Desalination and Water Treatment
www.deswater.com

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doi: 10.5004/dwt.2011.1420

29 (2011) 236–240
May

Effect of activation method on the pore structure of activated carbon from date pits application to the treatment of water

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Received 12 December 2009; Accepted in revised form 15 December 2010

ABSTRACT

Four active carbons have been prepared by carbonisation without adjuvant (DC) and by chemical activation of date pits with $ZnCl_2$ (DZ), KOH (DK), and H_3PO_4 (DP) in order to show the effect of variables such as the nature of the chemical reagent, extent of impregnation on the adsorbent surface area, and porosity of the resulting activated carbons. The pore structure of the activated carbons was characterized by CO_2 adsorption at 273 K and by N_2 adsorption at 77 K. The macro and mesoporosity were determined by mercury porosimetry. According to the nature of the adjuvant, the activated carbons present different porosity. Chemical activation of the date pits with KOH and H_3PO_4 produces an activated carbons having mesoporosity as well developed as in the $ZnCl_2$ activation. This last process led also to develop the microporosity more than KOH and H_3PO_4 activation. Adsorption at 298 K of potassium dichromate, triton X100 and potassium hydrogen phthalate from aqueous solutions on activated carbons has been studied. The adsorption capacity of the activated carbons depended on the surface area and porosity of the carbon, and the nature of the compounds adsorbed. The adsorption of potassium hydrogen phthalate and triton X100 on activated carbons DK, DP and DZ is comparatively better than potassium dichromate.

Keyword: Adsorption; Inorganic molecules; Organic molecules; Activated carbon; Chemical activation

1. Introduction

Adsorption of organic and inorganic pollutants by activated carbon has become one of the most reliable methods used in the field of water treatment [1]. Fruit stones are appropriate raw material for the production of activated carbons [2–5]. The use of these materials as adsorbents of inorganic and organic pollutants from water is due to their unique versatility resulting from their high surface area, porous structure, high adsorption capacity, and surface chemical nature, which can be appropriately modified by physical and chemical treatments to enhance the extent of a given adsorption process [6].

Both the nature of the precursors and the method of activation have a strong influence on the porous structure and adsorption properties of the resulting activated carbons.

Various methods of activation have been used to obtain activated carbons from agricultural waste products. The so-called chemical activation refers to the carbonisation of the precursor after addition of substances that restrict the formation of tar (H_3PO_4, $ZnCl_2$, KOH, etc.);

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in this way, a carbonised product with a well-developed porosity (after appropriate washing) may be obtained in a single operation. The chemicals incorporated into the interior of the precursor particle reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinking of the particle; in this way, the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large amount of porosity is formed [7].

In the present study we have investigated the influence of both the porous texture and the chemical nature of a series of activated carbons prepared from date pits on the adsorption process of potassium dichromate, triton X100 and potassium hydrogen phthalate from aqueous solutions at 298 K under static conditions.

2. Experimental

2.1. Preparation of activated carbons

Activated carbons used in this study were prepared from date pits. Date pits were crushed and sieved to a particle size of 0.5–1 mm in diameter. The precursor is impregnated with a chemical reagent in a solid form. The impregnated precursor was carbonised in horizontal furnace under a flow rate of (90 ml/min) of N_2 with a low heat of 5 K/min until the final temperature of the pyrolysis was reached. The holding time at the pyrolysis temperature is one hour. After cooling in N_2, the carbons were thoroughly treated by a diluted solution with chloride acid under reflux ebullition for three hours in order to extract the alkaline compound formed and reagent excess. The charcoals are recuperated after filtering and over washing with distillate boiling water until the test on the filtrate on silver nitrate is negative. Then they are dried in the oven.

Activated carbons will be referred to in the text as DC (these simples were pyrolyzed at 873 K with a heat low of 5 K/min), DP (these simples were impregnated with 14 mmol of H_3PO_4 and then pyrolyzed at 773 K), DK (these simples were impregnated with 9 mmol of KOH and then pyrolyzed at 1073 K with a heat low of 5 K/min), DZ (these simples were impregnated with 3.52 mmol of $ZnCl_2$ and pyrolyzed at 873 K with a low heat of 5 K/min).

2.2. Characterization of activated carbons

2.2.1. Textural characterization

Some of the textural characteristics of activated carbons are compiled in Table 1, which shows values for SN_2, the nitrogen surface area, obtained by applying the BET method to the N_2 adsorption isotherms at 77 K; SCO_2 obtained by applying the Dubinin–Radushkevich (DR) equation to the CO_2 adsorption isotherms at 273 K. The surface area was obtained with Micrometrics Accusorb.

