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Rey-Mafull, Carlos A.; Cesar-Llopiz, Julio; Dachamir-Hotza; García-Gallardo, Raquel; Tacoronte-Morales, Juan; Tobella-Sabater, Jorge; Rockwood-Sánchez, Jaison
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Thermodynamic Parameters of Adsorption from Systems Activated Carbon Chlordiazepoxide and Activated Carbon-Diazepam

Parámetros termodinámicos de adsorción de los sistemas carbón activado-clordiazepóxido y carbón activado–diazepam

MSc. Carlos A. Rey-Mafull[I], PhD. Julio Cesar-Llopiz[I], PhD. Dachamir-Hotza[II], MSc. Raquel García-Gallardo[III], PhD. Juan Tacoronte-Morales[IV], MSc. Jorge Tobella-Sabater[V], Téc. Jaison Rockwood-Sánchez[VI]

mafull@imre.oc.uh.cu; jcllopiz@imre.oc.uh.cu; dhotza@gmail.com; r.garcia@rg.quimefa.cu; jaison@fq.uh.cu

[I]Instituto de Ciencia y Tecnología de Materiales (IMRE-UH), La Habana, Cuba; [II]Universidad Federal de Santa Catarina (UFSC), Florianopolis-SC, Brasil; [III]Laboratorio Farmacéutico "Reinaldo Gutiérrez", La Habana, Cuba; [IV]Centro de Ingeniería e Investigaciones Químicas (CIIQ), La Habana, Cuba; [V]Laboratorios MEDSOL, La Habana, Cuba; [VI]Laboratorio de Bioinorgánica de la Universidad de la Habana, La Habana, Cuba

Resumen

Se estudian los parámetros termodinámicos de la adsorción de clordiazepóxido y diazepam en seis carbonos activados: Norit B, BDH, Merck, Panreac, M1 y M, en fluido gástrico simulado. Los materiales se caracterizan por: FTIR, pHzpc y adsorción de N_2 a 77 K. La porosidad fue interpretada por las ecuaciones de Dubinin-Radushkevich y BET. Los resultados muestran la relación entre el aumento de la temperatura, las características de cada adsorbente y el comportamiento de estos fármacos. Los valores positivos de todas las entalpías isostéricas de adsorción determinadas a partir de la pendiente de Van 't Hoff ($R^2 > 97$), indican la naturaleza endotérmica del proceso de adsorción, así como la $\Delta G < 0$ con el incremento de la temperatura. La $\Delta G < 0$ en todos los casos explica el carácter espontáneo del proceso de adsorción. Los valores positivos ΔS dejan claramente que la aleatoriedad se incrementó en la interfaz sólido-solución durante el proceso de adsorción.

Palabras clave: carbón activado, adsorción, parámetros termodinámicos.

Abstract

It is study the thermodynamic parameters of chlordiazepoxide and diazepam drugs adsorbed onto six activated carbons: Norit B, BDH, Merck, Panreac, M1 and M, from simulated gastric fluid at pH 1,2 for 4 h were characterized by FTIR, $pH_{zpc,}$ and adsorption of N_2 to 77 K. The results of porosity were interpreted with the Dubinin-Radushkevich's models and BET' equation. By UV visible spectra residual drugs were monitored. The results show relationship between: increased of temperature, the characteristics of each adsorbent and the behavior of these drugs in acid solution. The positive values of all the isosteric adsorption enthalpies determined from the slope *Van't Hoff* plot ($R^2 > 97$), indicate the nature endothermic process of adsorption. The $\Delta G<0$ in all cases explained the spontaneous character of the adsorption process and the positive values of ΔS state clearly that the randomness increased at the solid-solution interface during adsorption process.

Key words: activated carbon, adsorption, thermodynamics parameters.

• Introduction

Due to activated carbon's (a.c) ability to absorb a wide variety of drugs and chemicals, and the fact that it is not absorbed from the gastrointestinal tract, it has been widely used in the treatment of acute poisoning (overdose). In addition to the ability of activated carbon to prevent oral absorption of drugs, it was also reported that oral administration of activated carbon enhances the elimination of many drugs /1–4/. Depending on the chemical structure of a molecule and the surface structure of an activated carbon, a molecule may interact with the basal carbon planes (non specific interaction), with a particular polar functional group on the surface (specific interaction) /5-9/. Activated charcoal is an amorphous form of carbon in that it has no regular atomic structure. The chemical nature of activated carbon combined with a high surface area, porosity distribution and superficial chemistry makes it an ideal medium for the adsorption of organic chemicals /5-13/.

Generally, adsorption is a natural process and usually is accompanied by a decrease in free energy change and entropy of the system. There are a number of factors can influence the process of adsorption: the concentration of drug molecule, surface area of the adsorbent, temperature, pH, ionic strength, solubility, chemical state of both adsorbent and adsorbate molecules and the kinetic effect. The study of thermodynamic parameters involved in the process of adsorption may help to clarify and highlight which could be the mechanisms involved in this interaction surface /14-19/. The quantitative contribution of these values will provide the necessary information that will allow direct studies of materials more efficient and effective for removing organic compounds of high toxic level which are proposed in this paper.

