Preparation and characterization of activated carbon from waste biomass

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ABSTRACT

Lignocellulosic materials are good and cheap precursors for the production of activated carbon. In this study, activated carbons were prepared from the pyrolysis of soybean oil cake at 600 and 800 °C by chemical activation with K_2CO_3 and KOH. The influence of temperature and type of chemical reagents on the porosity development was investigated and discussed. K_2CO_3 was found more effective than KOH as a chemical reagent under identical conditions in terms of both porosity development and yields of the activated carbons. The maximum surface area (1352.86 $m^2\,g^{-1}$) was obtained at 800 °C with K_2CO_3 activation which lies in the range of commercial activated carbons. Elemental analyses of the activated carbons indicate insignificant sulphur content for all activated carbons. The ash and sulphur contents of the activated carbons obtained with chemical activation by K_2CO_3 were lower than those by chemical activation with KOH.

1. Introduction

Activated carbon, which can be produced from coal [1] or biomass [2], is a porous material. There has been a plethora of research on the efforts to obtain low cost activated carbons from various lignocellulosic materials [3–7]. Activated carbon materials can be produced by physical or chemical activation. Chemical activation has three main advantages. Firstly, it is carried out in a single step. Secondly, carbonization and activation are united [8]. Lastly, it is performed at relatively lower temperatures by comparing with physical activation. Chemical activation has been successfully applied to the production of activated carbons using various chemical reagents i.e., $ZnCl_2$, H_2SO_4, H_3PO_4, HCl. Recently, alkali hydroxides such as KOH, NaOH and alkali carbonates such as K_2CO_3 and Na_2CO_3 have increasingly been used as activation reagents turning out high specific surface areas of the prepared activated carbons. Activated carbons prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide were investigated [9]. It was reported that NaOH is more efficient in the activation of low structural-ordered materials, whereas KOH is more effective for the highly ordered materials, which indicates differences in the activation performance of both hydroxides. In another study, activated carbon from cork waste by chemical activation with K_2CO_3 has been investigated. It was reported that the increase of the calcination temperature promotes a continuous development of the porosity

[10]. Martinez et al. [11] studied the characteristics of activated carbons prepared from olive stones and walnut shells using KOH. The adsorptive properties of activated carbons from olive stones were higher than that of walnut shells. However, activated carbon from walnut shells had macro-porous structures with a pore size distribution more homogenous than that of olive stone.

In the present study, we have used waste biomass (soybean oil cake), which is by-product of vegetable oil industry, as a precursor for the production of activated carbons. The type of activating reagent (KOH or K_2CO_3) and the effect of temperature on the characteristics of the activated carbons were investigated.

2. Experimental

2.1. Materials

Waste biomass (soybean oil cake) sample was obtained from Altinyag Oil Company, Izmir, Turkey and used without further treatments. The proximate, ultimate and component analyses of soybean oil cake are shown in Table 1. Determination of each component of soybean oil cake was done using the method given in the literature [12]. All chemicals used in the investigation were of analytical grade.

2.2. Preparation and characterization of activated carbons

The preparation of the activated carbons from waste biomass (soybean oil cake) was carried out in four stages. The steps are as follows: (i) soybean oil cake and solutions of activating reagents (K_2CO_3 or KOH) were mixed for 24 h under continuous agitation

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Table 1
Proximate, ultimate and component analyses of soybean oil cake.

Proximate analysis (as received, wt%)	
Moisture	9.92
Volatile matter	69.81
Fixed carbon	14.44
Ash	5.83
Ultimate analysis (dry basis, wt%)	
C	44.48
H	6.28
N	8.21
S	0.54
O[a]	40.49
GCV[b] ($MJ\,kg^{-1}$)	19.72
Component analysis (dry basis, wt%)	
Extractives[c]	17.86
Hemicellulose	52.51
Lignin	2.80
Cellulose	21.58

[a] By difference.
[b] Gross calorific value.
[c] Toluene/alcohol (2/1) (v/v).

(1000 rpm). (ii) This mixture was dried at 110 °C for 24 h to prepare the impregnated sample. (iii) The impregnated sample was set in a reactor which was a fixed bed design of stainless steel with 6 cm diameter and 21 cm height. The impregnated sample was pyrolyzed at the temperatures of 600 and 800 °C for 1 h under nitrogen (N_2) flow of 30 mL min^{-1} at a heating rate of 5 °C min^{-1}. (iv) The carbonized sample was washed several times with hot distilled water, and finally with cold distilled water until the pH of the filtrate became neutral. The washed samples were dried at 110 °C for 24 h to prepare the activated carbons. After that, the activated carbons were boiled with HCl solution under reflux to remove impurities and reduce the amount of ash content of the activated carbons. Then, they were washed several times with hot distilled water, and finally with cold distilled water until chloride ions were not detected. The washed samples were dried at 110 °C for 24 h to prepare the activated carbons.

