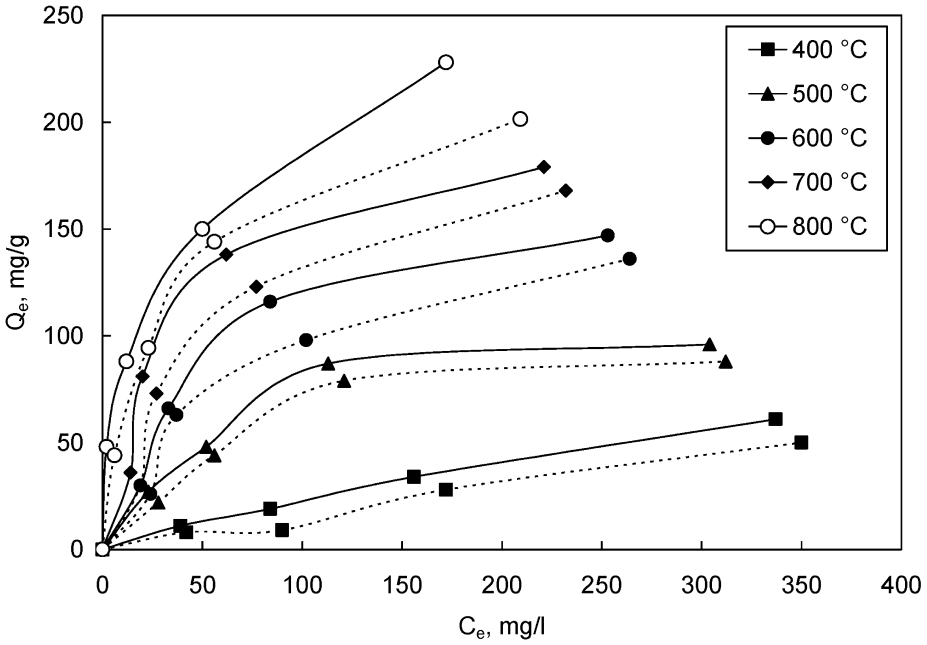

Figure 4. Effect of activation temperature on adsorptive capacity of methylene blue dye on activated product.

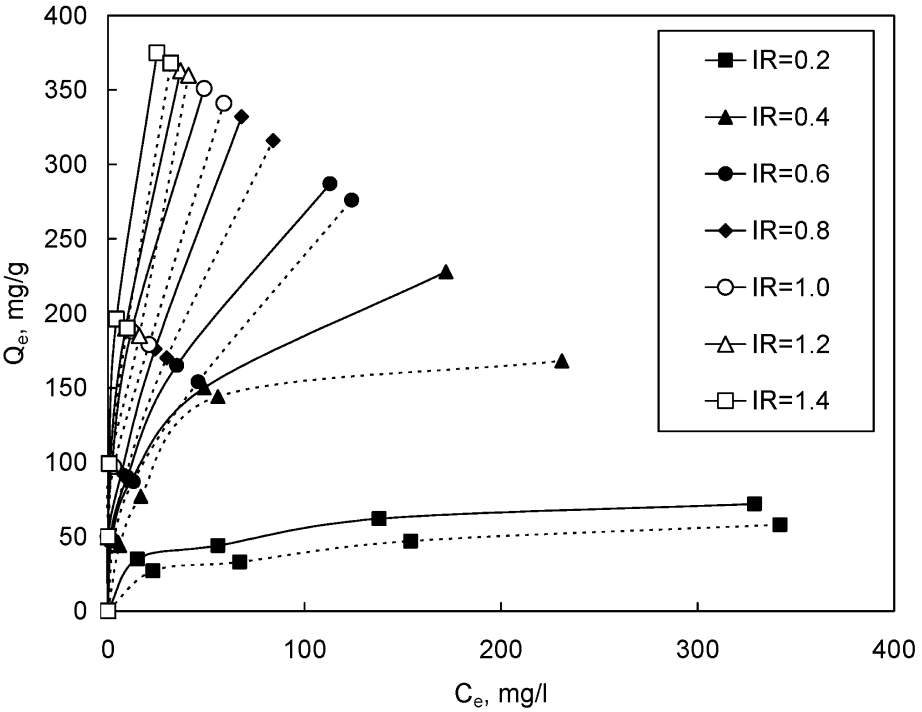

Figure 5. Effect of impregnation ratio on adsorptive capacity of methylene blue dye on activated product.