Benzodiazepines are medicines that help relieve nervousness, tension, and other symptoms by slowing activity of the central nervous system. Chlordiazepoxide (CDZ) and diazepam (DZP) was selected as a model compound in this research. Both are weak bases and may have some ionization state at pH 1,2. Although have the same basic molecular structure differ in terms of functional groups, substitution degree and solubility in water. The carbonyl group on the seven-member ring will likely hydrogen bond with the hydroxyl hydrogens on activated carbon. This belief is based on previous work which indicates that compounds having a carbonyl group are likely to interact with the hydroxyl groups on the activated carbon surface /20, 21/.

The aim of this study is to compare different commercial activated carbons to medical and pharmaceutical industries: Norit B EUR (Germany), Merck (Germany Germany), BDH (England), Panreac (Spanish), M (not purified-Cuba) and ML (purified-Cuba) in terms of their physicochemical characteristics and thermodynamic properties for the adsorption of CDZ and DZP in simulated gastric fluid (SGF) /22-24/.

• Materials and Method

Activated carbon

The activated carbon employed here was the industrial grade to application in medical pharmaceutical and biotechnological field. All materials studied are industrially produced and purchased in the market. Norit B test Eur (Germany), Panreac (Spain), BDH (England), Merck (Germany), ML (purified-Cuba) and M (not purified-Cuba). The activated carbon M (not purified) was supplied by the Plant Production Baracoa Activated Carbon and treatment subsequently by acid/base process (ML) /22-24/ The particle size of all samples is 100 % < 250 microns. All materials meet the requirements of USP 30 except M /25/.

Toxicity of Benzodiazepines

Chlordiazepoxide

Toxic reactions may be produced by plasma concentrations greater than 3 mg/L; plasma concentrations in the region of 20 mg/L may produce coma or death, but fatalities caused by **chlordiazepoxide** (figura 1a) alone are rare. Recoveries have occurred after the ingestion of single doses of about 2 g. The following postmortem **chlordiazepoxide** tissue concentrations were reported in a fatality in which death occurred 18 to 20 h after the ingestion of an unknown quantity of

chlordiazepoxide: blood 26,4 mg/L, bile 39 mg/L, kidney 11 µg/g, liver 10 µg/g, spleen 9 µg/g, urine 7,8 mg/L /26/. The following peak plasma concentrations were observed in a comatose adult subject who had ingested 1 g: **chlordiazepoxide** 20 mg/L after 6 h /27/.

Diazepam

Toxic effects may be produced by blood concentrations greater than 1,5 mg/L; fatalities caused by **diazepam** (fig. 1b) alone are rare, but may occur at blood concentrations greater than 5 mg/L.In a review of 914 drug–related deaths in which **diazepam** was involved it was found to be the sole cause of death in only 2 cases; postmortem concentrations of **diazepam** in the 2 cases were: blood 5 and 19 mg/L, liver 13 mg/kg in the first case /28/. In a fatality due to **diazepam** and alcohol ingestion, postmortem tissue–**diazepam** concentrations were: blood 1,3 mg/L, bile 4,5 mg/L, brain 2,4 µg/g, kidney 11,7 mg/kg, liver 11,4 mg/kg, urine 6,6 mg/L /29/.

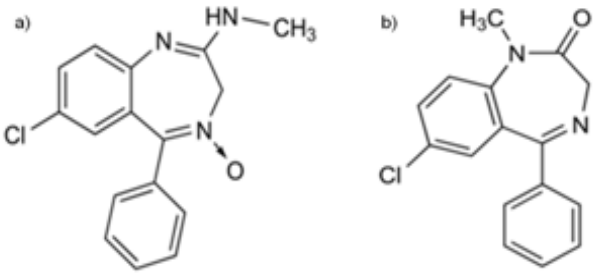

Fig. 1 Molecular structure of: a) chlordiazepoxide (pKa= 4,8) and b) diazepam (pKa= 3,3).

Simulated gastric fluid

The simulated gastric fluid was prepared according to the USP 30-NF 25; prepared with the active ingredient, CDZ (51 mg/L) and DZP (21mg/L), as described: 2 g of NaCl were dissolved in 7 mL of concentrated HCl, enrazing to 1 L with distilled water free of CO_2 by adjusting the pH of the solution to 1,2 /25/. Determination of UV spectrum (fig. 2) of CDZ and DZP and the calibration curve in SGF, was performed using a spectrophotometer UV/VIS [Ultrospec 2100 pro from Amersham Biosciences]. The optical density of all samples was determined with maximum absorbance at λ_{max} = 246, 308 nm (CDZ) and λ_{max} =242, 284, 366 (DZP) in the zone of Lambert Beer transmittance. The calibration curve was adjusted using least squares quadratic method, $R^2 > 99$. Each experiment was performed by triplicate.

