Arch. Pharm. Res. **14**(3), 249-254 (1991)

A Study on Adsorptive Properties of Activated Carbons Produced from Rice-Straw

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(Received August 8, 1991)

Abstract □ Activated carbons from rice-straw can be used as an adsorbents for the purification of water were prepared and evaluated. The adsorptive capacities of activated carbons were measured by iodine, potassium permanganate, phenol and metals. It was observed by electron microscope (SEM) and IR spectrum that organic components in the rice-straw and its carbonization product were disappeared, slit-shaped and porous structures were formed by activation. There was no relationship between temperature and adsorption of iodine but adsorption of potassium permanganate increased as temperature rose. The adsorption of the phenol was greater than 99%. The adsorption data of phenol at 25℃ obeyed the Freundlich's isotherm. Various metals except sodium were not removed by activated carbon.

keywords □ Activated cabon, rice-straw, phenol, metals, iodine, $KMnO_4$, isotherm, atomic absorption spectrometry, adsorptive capacity.

In the purification of water[1] for domestic use, for specialized industrial applications and treatment of wastewater to make it acceptable for release or resuse, the standard method for the removal of dissolved organic materials is adsorption on activated carbons. Activated carbons[2] are unique and versatile adsorbents because of their extended surface area, microporous structure, high adsorptive capacity, and high degree of surface reactivity. Their important applications[3] related to their use in the removal of odor, taste, color, and other undesirable impurities such as heavy metals, phenolic compounds and some miscellaneous organic compounds from potable waters and so on. Many impure compounds are of particular concern for possible toxicity, carcinogenicity, and mutagenicity.

The carbon is produced by the carbonization of the carbonaceous raw material anaerobically below 600℃, followed by the activation step of the carbonized product. The properties of the final product will be different, depending upon the nature of the raw material used, the nature of the activating agent, and the conditions of the activation process. Any cheap and readily available material with high carbon content, low in inorganics, can be used as a raw material.

Several studies[4-9] tried to evaluate the adsorptive capacity and the surface structure of the activated carbons produced from various raw materials.

The present work describes the preparation method for the new powdered activated carbons from rice-straw. In addition, their adsorption capacities and surface properties as an adsorbent for the removal of organic compounds and heavy metals from water were evaluated.

EXPERIMENTAL

Materials and apparatus

Rice straws of the *Onyza sativa* Tongil which gathered in Kyungbuk province as raw material were used for the production of chemical carbon. 4-Amino antipyrine (98% Janssen Chemica), phenol (USP crystal, Mallinckrodt Chemical) and metal standard solution (1000 rpm Hayashi Pure Chemical Inc.,) were used without further purification as obtained. All other chemicals were of reagent grade.

The absorption spectra and the absorbances were measuered on Hewlett Packard 8452 A diode array UV-visible spectrophotometer with 10 mm quartz

cells. IR absorption spectra were recorded with a Perkin Elmer 1310 IR spectrophotometer using KBr disc method over the range of 600-4000 cm^{-1}. AA spectrophotometer of Instrumental Laboratory Model 457 A was used to determine atomic absorbances. Scanning Electron Micrograph was observed by Akashi DS-130S.

Preparation of the activated carbons

About 50 grams of rice straws predried and cut into 0.1-0.3 cm in length were obtained in graphite crucibles with cap, than carbonization process was carried out in an electric Muffle furnace at 250-400 ℃ in the absence of any gas. Then the carbonized material was impregnated with the activating agent in the form of concentrated solution by mixing and kneading for more than two hours. The chemical impregnated material was pyrolyzed in a graphite crucible between 600-700℃ in an electric furnace. The final black powdered product was dried in an oven at temperatures below 110℃.

Determination of adsorptive capacity of activated carbons

A quantitative expression for the adsroptive capacity of activated carbons has been difficult to define. Favored conventional methods have been determination of the amount of iodine, potassium permanganate, and phenol etc. before and after adsorption.

The adsorption power of 100.0 mg of activated carbons was determined by reacting with 25 m/ of 0.1N standard iodine solution for 24 hours until saturated adsorption had equilibrated and titrating the iodine after filtration with 0.1N standard sodium thiosulfate solution.

