Research Article

SURFACE and INTERFACE ANALYSIS

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Surface properties of activated carbon prepared from wastes

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In this study, activated carbons were produced from animal wastes (cow dung) by chemical activation. The effects of the activating agent and the impregnation ratio were investigated at constant temperature of 700 °C. Chemical activations were carried out by mixing the solution of $ZnCl_2$ or KOH and animal wastes with a chemical agent/waste, ratio (wt/wt) varying from 0.5 to 2.5. The pore properties including the Brunauer-Emmett-Teller(BET) surface area, pore volume, pore size distribution and average pore diameter of the activated carbons were determined by physical adsorption of N_2 at −196 °C. The highest BET surface areas and total pore volumes were achieved as 1367 m^2/g and 0.788 cm^3/g for $ZnCl_2$-activated carbon and as 1916 m^2/g and 1.13 cm^3/g for KOH-activated carbon, respectively. The microstructure of the activated carbons was examined by SEM. The surface functional groups were determined by Fourier transform infrared spectra (FTIR). This study has demonstrated that high surface area activated carbons can be prepared from the chemical activation of animal wastes with KOH and $ZnCl_2$ as activating agents. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: activated carbon; dung; chemical activation; characterization

Introduction

Activated carbon is already a very important industrial raw material. It can be used as an electrode base material for super capacitors, as a catalyst support for fuel cells because of its porous features and for storage of large quantities of CH_4 and H_2 due to its adsorption capabilities.[1] Of the various porous materials, activated carbon is the most widely used for environmental applications such as gas separation, solvent recovery and water purification because of its high specific surface area and pore volume.[2] Many agricultural byproducts and animal wastes have been used as sources for activated carbon, such as date stones,[3] corn cob,[4] pistachio shells,[5] cassava peel,[6] olive cake,[7] broiler manure,[8] cow dung[9] and cattle manure.[10]

There are two processes for preparation of activated carbon: physical and chemical activation. The physical activation involves primary carbonization of the raw material followed by controlled gasification at higher temperature in a stream of an oxidizing gas. The chemical activation is carried out by impregnation of the precursor with a chemical (H_2SO_4, H_3PO_4, $ZnCl_2$, alkali metal hydroxides, etc.), then heat-treatment at moderate temperatures in a one step process.

Since animal husbandry is highly developed in Turkey, a substantial amount of animal wastes are produced each year. Approximately 7×10^6 tons of animal wastes have been produced annually in Turkey.[11] Generally, cow dung is used as domestic fuel in rural areas of Turkey. In this study, activated carbons were produced by chemical activation from cow dung. Process parameters such as chemical agent species and impregnation ratio were examined. The resulting activated carbons were characterized by several techniques.

Experimental

Activated carbon preparation

Cow dung was ground and sieved to the size of 0.6–0.8 mm and dried at 105 °C overnight before activation. Chemical activation was carried out using $ZnCl_2$ and KOH. Chemical activation was performed as follows: 20 g of dried material was mixed with $ZnCl_2$ or KOH solution with different impregnation ratios (0.5, 1.5 and 2.5) for about 4 h at 50 °C. The concentration of $ZnCl_2$ or KOH solution was adjusted to give a mass ratio of chemical activating agent to dung ranging from 0.5 to 2.5 (mass basis). The resulting homogeneous slurry was dried at 105 °C for at least 12 h. The sample was placed in a horizontal tubular furnace (Carbolite) and then carbonized at 700 °C under nitrogen flow. The activated carbons were washed with a 0.5 N HCl solution. Subsequently, the samples were repeatedly washed with hot distilled water until the pH of solution reached a range of 6–7.

Pore structure characterization

The pore structure characteristics of the carbons were determined by N_2 adsorption at −196 °C using Autosorb 1C (Quantchrome). Prior to gas adsorption measurement, the carbon was degassed at 300 °C in a vacuum for 3 h. N_2 adsorption isotherms were measured over a relative pressure (P/P_o) range between 10^{-6} and 0.995. The Brunauer-Emmett-Teller (BET) surface area, micropore volume and micropore surface area of the activated carbons were determined by application of the BET, and t-plot analysis, respectively. The BET surface area was determined in the relative pressure range from 0.01 to 0.15. The pore size distribution of the activated carbons was determined by density functional theory (DFT) method. All calculations were carried out using the software supplied by Autosorb-1C. The microstructure of the activated carbons prepared was examined by SEM (Jeol, JSM-5600LV). The

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surface functional groups were determined by Fourier transform infrared spectra (FTIR) (Perkin Elmer).