Bio-chars obtained from soybean oil cake without chemical activation at 600 and 800 °C were shown as BC1 and BC2, respectively. The activated carbons obtained from chemical activation with K_2CO_3 at 600 and 800 °C were denoted as SAC1 and SAC2, respectively. The activated carbons obtained from chemical activation with KOH at 600 and 800 °C were denoted as SAC3 and SAC4, respectively.

The experimental impregnation ratio was estimated from the following equation:

$$\text{experimental impregnation ratio} = \frac{(\text{weight of sample after impregnation}) - (\text{weight of waste biomass})}{\text{weight of waste biomass}}$$

The yield of the activated carbon was estimated from the following equation:

$$\text{yield of activated carbon (wt\%)} = \frac{\text{weight of activated carbon}}{\text{weight of waste biomass}} \times 100$$

The chemical recovery (wt%) was estimated from the following equation:

$$\text{chemical recovery (wt\%)} = \frac{(\text{weight of sample before washing}) - (\text{weight of sample after washing})}{\text{weight of impregnated chemical}} \times 100$$

A measurement of specific surface areas of the activated carbons produced from soybean oil cake has been made by N_2 adsorption (at 77 K), using a surface analyzer (Quantachrome Inst., Nova 2200e). The micropore volume (V_{micro}) was determined by using *t*-plot method. The results were obtained by using Novawin 2 software. The mesopore volume (V_{meso}) was calculated by subtracting V_{micro} from V_{total} ($V_{meso} = V_{total} - V_{micro}$).

The scanning electron micrograph (SEM) analyses of the activated carbons were recorded by using JEOL JSM-6060. Proximate analyses of the activated carbons were carried out according to ASTM D3174-04 for ash analysis and ASTM D3175-89a for volatile matter. The activated carbons were analyzed for carbon, nitrogen, hydrogen, sulphur, and oxygen (by difference) abundances using a LECO CHNS 932 Elemental Analyzer according to ASTM D5291.

3. Results and discussions

Preparation of the activated carbons from soybean oil cake by K_2CO_3 and KOH activation was carried out at 600 and 800 °C.

Table 2
Conditions used for the production of activated carbon from soybean oil cake with chemical activation.

Type of activated carbon	Activating reagent	Carbonization temperature (°C)	Theoretical impregnation ratio	Experimental impregnation ratio
BC1	–	600	–	–
BC2	–	800	–	–
SAC1	K_2CO_3	600	1.00	1.00
SAC2	K_2CO_3	800	1.00	1.00
SAC3	KOH	600	1.00	0.95
SAC4	KOH	800	1.00	0.95

Table 3
Yields of activated carbons and chemical recoveries in the chemical activation process.

Type of activated carbon	Activating reagent	Carbonization temperature (°C)	Yield of activated carbon[a] (wt%)	Chemical recovery (wt%)
BC1	–	600	29.72	–
BC2	–	800	27.77	–
SAC1	K_2CO_3	600	16.22	98.55
SAC2	K_2CO_3	800	11.56	99.65
SAC3	KOH	600	6.25	96.76
SAC4	KOH	800	4.11	96.08

[a] All yields calculated on a dry basis.

Table 4
Characteristics of bio-chars and activated carbons from soybean oil cake at 600 and 800 °C.

	Types of bio-chars and activated carbons					
	BC1	BC2	SAC1	SAC2	SAC3	SAC4
Proximate analysis (wt%)						
Volatile matter	12.30	6.56	21.02	13.71	18.57	17.43
Fixed carbon	79.05	85.39	77.78	85.31	77.77	79.89
Ash	8.65	8.05	1.20	0.98	3.66	2.68
Elemental analysis (wt%)						
C	64.56	68.85	69.68	81.03	72.98	79.28
H	1.68	0.99	1.99	0.53	1.89	0.84
N	8.48	5.51	3.86	0.06	4.61	0.20
S	0.14	0.06	0.06	0.05	0.19	0.04
O[a]	25.14	24.59	24.41	18.33	20.33	19.63
Typical properties						
Specific surface area (m^2 g^{-1})	9.47	5.37	643.54	1352.86	600.05	618.54
Total pore volume (cm^3 g^{-1})	0.009	0.001	0.336	0.680	0.299	0.291
Micropore area (m^2 g^{-1})	–	–	521.86	760.13	406.75	273.77
Micropore volume (cm^3 g^{-1})	–	–	0.272	0.400	0.213	0.143
Mesopore volume (cm^3 g^{-1})	0.009	0.001	0.064	0.280	0.086	0.148
Average pore diameter (Å)	19.05	5.23	10.43	10.05	9.98	9.41

