

Adsorption of Acetic acid onto Activated Carbons obtained from Maize cobs by Chemical Activation with Zinc chloride ($ZnCl_2$)

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Abstract

The batch isotherm studies of the adsorption of acetic acid on five samples of activated carbon prepared from maize cobs was carried out. The initial concentration of acetic acid was varied between 0.007 and 0.3948 mol/L. The comparison of the adsorption capacities of these samples with that of a commercial activated carbon of animal origin were performed to evaluate the effect of process parameters. From the experimental data, the isotherm parameters of Freundlich, Langmuir, Temkin and Dubinin-Radushkevitch were calculated for all the samples and compared. For all the samples, these data fitted well the four isotherm models in the range of the concentrations tested. There exists a correlation between the physico-chemical properties of the activated carbons and the sorption processes.

Keywords: Batch, isotherm, adsorption, activated carbon, acetic acid.

Introduction

The characterization of porous solids is very useful in the study of their physicochemical properties; whose properties explain the adsorption capacities and the suitability of the adsorbent for a particular process. Several methods of characterizations of porous solids have been used but the adsorption of an organic compound appears paramount because it improves the understanding of the effectiveness of the adsorption of materials and allows the investigation of the adsorption mechanism and the effects of the adsorption constants¹⁻³. Adsorption is highly recommended for elimination of organic and inorganic pollutants at low concentrations. It requires a microporous adsorbent, capable of exchanging ions and creating chemical bonds⁴⁻⁷.

There are a wide variety of adsorbent materials such as silica gel, zeolites, synthetic adsorbents (resins), clays, activated alumina, industrial wastes, bioadsorbents and activated carbon^{1,4,5,7,8,9,10}. Activated carbon (AC) adsorbents are frequently used in the extraction of chemical species in both gas and aqueous phases. This is because of their high adsorption capacity, their porous structure and accessibility of their surface^{11,12}. They are used in water treatment and in industrial applications such as in the extraction of metal ions, air handling, and purification¹³, the discolouration of food in the food industry and in the pharmaceutical industry^{8,12-14}. In addition, the raw material for preparation of AC is abundant and its preparation is cheap.

This work is based on the identification and on the comparison of the adsorption properties of ACs obtained from maize cobs

under different operating conditions and different impregnation ratios. Acetic acid is an organic pollutant with a specific surface area close to that of nitrogen most often used in adsorption experiments, hence it is used in this study to characterize ACs samples¹⁵. Acetic acid like phenol, iodine, p-nitrophenol, methylene blue, caffeine and halophenols are reference substances for adsorption in aqueous phase, satisfying the conditions of Giles hence its choice as solute^{2,16-21}. Other researchers highlighted the adsorbent properties of vegetal activated carbons (Triplochiton Scléroxylon and Terminalia Superba) by adsorbing acetic acid¹⁷.

In this study the adsorption properties of ACs of maize cobs using the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms were determined and the comparison of these properties with those of a commercial activated carbon has been analyzed. The influence of physico-chemical properties of the activated carbon in the sorption process were also carried out.

Material and Methods

Adsorbents: Activated carbons: Five samples of activated carbon from agricultural wastes origin (maize cobs) obtained by chemical activation by $ZnCl_2$ (M10-60-100, M10-24-100, MAPZC3, MAPZC4 and MAPZC5) and a commercial activated carbon from animal origin were used in this study. The characteristics of these samples are summarized in table-1.

Acetic Acid: The acetic acid or ethanoic acid used (99.5%) is a transparent and colourless liquid with a bitter and penetrating odour. It is inflammable and corrosive, having a density of 1.049 at 20°C with an auto inflammation temperature of 427°C.