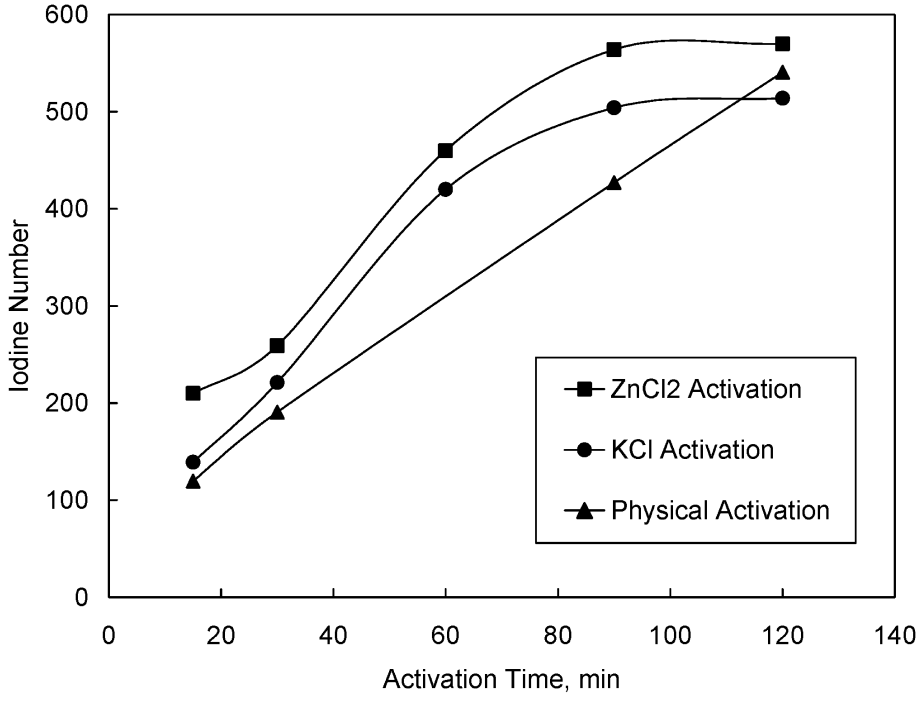

Figure 6. Effect of activation time on iodine number.

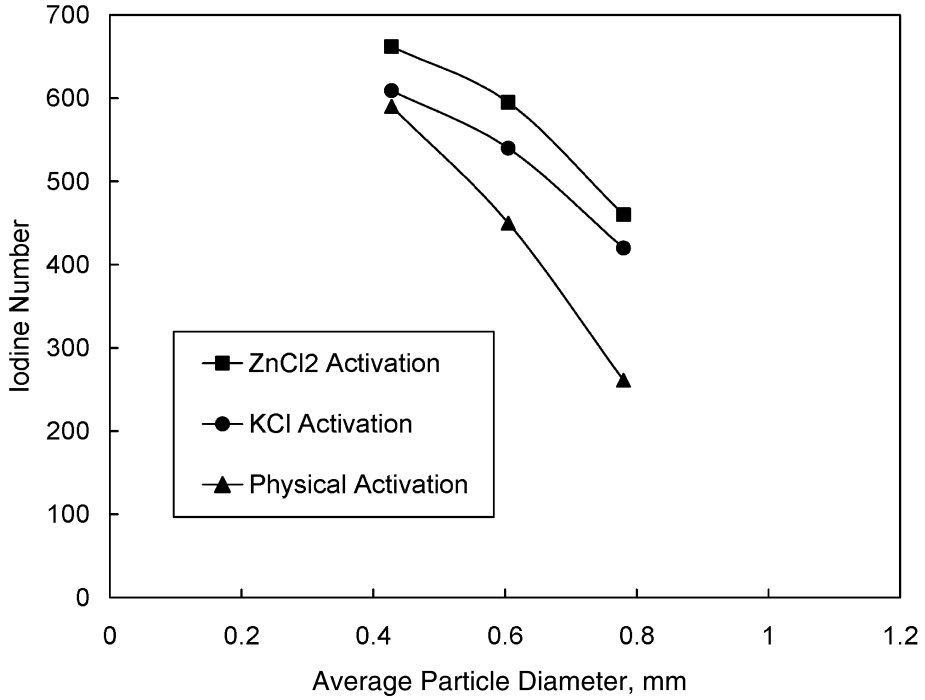

Figure 7. Effect of particle size on iodine number.