[a] By difference.
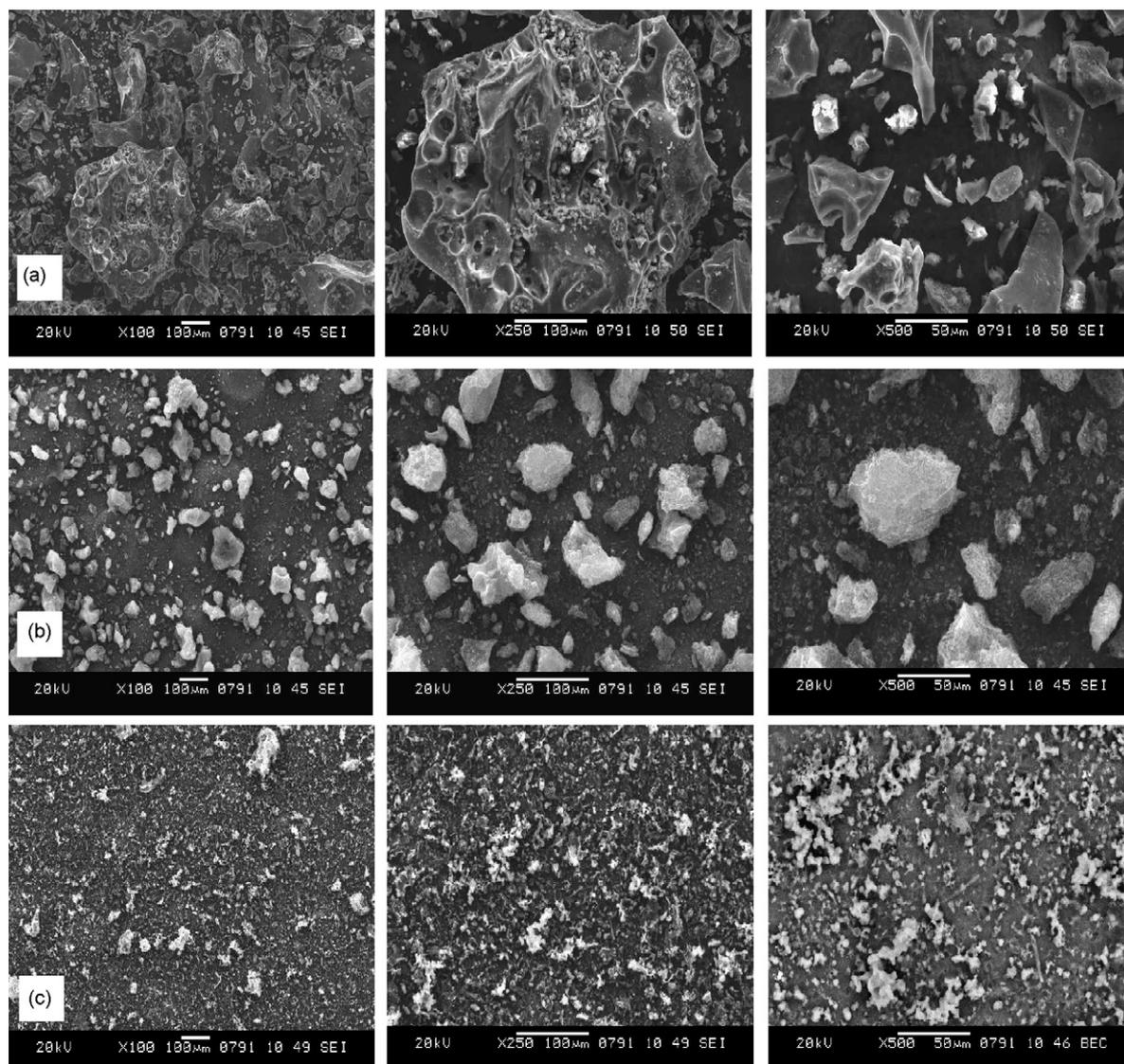
Fig. 1. SEM images of bio-char and activated carbons (a) BC2 (b) SAC2 (c) SAC4.