Table-1
Characteristics of different activated carbons samples

Adsorbent	Impregnation Ration (IR)	Physical aspect	pH	^c S.S.A by B.E.T (m ² /g)	Pores volume (cm ³ /g)	Cristallinity given by ^d XRD
M10-60-100	0.01	^a GAC	5.60	0.4312	0.000279	Amorphous
M10-24-100	0.005	GAC	5.50	5.2605	0.002713	Amorphous
MAPZC3	0.1	GAC	5.96	7.1314	0.002196	Amorphous
MAPZC4	0.15	GAC	5.96	11.6202	0.001852	Amorphous
MAPZC5	0.05	GAC	4.40	701.6853	0.393830	Amorphous
OA00	-	^b PAC	9.34	81.8638	0.176634	Cristallizes: hydroxyl-apatite, quartz, feldspar
Adsorbent	^e SEM results: surface aspect		^f EDX results		^g FTIR results : surface functional groups	
M10-60-100	Heterogeneous with macropores		C (80%); O (7%); Si(2%); Cl(6%); K (1%); Zn (2%)		-OH,-CH ₂ ,-CH ₃ ,-CO, CHO, -C ₆ H ₅ ,-CH-	
M10-24-100	Heterogeneous with macropores		C (80%); O (9%); Si (2%);Cl (6%); K (1%); Zn (2%)		OH,-CH ₂ ,-CH ₃ ,-CO, CHO, -C ₆ H ₅ ,-CH-	
MAPZC3	Heterogeneous with macropores and mesopores		C (80%); O(11%); C l(3%);Zn(2%)		-OH,-CH ₂ ,-CH ₃ ,-CO, CHO, -C ₆ H ₅ ,-CH-	
MAPZC4	Heterogeneous with macropores		C (60%); O (6%); Si (1%); Cl(4%); Zn (25%)		-OH,-CH ₂ ,-CH ₃ ,-CO, CHO, -C ₆ H ₅ ,-CH-	
MAPZC5	Homogeneous and compact with few micropores		C (80%); O (16%); Si(1%);Al(1%); Fe (1%);S(2%)		-OH,-CH ₂ ,-CH ₃ ,-CO, CHO, -C ₆ H ₅ ,-CH-	
OA00	Homogeneous with some micropores		C (10%);O (40%);Ca(29%);P(15%) Na (1%);Mg (1%)		-OH,-CH ₂ ,-CH ₃ ,-NH,-C≡C-, -CO,-CH-	

^aGAC: Granular activated carbon; ^bPAC: Powder activated carbon; ^cS.S.A: Specific Surface Area; B.E.T: Brunau-Emmet-Teller; ^dXRD: X-rays Diffraction; ^eSEM: Scanning Electronic Microscopy; ^fEDX: Energy Dispersive X-ray; ^gFTIR: Fourier Transformer Infrared; M10-60-100: Maize cobs activated carbon (light part) obtained with 10% ZnCl₂ solution and residence time=60minutes at T=500 °C; M10-24-100: Maize cobs (light part) activated carbon obtained with 10% ZnCl₂ solution and residence time=24 hour at T=500 °Cs; MAPZC3: Maize cobs (light part) activated carbon obtained with 2 g of solid ZnCl₂ at T=500 °C; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1 g of solid ZnCl₂ at T=500°C; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc

Batch Equilibrium Experiments: In each of the 8 (eight) screw cap Erlenmeyer flask of 250 ml, 0.1 g of activated carbon was placed and 20 ml of acetic acid solution added. The solution concentrations varied in increasing order, between 0.007 and 0.3948 mol/L. Each mixture was stirred with a magnetic stirrer at a temperature of 27 (±2) °C until equilibrium was attained. After agitation, each sample was filtered and the residual concentration measured by titration with sodium hydroxide solution.

The adsorbed quantities of acid, X, were obtained by subtracting the residual concentration at equilibrium C_e, from the initial concentration, C_o. Thus,

$$X = C_o - C_e \quad (1)$$

and Q_e, the quantity of acetic acid adsorbed per gram of adsorbent of mass m, from a an acetic acid solution of volume V, can be expressed as;

$$Q_e = \frac{C_o - C_e}{m} \cdot V \quad (2)$$

Results and Discussion

The properties of the activated carbon from maize cobs by the adsorption of acetic acid have been given by using the Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms. The equations of these isotherms and the parameters arising from their linear transformations are found in table-2.

Mode of adsorption: The sorption isotherm is the relationship between the sorbate in the liquid phase at equilibrium with the solid phase at constant temperature.

Figure-1 represents the adsorption isotherms of acetic acid onto activated carbon from maize cobs and onto a commercial activated carbon sample from animal origin OA00. Generally, for all the samples, the reduction in the number of available acid sites as the concentration of the acetic acid increases is observed. In addition, the higher the initial concentration, C_o, the higher the quantity adsorbed at equilibrium which indicates a strong adsorption between the active sites of the activated carbon and the molecules of acetic acid. But individually, each sample has particular characteristics and a specific mechanism of adsorption.