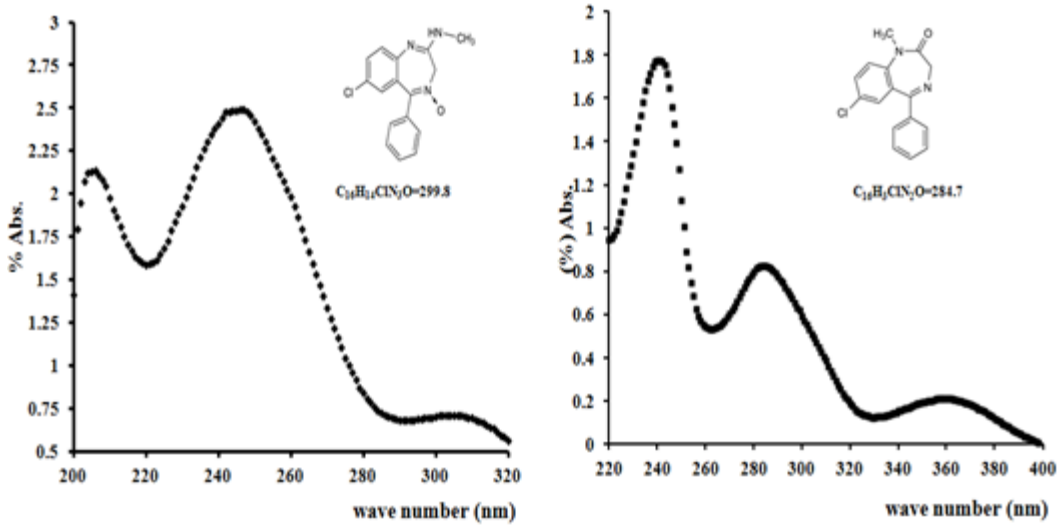

Fig. 2 UV-visible spectrum of chlordiazepoxide and diazepam.

Batch Equilibrium Adsorption Experiments and Analytical Method

The samples of ACs were analyzed granulometrically wet distribution, 100 % < 250 mμ. During adsorption process the amount of carbon used varied in the range of 0,06 g and was added to small vials, 6 mL, previously prepared with the drugs dissolved in SFG would be kept under constant stirring of 150 rpm for 4 h at different temperature 300; 306; 310 e 317 K. Once this time ending the samples were filtered to separate the solid phase and the liquid extract 5 mL solution for reading in the UV/VIS [Ultrospec pro from Amersham Biosciences].

Sampling was filtrated and removing 5 mL aliquots ending the experimental. Experimental solutions at desired concentrations were obtained by dilution of the stock solution with SGF preadjusted to pH 1,2. Previously established linear Beer-Lambert relationships were used in the concentration analysis. For the solutions with higher concentrations, dilution was required to operate the analysis in the Beer-Lambert region. % Absorbance readings are taken from the calibration curve which determines the equilibrium concentration corresponding to each of the points of the isotherm. The amount of adsorption at equilibrium, qe [mg/g], was calculated by eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad (1)$$

where C0 [mg/mL] initial concentration [t = 0] and Ce [mg/ mL] equilibrium [t=4 h],V [L] is the volume of the solution and M [g] is the weight of carbon.

Specific surface area determination activated carbon

Adsorption isotherms of N_2 (77 K) were obtained on a Quantachrome Autosorb surface analyzer system. The Brunauere Emmette,Teller (BET) (eq. (2), is the most usual standard procedure used when characterizing an activated carbon. The relative pressure $\left(\frac{P}{P_0}\right)$ range recommended in order to obtain the best straight line that is in the range of relative pressures of 0,05 to 0,3. To obtain the characteristic parameters of Eq. BET is necessary to plot $\left(\frac{P}{P_0}\right)$ *vs* $\frac{\left(\frac{P}{P_0}\right)}{V_0\left(1-\frac{P}{P_0}\right)}$ terms, where P (mm Hg) is the applied pressure, P_o (mmHg) vapor pressure of N_2 at 77 K, V_o (cm3/g) volume of adsorbed gas, V_m (cm^3) volume of gas adsorbed monolayer and C constant /30/.

$$\frac{\left(\frac{P}{P_0}\right)}{V_0\left(1-\frac{P}{P_0}\right)} = \frac{1}{(V_m C)} + \frac{C-1}{V_m C}\left(\frac{P}{P_0}\right) \qquad (2)$$

CO_2 Adsorption Isotherms (273K)

The isotherms were obtained on a surface analyzer ASAP 2010 Micromeritics System signature for CO_2 at 273 K. These isotherms were adjusted by the Dubinin-Radushkevich model of a single term developed on the basis of the theory of volumetric filling (TLLVM), which describes satisfactorily vapor adsorption microporous solid at temperatures below the critical temperature of the adsorbate, and which is expressed in Eq. (3), where Na: the amount adsorbed in the micropores at the equilibrium pressure Pe, Nm is the maximum adsorption in the micropores (mmol/g), n = 2: empirical parameter that depends on the structure of the adsorbent and the adsorbate, the adsorption characteristic energy E0 (kJ / mol) and the term A is the differential change of free energy, Eq. (4) /10, 30-34/.

$$N_a = N_m \exp\left(-\left(\frac{A}{E_0}\right)^2\right) \qquad (3)$$

$$A = -\Delta G = RT\ln\left(\frac{p_e}{p_0}\right) \qquad (4)$$

For the determination of maximum adsorption and the characteristic energy of the system use as logarithmic Eq. (5):

$$\ln N_a = \ln N_m - \left(\frac{RT}{E_0}\right)^2 \left(\ln \frac{P_0}{P_e}\right)^2 \quad (5)$$