Results and Discussion

N_2 adsorption–desorption isotherms

The adsorption isotherm is the information source about the porous structure of the adsorbent. Figure 1(a) and (b) shows the adsorption/desorption isotherms of N_2 for all activated carbons prepared at various KOH/dung and $ZnCl_2$/dung ratios, respectively. Isotherms of activated carbons activated with KOH and $ZnCl_2$ exhibit Type I isotherm. According to the IUPAC classification, the Type I isotherm is associated with microporous structures.[6] The major uptake occurs at relative pressure less than 0.1. The initial part of the isotherm represents micropore filling, and a low slope of the plateau indicates multilayer adsorption on the external surface. KOH-activated carbons show a steep and distinct increase in adsorption at about $P/P_o \approx 1$ as a result of a limited uptake of nitrogen indicating capillary condensation in the mesopores. Because of this characteristic, KOH-activated carbons contain more mesopore than $ZnCl_2$-activated carbons. Additionally, activated carbons prepared with KOH and $ZnCl_2$ present hysteresis loops indicating mesoporosity. Similar hysteresis loops were obtained by other researchers.[7,12]

Surface area and pore volume

Impregnation ratio (IR) was found to be the most important parameter in the carbonization of carbon precursor using chemical activation. The influence of IR on some of the physical properties of activated carbons including BET surface area (S_{BET}), micropore surface area (S_{micro}), total pore volume (V_T), micropore volume (V_{micro}) and average pore diameter (D_p) are given in Table 1. Activated samples used in this study were prepared by the impregnation method using different chemical ratios and then carbonized for 1 h at a temperature of 700 °C.

As shown in Table 1, the BET surface area of KOH-activated carbons increases from 1333 to 1996 m^2/g when KOH/dung ratio changes from 0.5 to 2.5. Total pore and micropore volumes of the KOH-activated carbons also increased with the impregnation ratio, showing a development of porosity. The pores are thought to be formed partly due to evolution of gaseous carbonization products (such as CH_4, CO_2, H_2, H_2O) through the carbonaceous masses and partly due to the metallic salts produced as a result of reactions during carbonization. Investigations showed that KOH is dehydrated to K_2O, which reacts with CO_2 produced by the water-shift reaction to give K_2CO_3. Removal of these metal salts from the internal volume of the carbon during the washing step creates the porosity in the structure. These results agree with those reported earlier.[13,14]

Table 1. Pore characteristics of the activated carbons

	IR	S_{BET} m^2/g	S_{micro} m^2/g	V_{micro} cm^3/g	V_{total} cm^3/g	D_p nm
KOH	0.5	1333	959	0.412	0.847	2.54
KOH	1.5	1569	1100	0.495	0.988	2.52
KOH	2.5	1916	1460	0.601	1.133	2.36
$ZnCl_2$	0.5	746	481	0.232	0.536	2.87
$ZnCl_2$	1.5	1005	829	0.340	0.543	2.48
$ZnCl_2$	2.5	1367	1136	0.502	0.788	2.30

The effects of chemical ratio on BET surface area and micropore volume of $ZnCl_2$-activated carbon are shown in Table 1. It shows that surface area as well as the total pore volume increased with the increase in chemical ratio and reached a maximum of 1367 m^2/g and 0.788 cm^3/g, respectively. The experimental results suggested that the use of $ZnCl_2$ developed new pores on choosing an appropriate $ZnCl_2$/dung ratio. Micropore volume percentage of the $ZnCl_2$-activated carbon increased from 43.28% to 63.70% with the chemical ratio. The increase in surface area and pore volume with impregnation ratio suggests that the porosity created by $ZnCl_2$ is due to the spaces left by zinc chloride after acid and water washing.

Pore size distribution

According to the definition by IUPAC, the adsorbent pores were classified into three groups: micropores (diameter <2 nm), mesopores (2–50 nm) and macropores (>50 nm). Figure 2 shows the pore size distributions of activated carbon samples. It appears that KOH-activated and $ZnCl_2$-activated carbons include micropores and mesopores. It was apparent that the average pore diameter was largely dependent on the chemical ratio as indicated in Table 1. As the impregnation ratio is increased from 0.5 to 2.5, the average pore diameter decreased from 2.87 nm to 2.3 nm for $ZnCl_2$-activated carbon and from 2.54 nm to 2.36 nm