Table-2

Isotherms equations used in the determination of the adsorbent properties of the activated carbon of maize cobs

Isotherm	Equations	Transformations		Slope	ordinates at the origin
		x-axis	y-axis		
Freundlich	$Q_e = a_F \cdot C_e^{b_F}$ (3)	$\ln C_e$	$\ln Q_e$	b_F	$\ln a_F$
Langmuir	$Q_e = \frac{K_L \cdot C_e}{1 + a_L \cdot C_e}$ (4)	$\frac{1}{C_e}$	$\frac{1}{Q_e}$	$\frac{1}{K_L}$	$\frac{1}{Q_0}$
Temkin	$Q_e = \frac{R \cdot T}{b_T} \ln(A_T \cdot C_e)$ (5)	$\ln C_e$	Q_e	$\frac{R \cdot T}{b_T}$	$(\frac{R \cdot T}{b_T}) \ln A_T$
Dubinin-Radushkevich	$Q_e = Q_{DR} \cdot \exp \left[-B_{DR} (R \cdot T \ln(1 + \frac{1}{C_e})^2) \right]$ (6)	$[\ln(1 + \frac{1}{C_e})]^2$	$\ln Q_e$	$-B_{D-R} \cdot R^2 \cdot T^2$	$\ln Q_{D-R}$

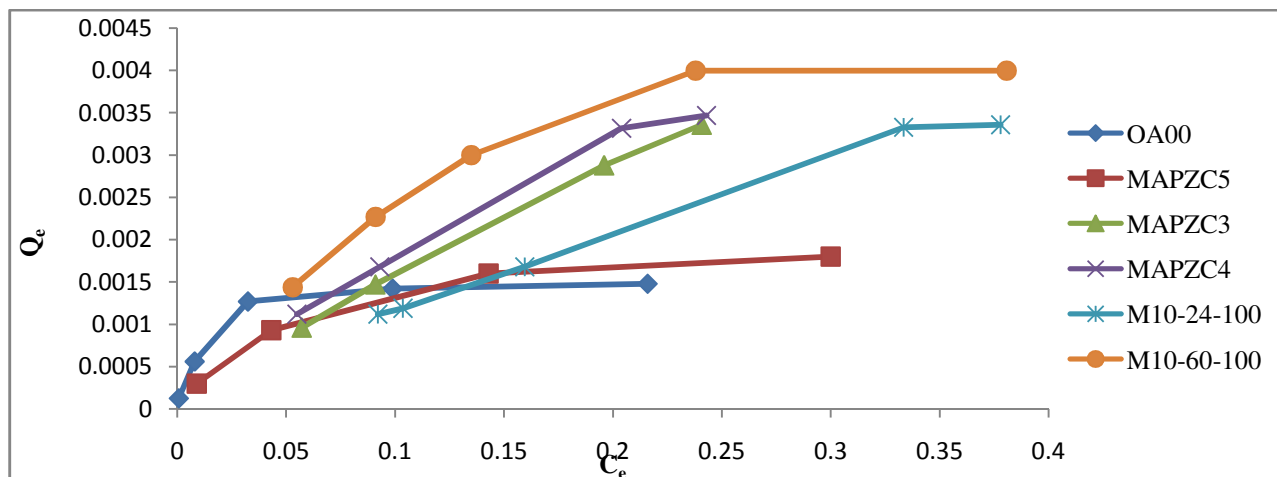


Figure-1
 Isotherms of adsorption of the acetic acid on the activated carbon of maize cobs and of sample OA00

The first part of these isotherms of samples MAPZC4, MAPZC5, MAPZC3 and M10-60-100 (figure-1) appears to be of type I, characteristic of a medium containing mainly micropores (pore radii less than 2 nm).