Obtaining a straight line if the model is applicable, when plotted on a graph ln N_a *vs*. ln P0/Pe and whose intercept allows the calculation of maximum adsorption and slope characteristic energy E_0. Generating power E0 feature is related to the half aperture of the pores Wm (nm), Eq. (6), and the micropore volume (cm^3/g), where Vm is the molar volume (cm3/mmol) of the adsorbate at T (K) absolute. After calculating the maximum adsorption and the characteristic energy, the radius of gyration R_g (nm) is calculated using Dubinin-Steockli Eq. (7), where:

$$W_m = 4{,}669\,9 \exp^{-\left(0{,}066\,6 * E_0\right)} \quad (6)$$

$$R_g = 0{,}05 + 0{,}5 W_m \quad (7)$$

FTIR

FTIR spectra for different activated carbon samples (4 000–400 cm^{-1}) were recorded on a FTIR spectrophotometer (Nicolet 50X). The transmission spectrum of the samples was recorded using KBr pellet containing 0,1 wt % of carbon. Those pellets were dried overnight at 100 °C before the spectra were recorded.

Thermodynamic Parameters of Adsorption

The change in Gibbs free energy of the sorption process is related to the sorption equilibrium constant K_{ads} by the classical Van`t Hoff equation, Eq. (8) /36-38/.

$$\Delta G^0_{ads} = -RT \ln K_{ads} \quad (8)$$

Since $\Delta G^0_{ads} = \Delta H^0 - T\Delta S^0$ one gets where K_{ads} is obtained from the following relationships using the experimental data, Eq. (9-11):

$$\ln K_{ads} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (9)$$

$$K_{ads} = \left[\left(\frac{C_0 - C_e}{C_e}\right)\right]\left[\frac{V\rho}{w}\right] = \frac{q_e \rho}{C_e} \quad (10)$$

Substituting

$$\ln\left[\frac{q_e}{C_e}\right] = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (11)$$

where ρ is the density of the solution (g/L), ΔG^0 the free energy change (KJ/mol), ΔH^0 the standard enthalpy change (KJ/mol), T the absolute temperature (K), K_{ads} is the equilibrium constant of interaction between the adsorbate and the ACs surface and R is the universal gas constant (8,31 J/mol K) and ΔS^0 the entropy of the system. The ΔH^0 can thus be determined from the slope of the Van`t Hoff plot ln (q_e/C_e) *vs* 1/T and the intercept represent the entropy variation ΔS^0.

• Results and Discussion

Specific Surface Area Determination and Volume Distribution of Activated Carbon

The N_2 adsorption isotherms at 77 K are shown in fig. 3. The values obtained after evaluating Equation BET in its linear form are reported in table 1. Surface areas are in a normal range for this type of material. We distinguish 3 groups of surface areas corresponding to: a very high surface area of 1 400 m^2/g (NB), a second value of surface area of 720 m^2 / g (ML) and a third group with very close together and around 540 m^2/g (Ch3J, M and Panreac). With regard to surface area ratios established between these materials, with reference to the value of surface area of NB, and following the same old order is: 1 (NB); 1,98 (M1) and 2,65 (Ch3J); 2,63 (M); 2,65 (Panreac), respectively. Among the materials ML and M there is a difference between their surface areas of 102 m^2/g. This difference is mainly because ML is an activated carbon chemically purified /20-22/. Much of the inorganic material originally present in M were removed during the acid leaching process for exposing the removal a large part of the porosity obstructed in this particular case amounts to 34 %. These new unlocked pores allow access of the N_2 molecule (16,2 A^2 and 0,3 nm), without imposing any restrictions, thus contributing to further development of the internal surface area of 1,34 ML at times the internal surface area M. The surface area is simply the result of the entire area occupied by nanopores once the molecule is introduced into these N_2 to fill the volume corresponding to a monolayer (V_m), table 1.