Theoretical and experimental impregnation ratios for KOH and K_2CO_3 impregnations are given in Table 2. As can be seen from Table 2, experimental impregnation ratio was lower than theoretical impregnation ratio for KOH impregnation. However, experimental impregnation ratio was the same as theoretical impregnation ratio for K_2CO_3 impregnation.

The yields of the activated carbons and the chemical recoveries in the activation process are shown in Table 3. The chemical recovery was found to be between 96.76 and 99.65 wt%. With increasing the temperature from 600 to 800 °C, the yields of bio-char and activated carbon samples decreased. The yield of bio-char decreased slightly with an increase of carbonization temperature. The yields of the activated carbons produced by chemical activation were lower than those of bio-chars for all carbonization temperatures. This shows that both K_2CO_3 and KOH worked effectively as activating reagents at the carbonization temperatures of both 600 and 800 °C. The yields of the activated carbons produced by K_2CO_3 activation were higher than those of the activated carbons produced by KOH activation.

The development of porosity of the activated carbons by KOH activation is associated with gasification reaction. It is assumed that KOH is reduced to metallic potassium during the carbonization process. The reaction of KOH and carbon occurs according to the following reaction:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad [13, 14]$$
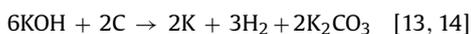
The characteristics of the activated carbons are presented in Table 4. For comparison purpose, the characteristics of the bio-chars (BC1 and BC2) prepared at 600 and 800 °C without chemical activation are also shown in Table 4. As expected, the specific surface areas of bio-chars were quite low. The type of activating reagent and carbonization temperature influenced the surface areas and porosity characteristics of the activated carbons produced by chemical activation. As can be seen from Table 4, specific surface areas of the activated carbons increase with increasing the carbonization temperature from 600 to 800 °C. The specific surface areas of the activated carbons obtained by chemical activation with K_2CO_3 were higher than those of the activated carbons produced by chemical activation with KOH under identical conditions. With increasing the carbonization temperature from 600 to 800 °C, specific surface area of the activated carbon produced by chemical activation with K_2CO_3 increased more than two folds. However, the surface area of the activated carbon produced by KOH activation KOH increased from 600.05 to 618.54 $m^2 g^{-1}$ with increasing the temperature from 600 to 800 °C. The maximum specific surface area was found in the case of K_2CO_3 activation at 800 °C. The specific surface areas of commercially produced activated carbons are typically range from 500 to 2000 $m^2 g^{-1}$ [15,16]. Thus, the production of the activated carbons with high surface areas from a low cost and renewable material is indeed of importance from the view point of economic and environmental aspects. It is found that the micropore is well developed for the activated carbon produced by K_2CO_3 activation with increasing the carbonization temperature from 600 to 800 °C. The micropore volume of the activated carbon produced by KOH activation decreased but mesopore volume increased. Activated carbon was prepared from cassava peel by chemical activation with KOH at the temperatures of 450–750 °C [17]. It was found that the micropore volume of activated carbon increased until carbonization temperature reached to 650 °C and at higher temperature, the micropore volume decreased. The temperature higher than 650 °C led to widening of micropore to mesopore. Our results for KOH activation are in good agreement with this previous report [17]. Also, the ash contents of bio-chars were higher than those of the activated carbons produced by chemical activa-

tion. The ash contents of the activated carbons produced by KOH activation were higher than those of the activated carbons produced by K_2CO_3 activation. Elemental analyses of the activated carbons indicate insignificant sulphur content for all activated carbons.

The SEM was used to investigate the surface topography of bio-char and activated carbons. The SEM images of BC2, AC2 and AC4 are shown in Fig. 1. There was observed a significant difference between the surface topography of bio-char and activated carbons. The surface of BC2 is rough with lots of big particles and holes. The SEM images of SAC2 and SAC4 show that it has amorphous nature of carbon with lots of micropores.

4. Conclusions

Activated carbons were prepared from the pyrolysis of soybean oil cake at 600 and 800 °C by chemical activation with K_2CO_3 and KOH. The yields of the activated carbons produced by chemical activation were lower than those of bio-chars for all carbonization temperatures. K_2CO_3 was found more effective than KOH as a chemical reagent under identical conditions in terms of both porosity development and yields of the activated carbons. The ash and sulphur contents of the activated carbons obtained by chemical activation with K_2CO_3 were lower than those with chemical activation by KOH. The maximum surface area of 1352.86 $m^2 g^{-1}$ was obtained at 800 °C with K_2CO_3 activation which lies in the range of commercial activated carbons.

Consequently, the activated carbons produced from waste biomass can be used as adsorbents for various environmental applications including removing hazardous compounds from industrial waste gases or wastewater.

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