There is a saturation offset at concentrations $C_e = 0.2, 0.2, 0.1$ and 0.24 mol/L for samples MAPZC4, MAPZC5, MAPZC3 and M10-60-100 respectively, marking the end of the formation of molecular monolayer on the AC surface. It is important to note that the filling of the monolayer is almost linear for samples MAPZC3 and MAPZC4. For these four samples, the actual adsorption of acetic acid begins at higher concentrations with the formation of multilayer (figure-1). But here for all samples (except OA00 isotherms unlike conventional types I), adsorption does not occur only at low concentrations, which means that the mesopores (pore radii between 2 nm and 50 nm) represent a fairly high percentage and also participate significantly in the adsorption phenomenon. The third part of the curve representing the phenomenon of physisorption is nonexistent. These

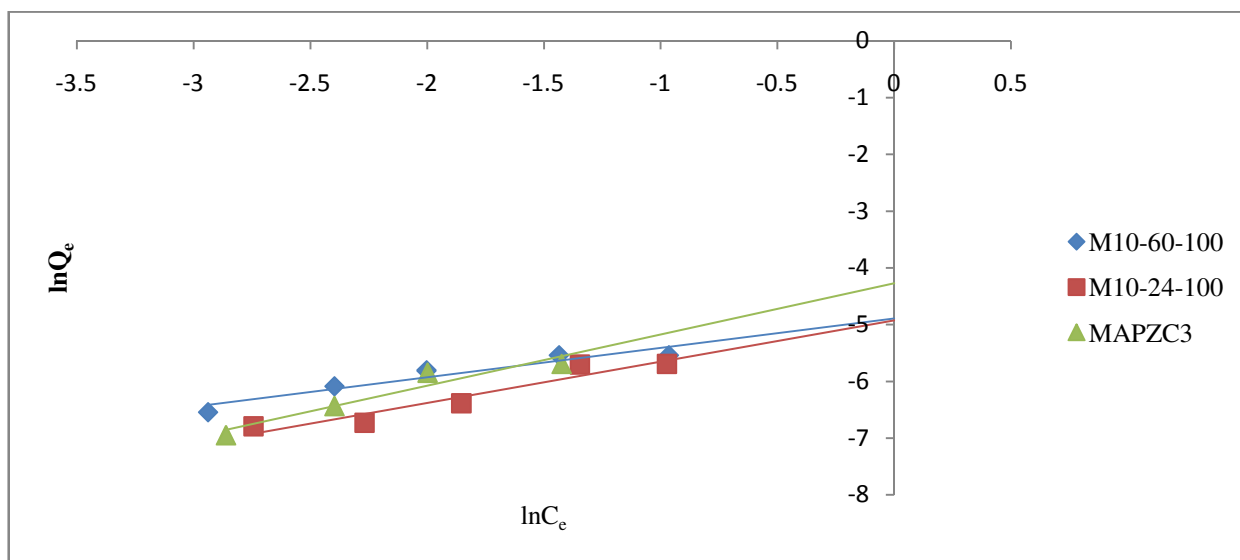
observations showed a macro environment and a multilayer adsorption with progressive thickening of the adsorbed layer. The adsorption isotherm of sample M10-24-100 appears to be of type III (multilayer adsorption resulting in macropores as majority and weak interactions between acetic acid and carbon) but the presence of a horizontal saturation plateau at the equilibrium concentration of $C_e = 0.3375$ mol/L would suggest adsorption of type V (middle mesoporous with weak interactions between acetic acid and activated carbon with formation of multilayer at low concentrations) but with no vertical saturation plateau. This ambiguity is actually due to the fact that the mesopores and macropores are both in considerable quantities in this coal: the mesopores leading to an adsorption of type V and macropores in an adsorption of type III. The same authors quoted previously obtained identical curves during the adsorption of acetic acid on activated carbon of vegetal origin (Triplachiton Scléroxylon and Terminalia Superba) and also showed that adsorption increased when initial concentration increased¹⁷. These authors showed that the adsorption is of type

I according to the classification of Langmuir (adsorption with monomolecular saturation of the monolayer of activated carbons during the filling)¹⁷.