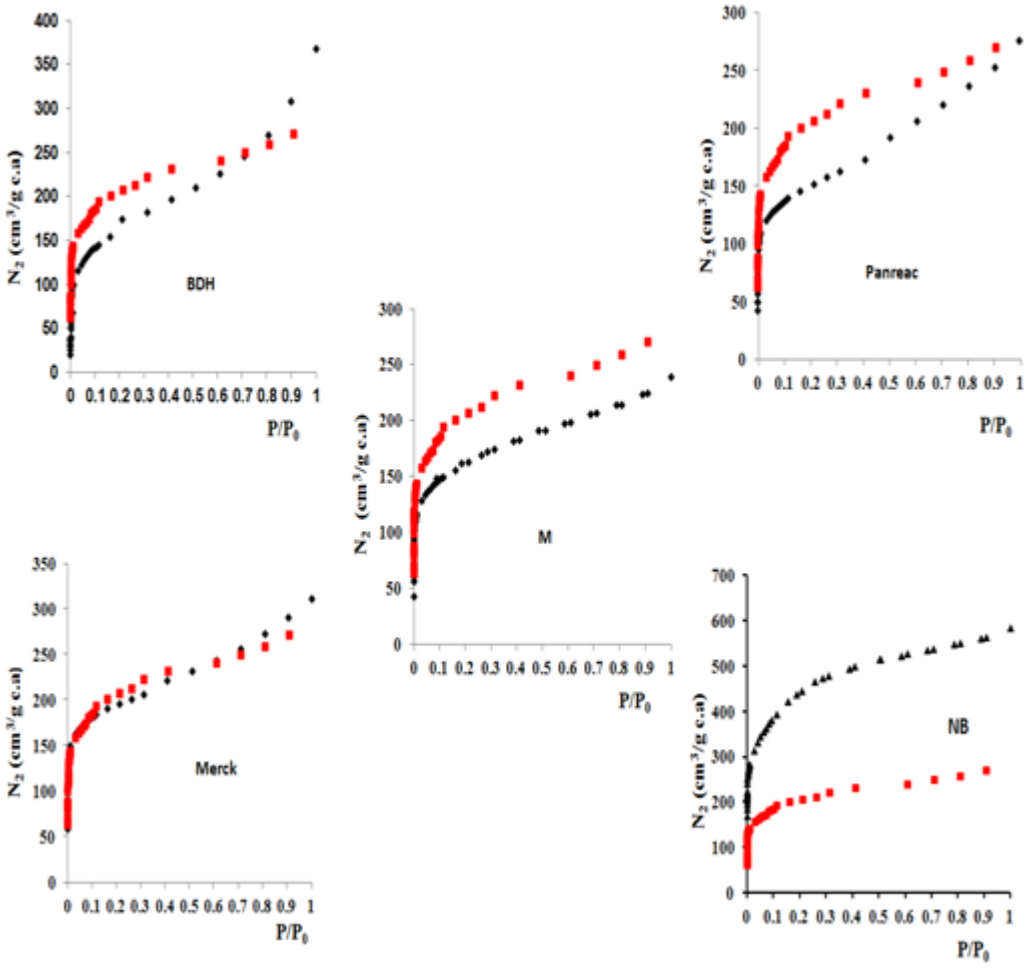

Fig. 3 N_2 adsorption isotherms at T = 77 K, ML (■).

TABLE 1 SURFACE AREA OF ACTIVATED CARBONS AND VOLUME OF MONOLAYER N_2 AT 77 K OBTAINED FROM EQUATION BET

Adsorbente	Surface area (m^2/g)	Monolayer volume (cm^3/g)
Norit B	1 430	328
ML	721	165
M	539	123
Merck	614	141
BDH	543	125
Panreac	539	123

The pore distribution and sizes of the same were calculated by different methods: DFT (density functional theory), HK (Howart - Kawasoe) and MP (micropore method), table 2. The calculation of micropores (0,3 to 2 nm) from the adsorption isotherm of CO_2 at 273 K reveals no substantial differences with those values calculated from the isotherm of N_2, which is indicative that these materials are predominantly microporous.

Although they do not fail to show a development of narrow mesopore (2 to 3 nm), fig. 4. It is precisely in this zone where most of these materials show a very similar textural development, with the exception of NB is further noted that the coals M and ML, in the area corresponding to pores with sizes between 2,3 to 3 nm, an increase in the volume of mesopores caused mainly during chemical cleaning of ML. Also found between 0,5 to 1 nm a significant increase in the volume of micropores in ML caused by the same reasons. Starting from 2 nm the rest of the coals are very specific trends in the development of micropore volume with significant variation between them, mainly due to the history of their derivation. These commercial materials are obtained by different activation processes and initial raw materials.