100.0 mg of activated carbons are added to 25 m/ of 0.1N standard potassium permanganate solution, after maintaining a saturated adsorption for 24 hours and then filter the solution through clean sintered glass funnel. Amount of unadsorbed potassium permanganate was calculated by titration.

5 ppm phenol solution is prepared which was contained 0-40 ppm activated carbons. After 24 hours stirring, filtered, and determination of phenol was carried out by modified Emersson's spectrometric method[10] at the maximum wavelength of 458 nm.

10 ppm metal standard solutions are prepared and mix with activated carbon for 24 hours. Atomic absorbance was measured with AA spectrophotometer; band pass were 0.5-1 nm, fuel and support were acetylene with air. Wavelengths for the determination of Na, Ca, Cu, Mn, Cd, Pb, Zn were 589.2, 422.7, 324.7, 228.8, 279.5, 217.0 and 213.9 nm, respectively.

RESULTS AND DISCUSSION

Optimal conditions on the preparation of activated carbons

The influence of the carbonization temperature was shown in Table I. The determination of the adsorptive capacity of activated carbons was accomplished by varying the carbonization time, activation temperature, activation time.

The adsorptive capacity was maximal at carbonization time for 45 min and at activation temperature around 650℃.

Activating agents

Reagents commonly used to activate the carbonized materials were examined for their effect on the adsorptive capacity. Chemical activation is usually carried out when the raw material is of wood origin[2]. The starting material is impregnated with the activating agent in the form of concentrated solution usually by mixing and kneeding. This results in the degradation of the cellulosic material. When zinc chloride was the activating agent, the highest adsorption capacity was obtained. These results are better than different activation process and therefore more porous structure is developed. The other conditions were kept constant, while content of zinc chloride varied. At zinc chloride content of 200% by weight of raw material, highly adsorption capcaities of acivated carbon were obtained as shown in Table I.

Scanning electron micrographs

Active carbons are characterized by their strong adsorption capacity, which occurs mostly in cavities of molecular dimensions called micropores. Depending upon their preparation, active carbons also contain larger pores, known as mesopores and macropores in the classification[11] proposed by Dubinin and now adopted by IUPAC. From six different scanning electron micrographs of different activated

Table I. Various conditions on the preparation of activated carbons and adsorptive capacity on the adsorption of iodine and potassium permanganate

Sample	Activation Agent	Carbonization Added (wt/wt %)	Carbonization Temp. (C)	Carbonization Time (min)	Activation Temp. (C)	Activation Time (min)	Adsorptive capacity I_2 (mean± sd mg/g)*		Adsorptive capacity $KMnO_4$ (mean± sd mg/g)*	
1	$ZnCl_2$	300	250	30	650	60	216.54	1.08	304.18	0.20
2	$ZnCl_2$	300	300	30	650	60	223.36	0.51	310.05	0.33
3	$ZnCl_2$	300	350	30	650	60	220.01	0.19	295.54	0.51
4	$ZnCl_2$	300	400	30	650	60	217.05	0.29	308.51	0.39
5	$ZnCl_2$	300	300	30	600	60	227.82	2.38	295.69	3.25
6	$ZnCl_2$	300	300	30	650	60	215.79	0.76	310.72	1.09
7	$ZnCl_2$	300	300	30	700	60	206.00	0.64	286.89	2.03
8	$ZnCl_2$	300	300	30	650	60	202.61	0.69	285.39	1.41
9	$ZnCl_2$	300	300	45	650	60	226.10	0.93	301.93	1.24
10	$ZnCl_2$	300	300	60	650	60	210.04	1.06	281.82	1.52
11	$ZnCl_2$	300	300	45	650	30	207.79	1.46	309.74	1.09
12	$ZnCl_2$	300	300	45	650	45	185.33	0.47	269.08	1.52
13	$ZnCl_2$	300	300	45	650	60	179.27	1.48	279.47	0.50
14	$Ca_3(PO_4)_2$	200	300	45	650	30	187.38	0.33	259.35	3.41
15	$ZnCl_2$	200	300	45	650	30	210.42	1.78	320.71	0.41
16	Na_3PO_4	200	300	45	650	30	188.03	0.51	254.52	4.50
17	H_3PO_4	200	300	45	650	30	164.04	1.30	271.02	2.46
18	K_2S	200	300	45	650	30	189.06	0.82	264.60	2.18
19	$ZnCl_2$	100	300	45	650	30	198.35	1.13	270.90	1.18
20	$ZnCl_2$	200	300	45	650	30	216.67	0.38	318.47	0.45
21	$ZnCl_2$	300	300	45	650	30	218.99	0.62	295.63	2.47