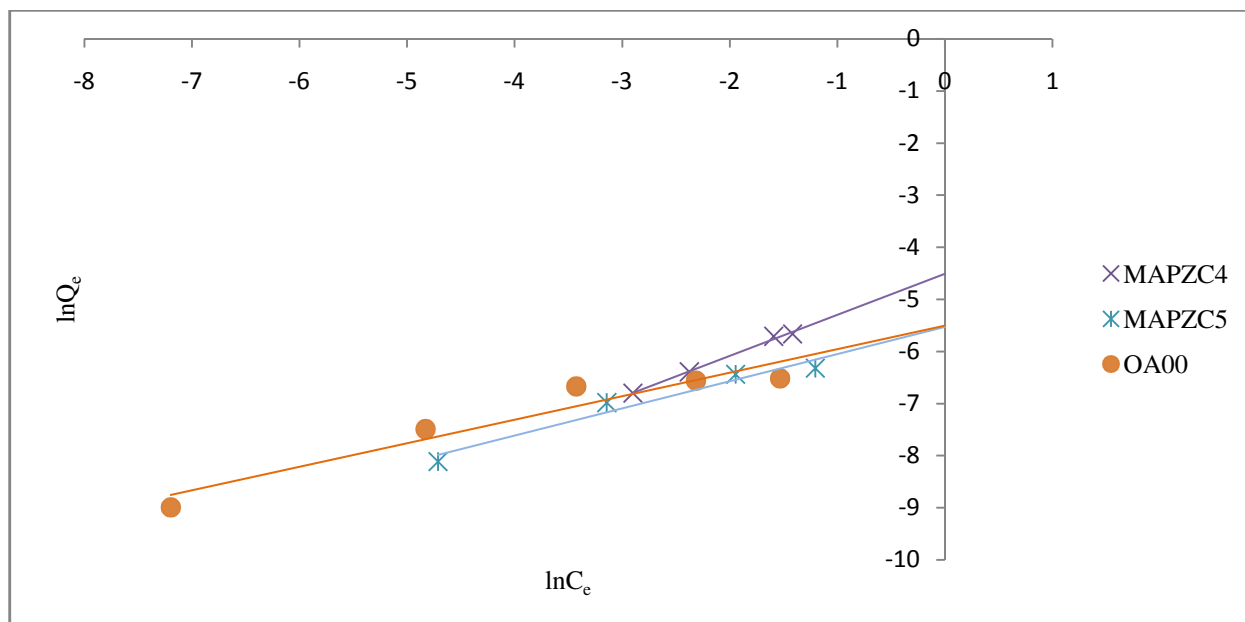
with respect to the acetic acid, even less on the nature of equilibrium forces of the bonds between the sites of AC and the acetic acid.

Influence parameters of preparation on the adsorption of the acetic acid: The observation of the quantities of acetic acid adsorbed at equilibrium (figure-1) shows that coals having weak impregnation ratios (IR) ($ZnCl_2$ /maize cob in table-1) tend to adsorb much more, the acetic acid. But these great values do not give any information on the affinity of these activated carbons

Adsorption properties: The various constants characteristics of adsorption for each model and each sample were obtained by using MS Excel of Windows. All the constants deduced from the linear transforms of the different isotherms (figure-2 to figure-5) are found in table-3

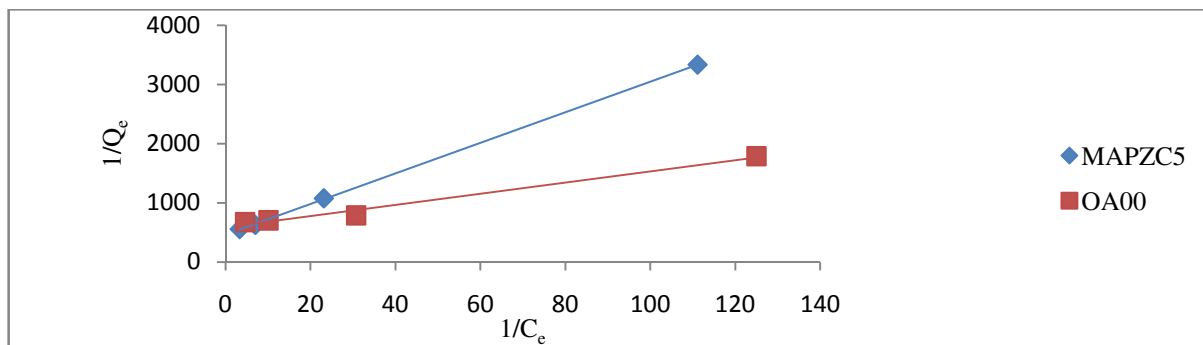


(a)