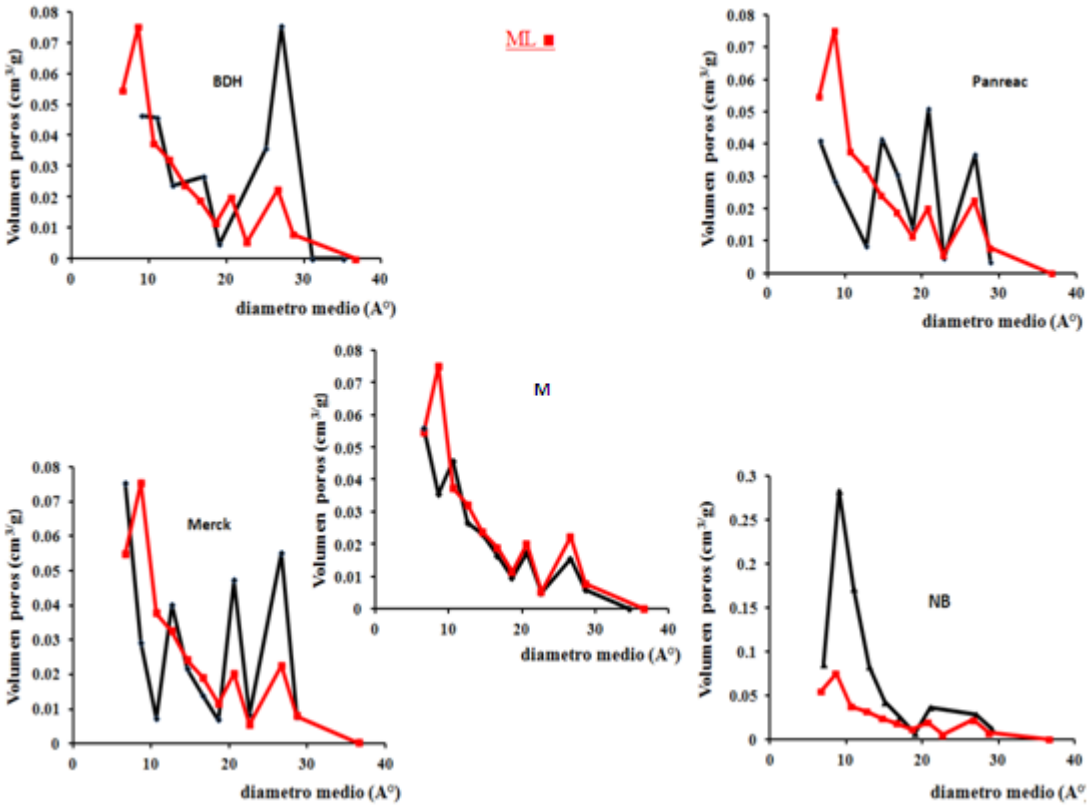

Fig. 4 Comparative study of the distribution of pores (MP method) by N_2 adsorption at 77 K, ML (■).

Identification of surface functional groups

In order to check the change in surface chemistry of the samples was determined FTIR spectra for the six samples of activated carbon, which have similarities and differences in the appearance of bands and variation in the intensity of the peaks.

Common bands were identified for the six activated carbons (3424, 2 852, 2921 and 1125 cm^{-1}), table 3. The band in 3424 cm^{-1} is assigned to carbonyl group -OH stretching. The peaks at 2852 and 2921 cm^{-1} due to the presence of aliphatic CH, CH_2, and CH_3 groups, and the one at1125 cm^{-1} is expected related to carboxylic –OH group /50-54/.

TABLE 2. TOTAL PORES VOLUME AND AVERAGE PORE SIZE OBTAINED FROM DIFFERENT METHODS: TDF: DENSITY FUNCTIONAL THEORY[1], HK METHOD: HOWART - KAWASOE[2] AND MP: MICROPORES METHOD[3]

Adsorbent	Pores volume (cm^3/g)	Average pore size (A°)
NB	0,81 [1]	7,51
	0,65 [2]	5,63
	0,77 [3]	
ML	0,40 [1]	7,85
	0,30 [2]	3,67
	0,31 [3]	
M	0,33 [1]	7,50
	0,24 [2]	5,43
	0,26 [3]	
Merck	0,42 [1]	7,51
	0,24 [2]	5,63
	0,31 [3]	
BDH	0,35	7,54
	0,23	5,21
	0,29	
Panreac	0,39 [1]	7,51
	0,23 [2]	5,43
	0,26 [3]	

Peak appears for wave numbers between 3 200 and 3500 cm^{-1} corresponding to the stretching vibration of OH functional group /39-42/. The sample BDH shows a peak is observed at 1710 cm^{-1} can be assigned either to lactone or to nonaromatic carboxyl groups, for which the C=O stretching has been reported to occur at 1712 cm^{-1} /38, 40/. The bands from 1 600 to 1 650 cm^{-1} can be assigned to C=O quinonics groups and it is common to the three carbons. The band 1 577 cm^{-1}, which belongs to BDH has not been interpreted unequivocally. This has been assigned to aromatic ring stretching couplet to highly conjugated carbonyl groups /40/. The peak 1 460 cm^{-1} which correspond to –OH carboxylic groups and C-H bond vibration /41/. Peak 1 435 cm^{-1} (M) correspond to inorganic ester presence. At 1 038 cm^{-1} BDH presents a peak which corresponds to alcoholic C-O vibration stretching. The peaks <950 cm^{-1} belong to vibrated aromatic ring /39-45/.

TABLE 3. CHARACTERISTIC BANDS AND ASSOCIATED FUNCTIONAL GROUPS IDENTIFIED BY FTIR SPECTROSCOPY

Bands (cm^{-1})	functional groups	Activate carbon					
		NB	Merck	Panreac	BDH	ML	M
3 400-3 500	-OH fenólicos	x	x	x	x	x	x
2 800-3 000	C-H, $-CH_2$, $-CH_3$ alifáticos	x	x	x	x	x	x
1 698	Aryl ketone C=O stretch	x					
1 720-1 730	C-O carbonilos	x					

(continuación tabla 3)

1 710	can be assigned either to lactone or to nonaromatic carboxyl groups, for which the C=O	x			x		
1 600-1 650	C=O quinónicos	x		x	x	x	
1 635	enlace del tipo N–H			x		x	
1 631	C=O stretching of amide	x				x	
1 580-1 585	anillos aromáticos acoplados a grupos carbonilos C=O altamente conjugados	x	x		x	x	x
1 460	OH en grupos carboxilos y vibraciones del enlace C-H	x	x		x	x	
1 440	Carboxylic -OH						x
1 100-1 200	C-O fenólicos o éteres	x		x	x	x	
1 125	OH carboxílico	x	x		x	x	x
1 040	C-O alcohólicos				x		
< 950	vibración anillos aromáticos C-H		x			x	x

Note: common bands x

Thermodynamics Properties

The thermodynamic properties analyzed are shown in tables 4-5 and fig. 5-8. In all cases it is observed that the adsorption enthalpies are positive for both the adsorption CDZ to DZP Theses indicate that the adsorption is endothermic in nature. When the magnitud of the ΔH values lies in the range of 2,1 to 20,9 and 80 to 200 KJ/mol for physical and chemical adsorption respectively /44, 45/. Enthalpy of adsorption is found to be in the range of 39,30 to 97,63 KJ/mol for the removal of CDZ and 9,83 to 67,44 KJ/mol for the removal of DZP respectively, indicating that DPZ need to involve less energy for adsorption. The enthalpy values obtained for the case of DPZ are less than 80 KJ/mol but in the majority of cases greater than 20 KJ/mol, except for BDH and Merck.