*n=4

carbons as illustrated in Fig. 1, it was observed in the case of the active carbon treated with zinc chloride as activating agent that there were a lots of slit-shaped mesopores of approximately 30 nm in diameter and perpendicular to the plane of the micrograph. It is considered these porous structures contribute to the adsorption.

IR spectra

Attemps[2] have been made to identify and estimate the surface fuctional groups using several physicochemical techniques, which include neutralization, potentiometric, thermometric titration, polarography, IR spectroscopy, and X-ray spectroscopy. We have previously studied[7] activated carbons produced from rice-chaff by IR spectroscopy. In the present work, from IR spectroscopic investigation nealy most stretching bands except slight band at 1080 cm^{-1} were not observed in the activated carbon (Fig. 2). We believe that all organic species in the rice-straw and its carbonization product were completely removed and slit-shaped and porous structures were formed by activation.

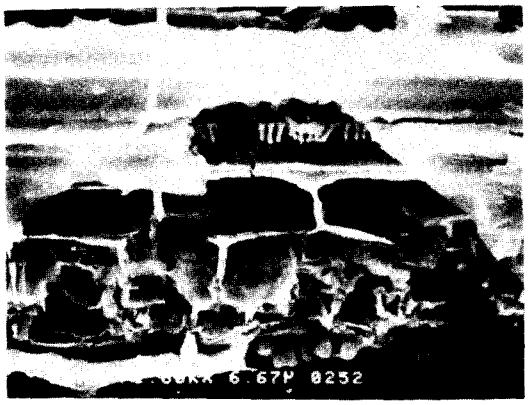
Effects of temperature on the adsorptive capacity

The adsorptive capacity was also measured as a fuction of temperature over the range 10-50℃. There was no relationship between temperature and adsorption of iodine but adsorption of potassium permanganate increased with increasing temperature (Fig. 3). The adsorptive enthalpy(H_{ad}) were computed by the following van't Hoff equation.

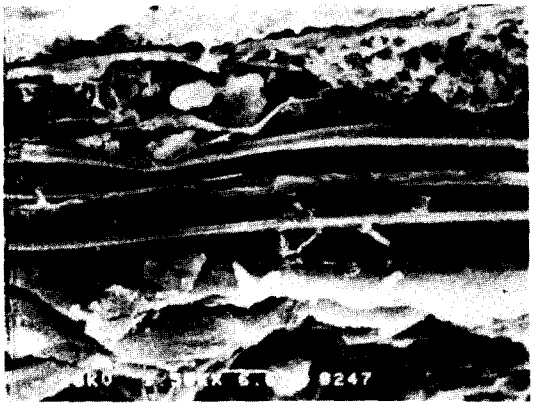
$$d \ln C/d(1/T) = -H_{ad}/R$$

where C is adsorptive concentration at equilibrium and at a given temperature (T). Computed H_{ad} values for the adsorption of iodine and potassium permanganate were 12.0154 kJ mol^{-1}, and 8.7189 kJ mol^{-1}, respectively.

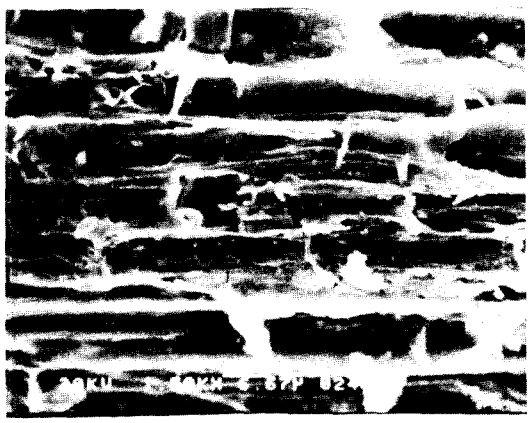
Historically the measurement of adsorptive capacity of iodine was first empolyed in 1920 to collect iodine from petroleum brine[3]. Natural oilwell brine contains about 13-53 μg/ml iodide which can be recovered by adsorption on active carbon. This me-