V_{meso} and V_{macro}, the pore volumes contained in pores with diameters within 3.7 and 50 nm, and higher than 50 nm, respectively, were obtained from mercury porosimetry.

2.2.2. Structural characterization

The microstructures of the activated carbons produced from date stones were examined using a scanning electron microscope (Philips SEM 505).

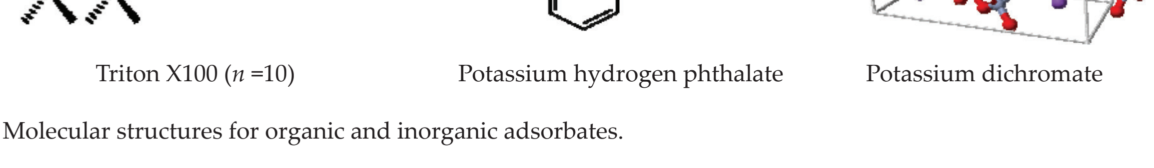
2.3. Adsorption of organic and inorganic pollutants under static conditions

The adsorption processes from aqueous solutions of the different organic and inorganic compounds, potassium dichromate ($K_2Cr_2O_7$), triton X100 ($C_{14}H_{22}O(C_2H_4O)$ ($n = 10$) and potassium hydrogen phthalate ($KC_8H_5O_4$), on the activated carbons were carried out at 298 K.

The molecular structures for organic and inorganic adsorbates used in this work

Potassium dichromate, triton X100 and potassium hydrogen phthalate were reagent grade chemicals from Fluka.

For this purpose, aqueous solutions with different initial known concentrations were used. Adsorption isotherms were determined by using stoppered flasks containing 0.1 g of carbon/100 cm^3 of solution. They were kept in a thermostat shaker bath at 298 K for 2 d, after which the equilibrium concentrations were determined spectrophotometrically, at the maximum absorbance wavelength (λ) shown in Table 2, using a Jasco V-530, spectrophotometer [6]. Table 2 also shows some physical characteristics of organic and inorganic compounds used.



Triton X100 (n =10) Potassium hydrogen phthalate Potassium dichromate

Fig. 1. Molecular structures for organic and inorganic adsorbates.

Table 1
Textural characteristics of the activated carbon samples from date pits

Sample	Yield (%)	SN_2 (m^2g^{-1})	SCO_2 (m^2g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_{macro} (cm^3g^{-1})	V_{tot} (cm^3g^{-1})
DC	42	640	1167	0.45	0.08	0.12	0.65
DZ	20	882	1509	0.59	0.09	0.38	1.06
DK	12	1032	1450	0.56	0.31	0.34	1.21
DP	17	700	1230	0.49	0.35	0.36	1.20