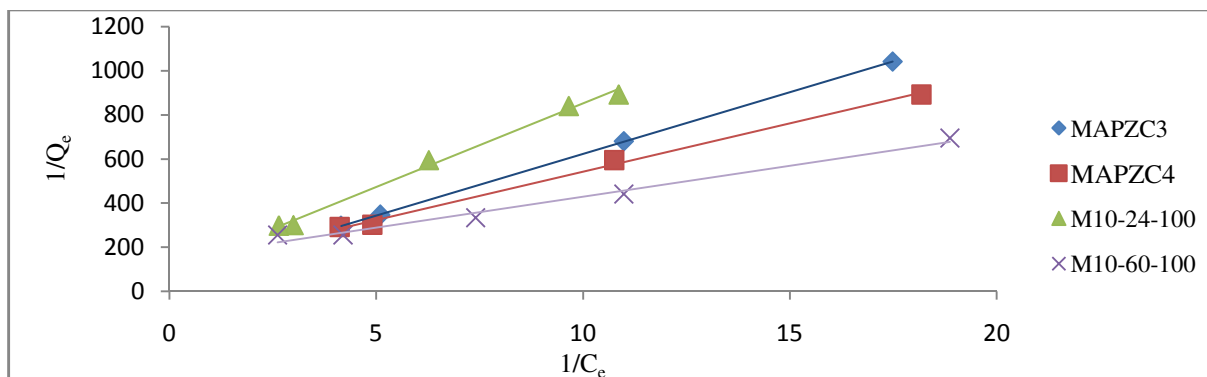


(b)

Figure-2
Linear transforms of Freundlich isotherm



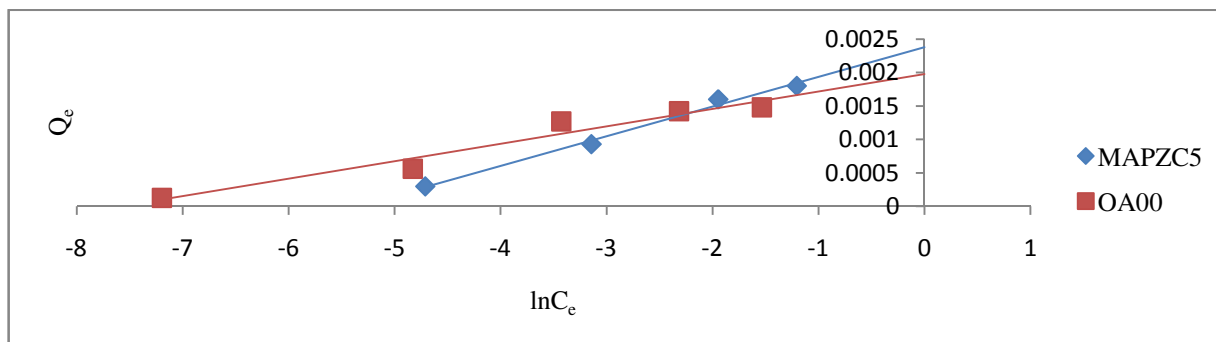
(a)



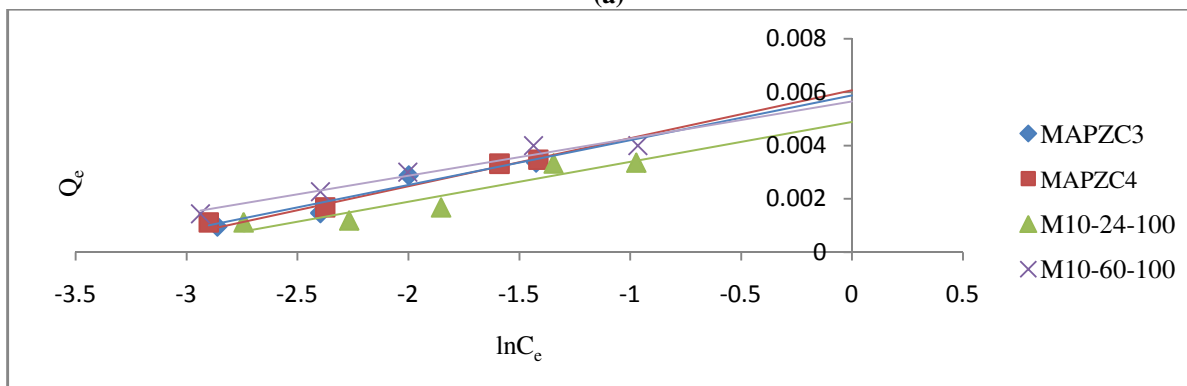
(b)