Generally, the ΔG is in the range of 0 to -20 KJ/mol and -80 to - 400 KJ/mol for physical and chemical adsorption /46-49/. The values of ΔG calculated are in the range of physical adsorption (tables 4-5). The positive value of ΔS0 suggest (tables 4-5), decreased randomness at the solid/ solution interface, and decrease in the degree of freedom of the adsorbed species. The value of ΔG is found to be in the range of -16,60 to -18,18 kJ/mol for the entire temperature range studied. The negative value of ΔG indicates the feasibility and spontaneity of the adsorption process in both cases /49, 50/.

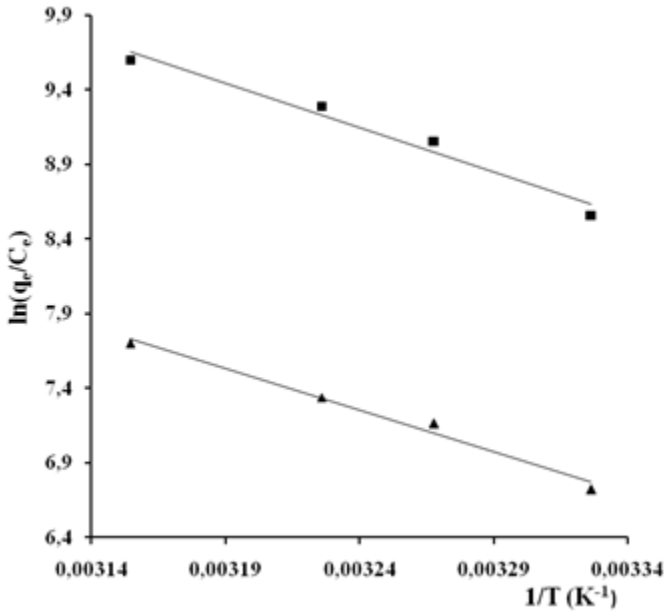

Fig. 5 Plot of ln (qe/Ce) *vs* 1/T for chlordizepoxide (ΔH_{ads} < 50 kJ/mol) on P(■) ML(▲).

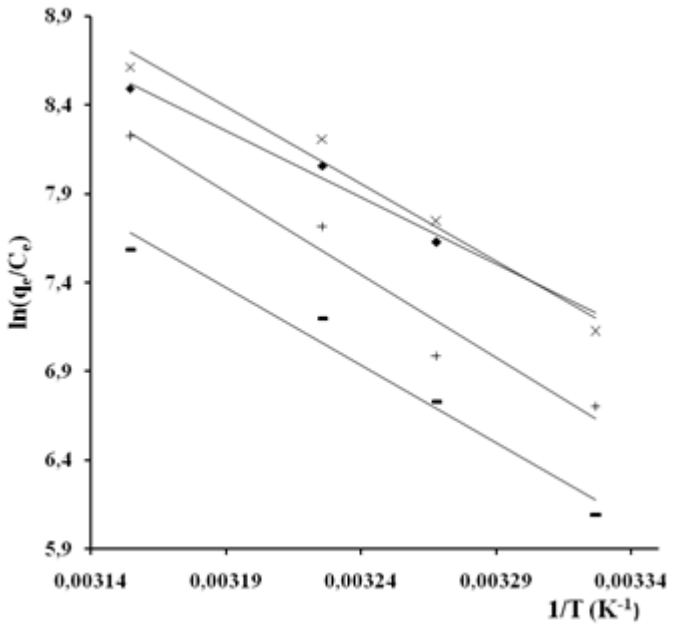

Fig. 6 Plot of ln (qe/Ce) *vs* 1/T for chlordiazepoxide (ΔH_{ads}>50 kJ/mol) on NB (♦) BDH (+) Merck (x) M (-).

TABLE 4. THERMODYNAMICS PARAMETERS FOR THE ADSORPTION OF CDZ ONTO ACS IN FGS

Adsorbate	Thermodinamics parameters				
	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)	$T\Delta S^0$ (K) (J/mol)	ΔG^0 (KJ/mol)	R^2
NB	97,63	380	113,91	-17,49	0,982
			115,95	-19,39	
			117,47	-20,76	
			120,12	-22,37	
ML	46,28	210	63,20	-16,79	0,980
			64,33	-18,21	
			65,18	-18,91	
			66,65	-20,28	
M	72,78	290	88,18	-15,22	0,974
			89,76	-17,11	
			90,94	-18,55	
			92,99	-19,99	
BDH	77,52	313	94,10	-16,75	0,964
			95,78	-17,77	
			97,04	-19,88	
			99,23	-21,66	
Merck	74,05	307	92,12	-17,80	0,971
			93,78	-19,69	
			95,00	-21,15	
			97,15	-22,69	
Panreac	39,30	200	61,25	-18,63	0,975
			62,35	-23,33	
			63,17	-23,93	
			64,59	-24,73	