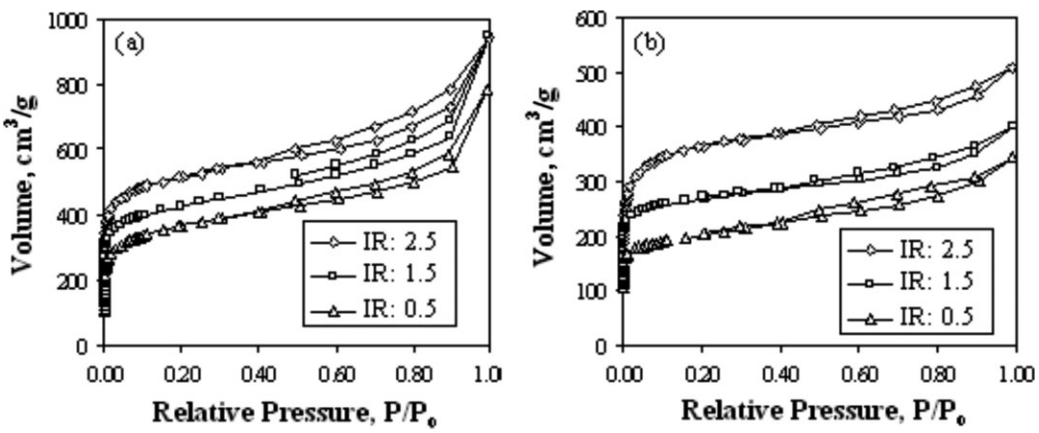


Figure 1. Adsorption–desorption isotherms of (a) KOH-activated carbon, (b)$ZnCl_2$-activated carbon.

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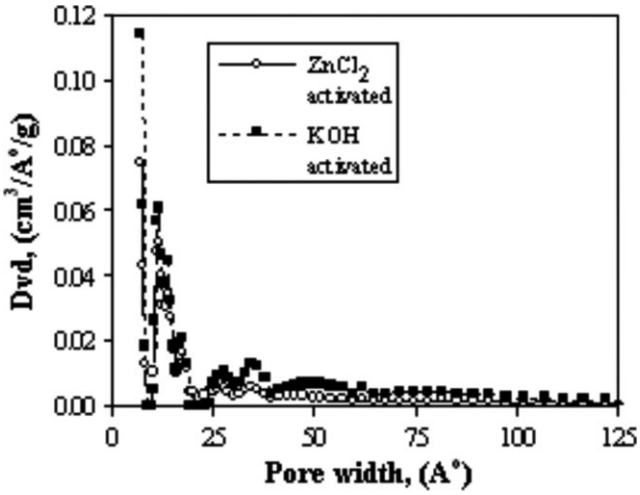


Figure 2. Pore size distribution of the activated carbons.

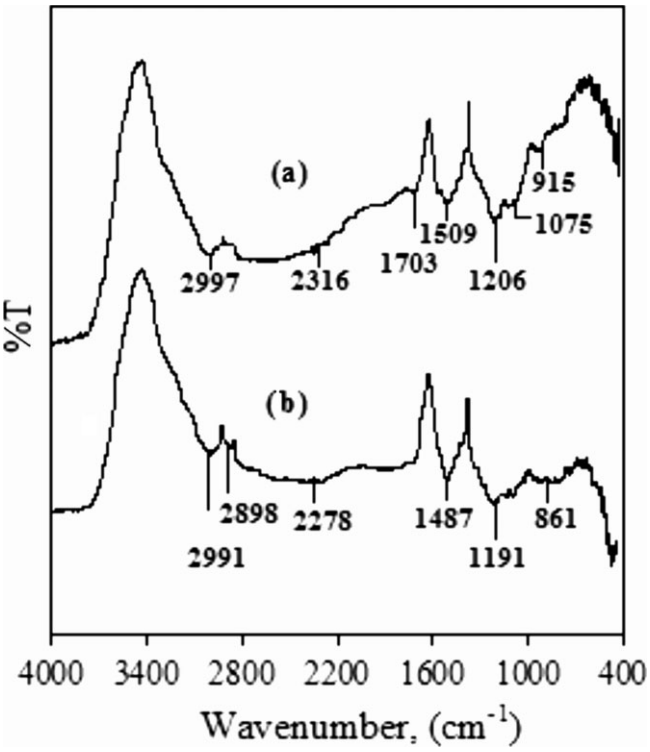


Figure 3. FTIR spectra of the activated carbons. (a) KOH-activated carbon, (b) $ZnCl_2$-activated carbon.

for KOH-activated carbon, respectively. The percentage of the micropore volumes of the activated carbons increased from 43.28% to 63.70% for $ZnCl_2$-activated carbons and from 48.6% to 53.92% for KOH-activated carbons, respectively. The effect of impregnation ratio on micropore development was reported by other researchers.[10]

FTIR analysis

The FTIR spectra of activated carbons are shown in Fig. 3. The spectra were recorded on a Perkin Elmer 100 FTIR spectrometer in the 400–4000 cm^{-1} wavenumber range using DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique. Spectra of activated carbons were obtained using KBr dilution and finely powdered KBr as reference.