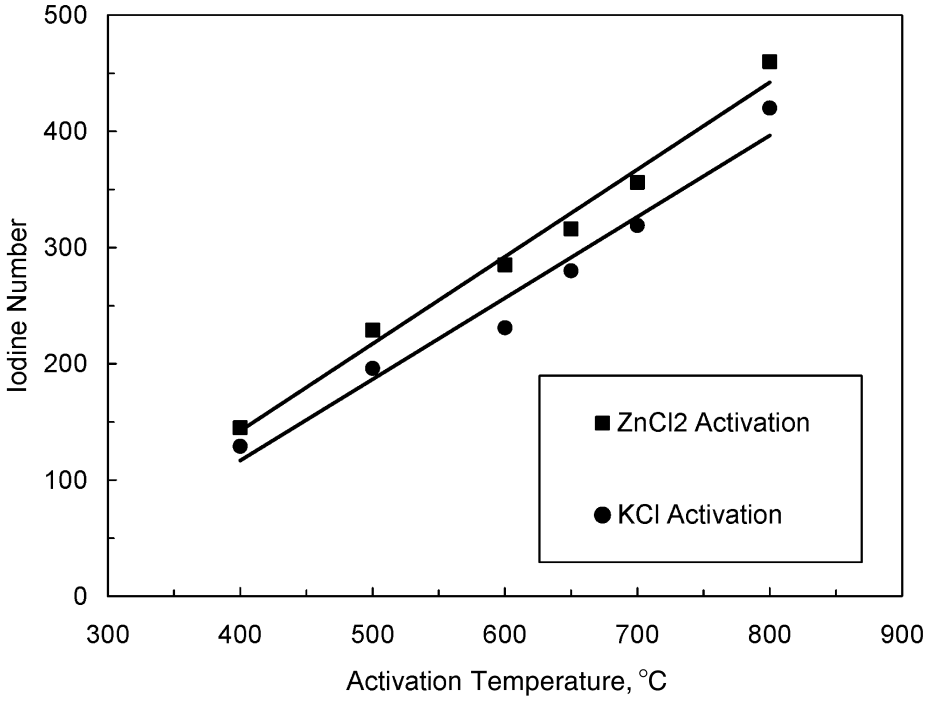

Figure 8. Effect of activation temperature on iodine number.

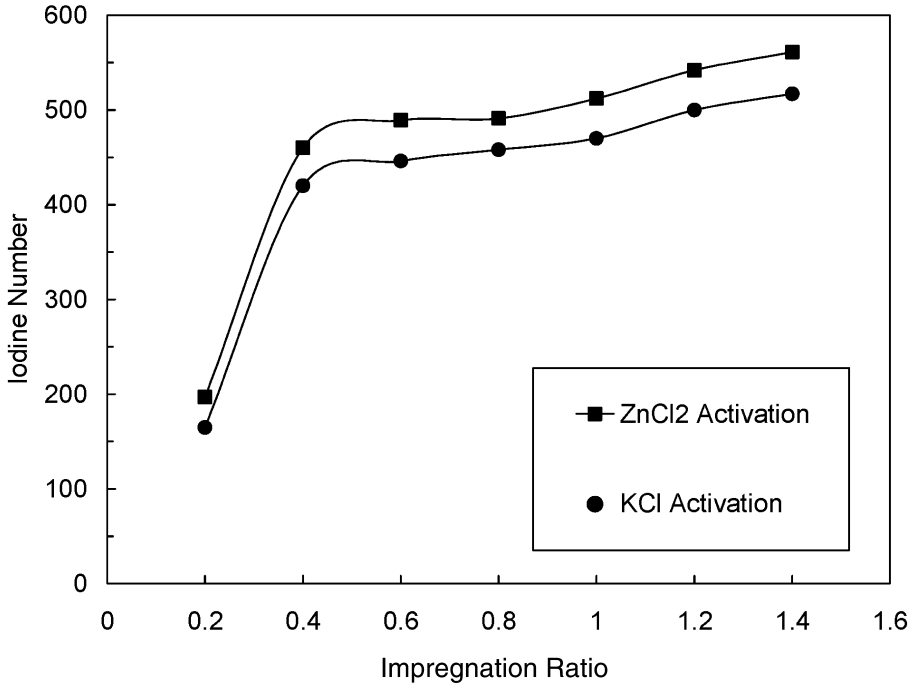

Figure 9. Effect of impregnation ratio on iodine number.

development of porosity, and it was higher for $ZnCl_2$ than KCl, which suggests that activated carbons produced by impregnation with $ZnCl_2$ developed higher porosity than with KCl.

Chemical and Physical Activation

By comparing the results obtained from chemical activation using $ZnCl_2$ or KCl with those obtained using physical activation (Al-Khalid et al., 1998), it was found that chemical activation gives better yield and higher adsorption capacities towards methylene blue or iodine as shown in Table 1, Figure 6, and Figure 7 under similar conditions of temperature and residence time.

Conclusions

Activated carbon has been successfully produced from olive-seed waste residue. Based on adsorptive capacities toward methylene blue dye and iodine number, it was shown that an acceptable activated can be produced from such materials. The chemically prepared activated carbon from olive-seed waste residue was more effective than previously prepared activated carbon by physical activation. Impregnating the starting materials with $ZnCl_2$ showed better results than using KCl.

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