3. Results and discussion

3.1. Activated carbon characterization

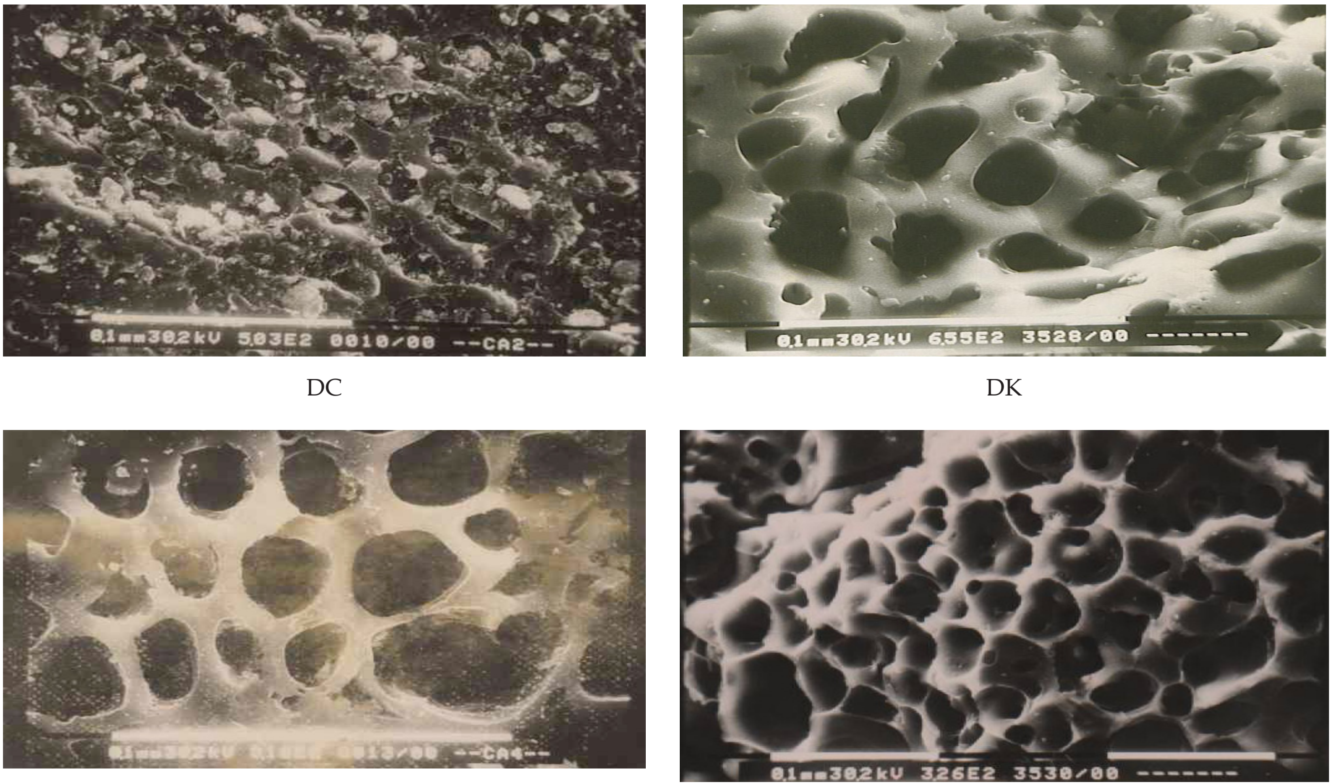
Table 1 reports the characterization of the porous structure of the activated carbons.

The DC char shows an interesting BET surface area for use as a precursor for activated carbon through further activation.

The main factor affecting the surface area and the micropore size distribution is the nature of chemical reagent introduced in the precursor during impregnation. Chemical activation of the date pits with $ZnCl_2$ produces an activated carbon having microporous volume more important (0.59 cm^3/g) than activated carbon DC whose volume is in the order of 0.45 cm^3/g. similar results have been found by other authors [8–10] showing that the chemical activation with $ZnCl_2$ produced activated carbons of natural microporous.

We also note that potassium hydroxide and phosphoric acid activation produced activated carbons with more important mesoporous volume than the one impregnated by $ZnCl_2$. The development of the porosity of date pits by chemical activation with $ZnCl_2$, H_3PO_4 or KOH is discussed in detail in previous papers [11–13].

Fig. 2 shows a SEM micrograph of a char particle. The morphological structure of activated carbon DC resembles fairly closely the characteristic appearance of lignocellulosiques material indicating that the structure of the precursors is basically preserved in the devolatilized solid.



DC DK

DZ DP

Fig. 2. SEM micrograph of activated carbon.

Table 2
Physical characteristics of organic and inorganic compounds

Compound	λ (nm)	Solubility at 298 K g/100g H_2O
Triton X100	275	2.3
Potassium hydrogen phthalate	280	25
Potassium dichromate	274	4.9

SEM micrograph of the activated carbon DK, DZ and DP demonstrates the considerable attack undergone by the solid. The original cell structure is completely preserved and some of the pores on the surface have been enlarged.

The micrograph in Fig. 2 suggests that the large pores on the surface are connected to a whole network of smaller pores in the interior of the carbon.

Thus, widening of the micropore size together with the development of meso- and macroporosity are important features as regards to the potential use of these activated carbons as adsorbents for liquid phase applications such as water and waste water treatment. The apparent surface areas compare well with those of many commercial activated carbons used in these applications [14–16].

3.2. *Adsorption of organic and inorganic compounds*

Adsorption isotherms of potassium dichromate, triton X100 and potassium hydrogen phthalate, on activated carbons DK, DZ, and DP are depicted in Fig. 3.

The adsorption isotherm plots present an L-shape, according to the Giles classification [17]; competition between compounds and water molecules for active sites on carbons is therefore weak and they were very well fitted by the Langmuir equation, from which the adsorption capacity, X_m, and the constant, B, were calculated. These parameters are compiled in Table 3.