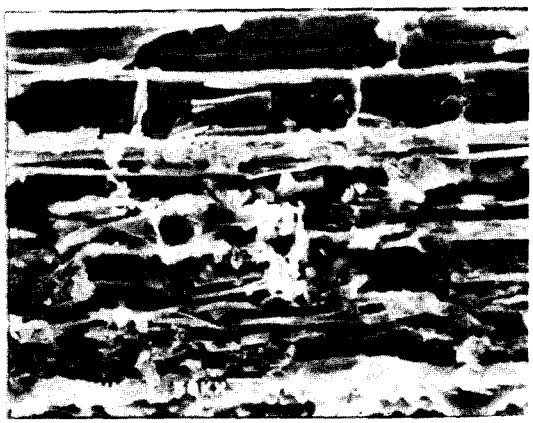
a) Carbon



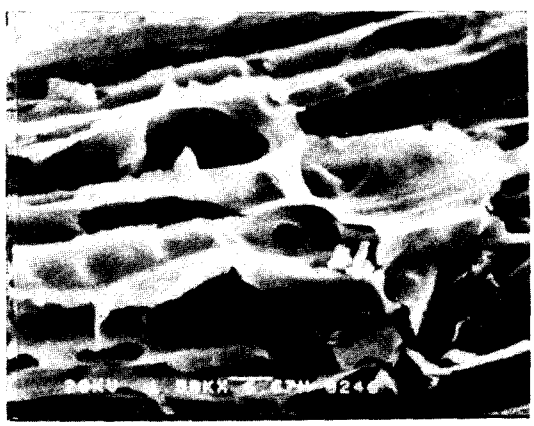
b) $Ca_3(PO_4)_2$



c) Na_3PO_4



d) H_3PO_4



e) K_2S

f) $ZnCl_2$

Fig. 1. Scanning electron micrographs of different activated carbons treated with various activation agents.

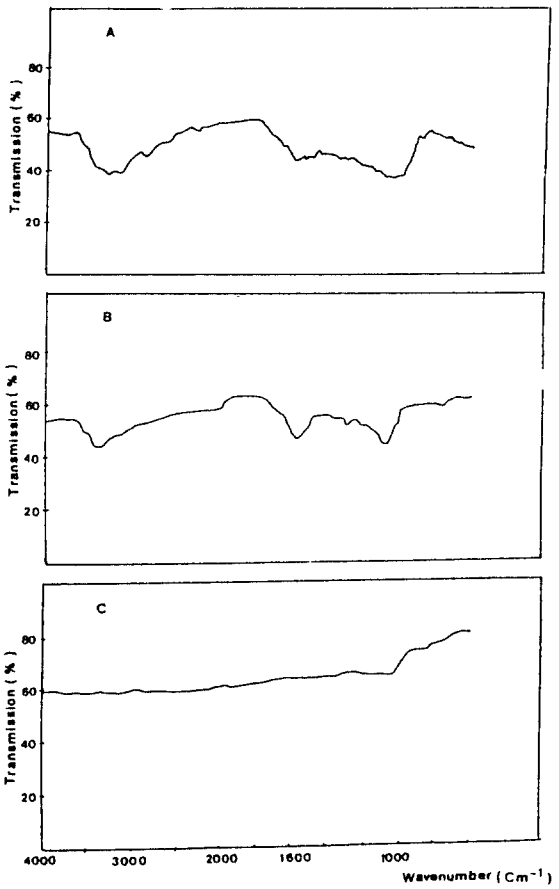


Fig. 2. IR spectra of a) rice straw, b) carbonization product of rice straw (300°C, 45 min), c) activation product of b) (650°C, 30 min).