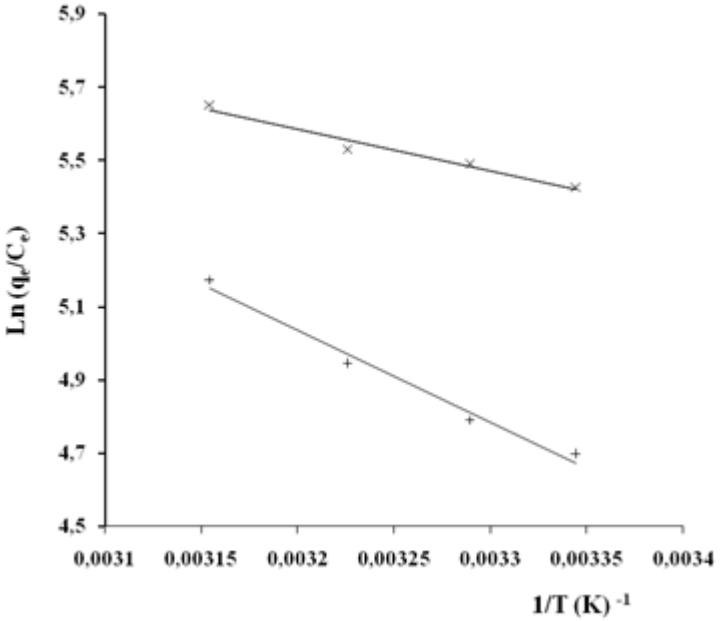

Fig. 7 Plot of ln (qe/Ce) *vs* 1/T for diazepam (ΔH < 20 kJ/mol) on BDH (+) Merk (x).

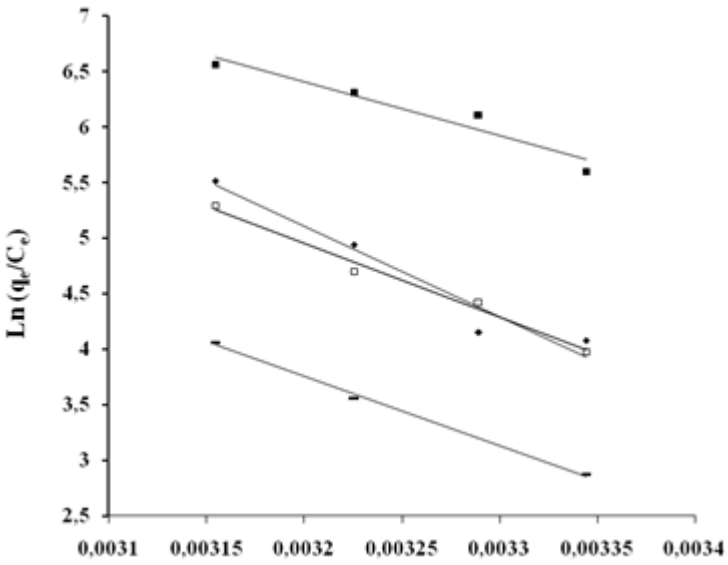

Fig. 8 Plot of ln (qe/Ce) *vs* 1/T for diazepam (ΔH > 20 kJ/mol) on (NB (♦) ML (■) M (-) Panreac (□)

TABLE 5 THERMODYNAMICS PARAMETERS FOR THE ADSORPTION OF DZP ONTO ACS IN FGS

Adsorbate	Thermodinamics parameters				
	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)	$T\Delta S^0$ (K) (J/mol)	ΔG^0 (KJ/mol)	R^2
NB	67,44	260	77,03	-10,13	
			78,31	-10,50	0,977
			79,86	-12,72	
			81,66	-14,53	
ML	55,39	220	65,30	-9,88	0,986
			66,39	-11,16	
			67,70	-12,10	
			69,23	-13,94	
M	51,84	200	58,89	-7,13	0,997
			59,87	-9,86	
			61,05	-9,18	
			62,43	-10,70	
BDH	20,87	110	32,55	-11,67	0,990
			33,09	-11,98	
			33,75	-12,84	
			34,51	-13,63	
Merck	9,83	80	23,31	-13,48	0,964
			23,70	-13,87	
			24,16	-13,88	
			24,71	-14,89	
Panreac	40,16	180	54,34	-13,91	
			55,25	-15,42	0,973
			56,34	-16,26	
			57,61	-17,29	

Conclusions

The positive values of all the isosteric adsorption enthalpies to both drugs indicate the nature endothermic process of adsorption and also the decreased of the free Gibbs energy (ΔG) with increased of temperature. Isosteric enthalpy of adsorption is found to be in the range of 39,30 to 97,63 KJ/mol for the removal of CDZ and 9,83 to 67,44 KJ/mol for the removal of DZP respectively, indicating that DPZ need to involve less energy for adsorption.

The enthalpy values obtained for the case of DPZ are less than 80 KJ/mol but in the majority of cases greater than 20 KJ/mol, except for BDH and Merck. To CDZ all values were more than 20 KJ/mol and less than 80 KJ/mol.

The variation of the ΔG<0 in all cases explained the spontaneous character of the adsorption process.

The positive value of ΔS^0 suggests decreased randomness at the solid/solution interface with some structural change in the adsorbate and adsorbent and increased entropy change with the increase of substitution degree.

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