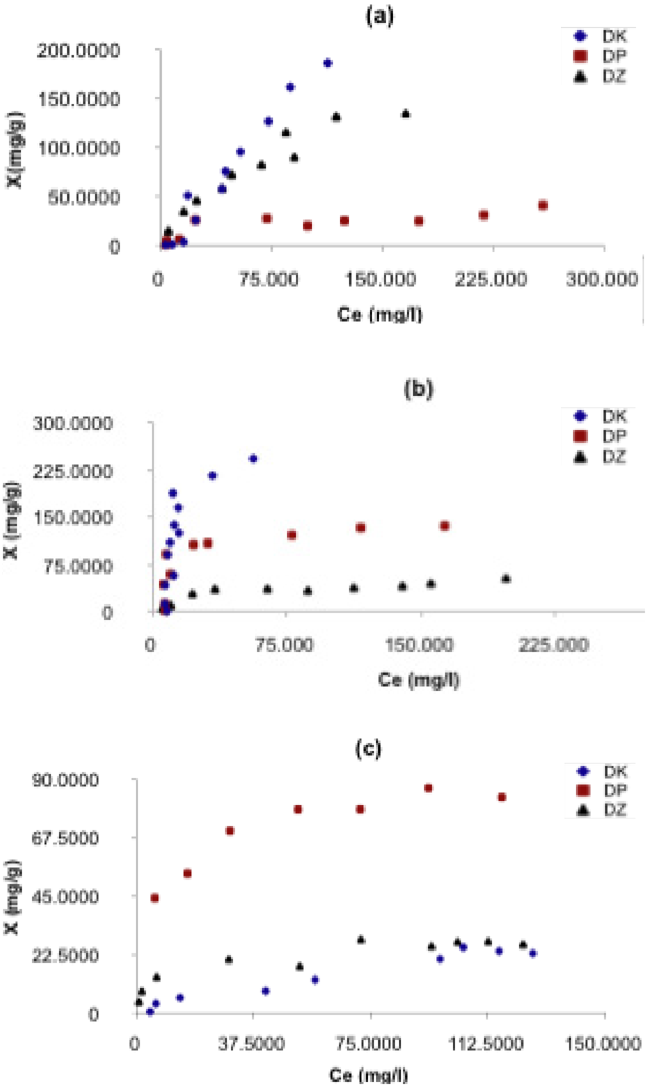


Fig. 3. Adsorption isotherms of (a) potassium hydrogen phthalate, (b) triton X100, (c) potassium dichromate at 298 K on activated carbons.

Table 3
Results obtained from the Langmuir equation applied to the adsorption isotherms of organic and inorganic compounds on activated carbons

Sample	Compounds	X_m (mg.g^{-1})	B (L.mg^{-1})	R^2
DP	Phthalate	54.94	0.02	0.9997
	Triton X100	58.14	0.02	0.9996
	Potassium dichromate	33.36	0.027	0.9967
DZ	Phthalate	120.09	0.16	0.9998
	Triton X100	188.68	0.25	0.9996
	Potassium dichromate	36.48	0.043	0.9977
DK	Phthalate	180.49	1.21	0.9999
	Triton X100	322.58	0.34	0.9998
	Potassium dichromate	65.92	0.01	0.9985

High correlation was found between X_m (amount adsorbed) and BET areas; the value of X_m for the different compounds increases with the surface area and porosity of the activated carbons. Thus, activated carbon DK with the highest surface area and the most developed porosity has the highest adsorption capacity for all compounds.

Reproducibility of the amount of potassium dichromate, triton X100 and potassium hydrogen phthalate adsorbed was fairly good, within an error of about 5% on activated carbon DK, DZ and DP.

The adsorption capacity of a given activated carbon for the different compounds is, in general, related to the nature of the compounds adsorbed.

The adsorption of potassium hydrogen phthalate and triton X100 (organic compounds) on activated carbons DK, DZ and DP is comparatively better than potassium dichromate (inorganic compound).

4. Conclusion

Date pits have a high potential as stated for activated carbons showing good performances as adsorbent for the removal of waters containing organic and inorganic pollutant compounds.

The characteristics of the activated carbons obtained depend on the activation process and the nature of the chemical reagent.

Chemical activation of the date pits with $ZnCl_2$ or KOH produces an activated carbon having a high specific surface area reaching about 880 and 1030 m^2/g for DZ and DK carbon, respectively.

The adsorption capacities of the activated carbon for the organic and inorganic pollutants studied depended on the degree of activation of the activated carbon and the nature of the compounds adsorbed. Thus, the adsorption capacity rose with increased development of carbon surface area and porosity.

The adsorption of organic compounds on activated carbons is comparatively better than for inorganic compounds.

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