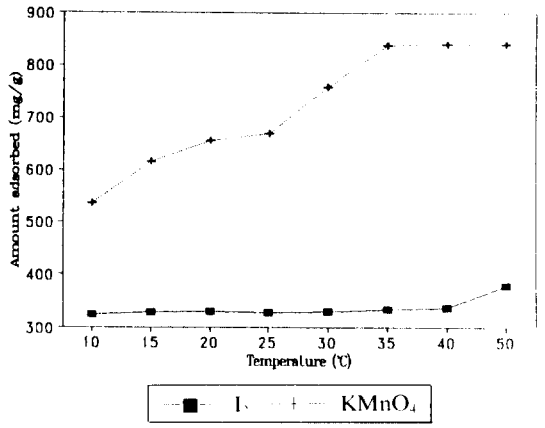


Fig. 3. Influence of temperature on the adsorption of iodine and potassium permanganate.

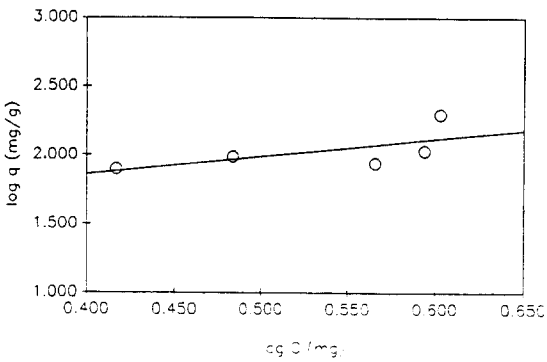


Fig. 4. The plot of Freundlich's isotherm on the adsorption of phenol at 25°C.

thod then became one of official test methods to evaluate the adsorptive capacity of the new activated carbon or to investigate activating conditions. In the case of potsssium permanganate test, the adsorption capacity was indicated the removability of undesirable coloring matter in the food industry. Therefore it was found out that activated carbon produced from rice-straw could be used in the recovery of matter and the removal of color.

Removability of phenol and metals from water

The wasterwater from industries contains substantial amounts of metalic and phenolic compounds, which include methyl phenols, ethyl phenols, and dimethyl phenols. These compounds cause several harmful effects in living beings. Therefore, their removal is part of water pollution control. Singer and Yen[12] investigated the adsorption of a number of alkyl phenols on powdered activated carbon in the concentration range 20-60 mg/*l*.

In the present study, the solution was contacted with the activated carbon for 24 hr, after which an aliquot was examined for phenol concentration using UV-visible spectrophotometery. The adsorption of the phenol was greater than 99% in all cases examined. The adsorption data at 25℃ obeyed the Freundlich's isotherm equation (Fig. 4) given by

$$\log q = 1.2763 \log C + 1.3511$$

where q is the weight fraction adsorbed (the mass of solute adsorbed per unit mass of adsorbent) and C is the solution's concentration.

Similarly the metalic standard solution was treated with the activated carbon, after that an aliquot

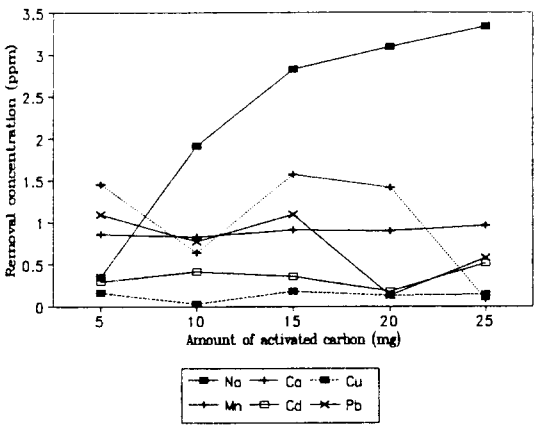


Fig. 5. Relationship between removal concentration and amount of activated carbon on the adsorption of various metals.

was examined for metal concentration by AA spectrophotometry at the identical wavelength. Various metals except sodium measured were not removed (Fig. 5).

The ion size of Na^+ was reported as 500 pm while those of Ca^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, and Pb^{2+} were 600 or 450 pm[13]. Interrelation was not obvious between the ion size and the pore size in the activated carbon which had larger pore size of about 30 nm in diameter. The adsorption mechanism of metal ions on the active carbon surface must be further studied and/or other pretreatment of the active carbon may be required.

ACKNOWLEDGEMENT

This research was supported by the grant from Seoul Woman's University in 1990.

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