The bands around 2898–2991 cm^{-1} for $ZnCl_2$ and 2997 cm^{-1} for KOH-activated carbons were observed and assigned for aliphatic groups stretching vibration, respectively. Small weak bands appearing in two spectra around 2278 and 2316 cm^{-1} is generally ascribed to symmetric or asymmetric stretching of aliphatic band in -CH, $-CH_2$ or $-CH_3$. The small band appearing around 1700 cm^{-1} was attributed to carbonyl (C═O) groups. The peaks at 1487 and 1509 cm^{-1} may be attributed to aromatic ring or C═C stretching vibration for $ZnCl_2$ and KOH-activated carbons, respectively. The band around 1200 cm^{-1} is typically attributed to C–O band. The last bands at 915 and 861 cm^{-1} could be attributed to C–H stretching vibrations.

The spectrum of $ZnCl_2$-activated carbon is quite similar to that of KOH-activated carbon. This indicates that the chemical agent ($ZnCl_2$ or KOH) has not much effect on the surface functional groups and structures in the resultant products.

SEM analysis

The SEM of the surface appearances of the carbons prepared from cow dung by chemical activation using KOH and $ZnCl_2$ are given in Fig. 4. Carbons shown in the figure were prepared at a carbonization temperature of 700 °C with the impregnation ratio of 2.5. It can be seen from the micrographs that the external surface of the $ZnCl_2$-activated carbon is full of cavities. It seems that the cavities on the surface of the $ZnCl_2$ carbons resulted from the evaporation of $ZnCl_2$ during carbonization, leaving the space previously occupied by the $ZnCl_2$. The external surface of the KOH-activated carbon is more intact than that of $ZnCl_2$ carbon. However, there are numerous small pits distributed over the surface, indicating the occurrence of carbon gasification on the external surface during carbonization.

Conclusion

High porosity activated carbons were prepared from cow dung by activation with two chemical activation agents, $ZnCl_2$ and KOH. Cow dung is found to be a good raw material for developing activated carbons with a desirable pore size distribution.

The adsorption isotherms of carbons activated with KOH and $ZnCl_2$ generally exhibit Type I isotherm. When the impregnation ratio was increased from 0.5 to 2.5, the BET surface area of the activated carbon was increased from 746 to 1367 m^2/g for $ZnCl_2$-activated and from 1332 to 1916 m^2/g for KOH-activated carbons, respectively. Similarly, micropore and total pore volumes of the activated carbons were increased with the impregnation ratio. As the porosity was developed via acid washing the spaces which were occupied by impregnated $ZnCl_2$ or KOH, the washing process following carbonization has a significant influence on the surface properties of resulting carbon. On the other hand, KOH is more effective on the cow dung at the activation temperature of 700 °C. According to the pore size distribution, KOH and $ZnCl_2$-activated carbons include both micropore and mesopore, and microporosity increases with the impregnation ratio. SEM study shows that the external surface of the resulting activated carbons is full of cavities, especially for the carbon activated with $ZnCl_2$. FTIR spectra showed that the carbons activated with KOH and $ZnCl_2$ develop similar surface groups.

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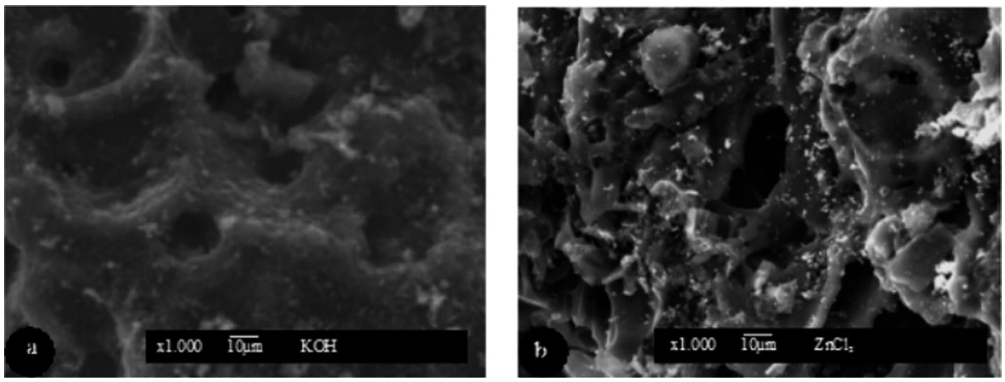


Figure 4. SEM photographs of the activated carbons. (a) KOH-activated carbon, (b) $ZnCl_2$-activated carbon.

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