Figure-3

Linear transforms of Langmuir isotherm



(a)



(b)

Figure-4

Linear transforms of Temkin

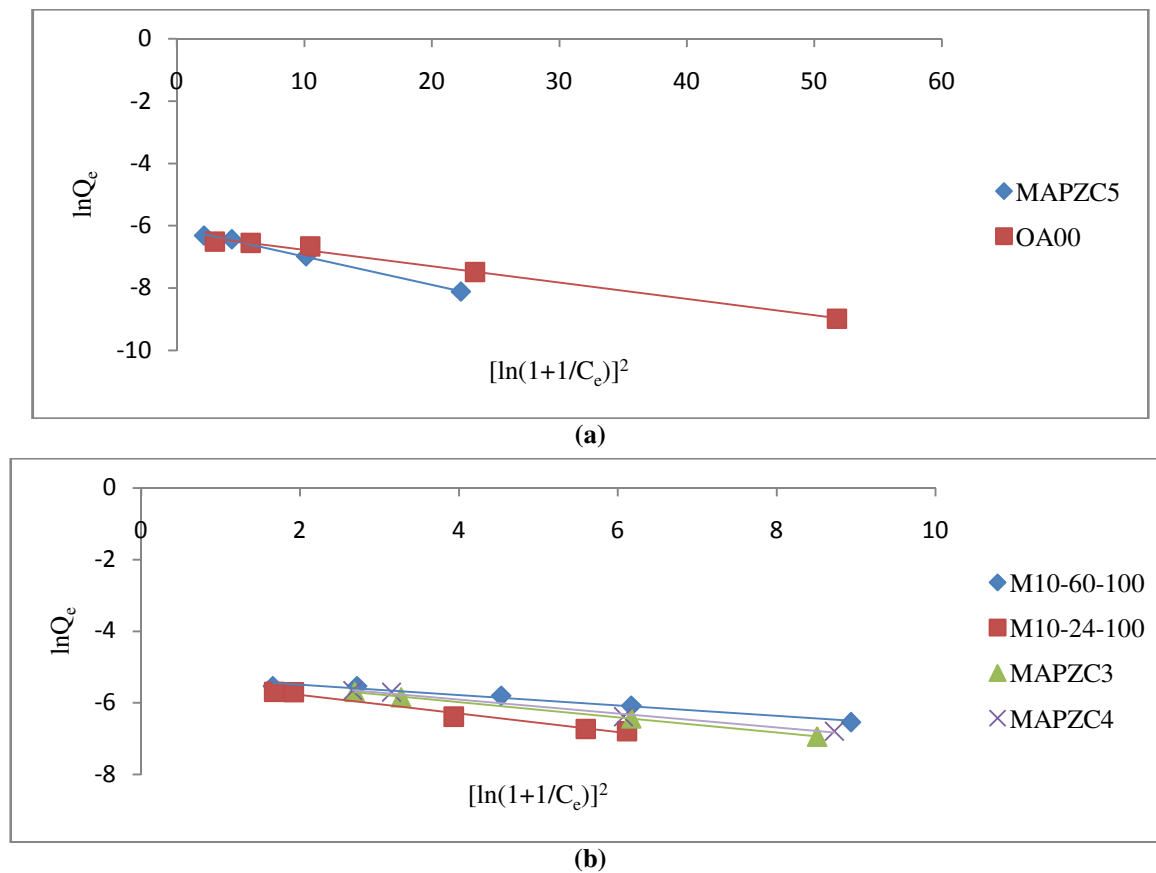


Figure-5
Linear transforms of Dubinin-Radushkevitch

Table-3
Adsorption constants

Adsorbent	Langmuir				Freundlich		
	K_L mL/g	A_L L/mol	Q_L mmol.g ⁻¹	R^2	b_F	a_F mmol/g (.mol/l) ^{-1/n}	R^2
M10-60-100	35.57	5.26	6.77	0.983	0.572	0.0075	0.910
M10-24-100	13.20	1.24	10.62	0.994	0.822	0.0072	0.914
MAPZC3	18.36	1.17	15.65	0.999	0.903	0.0139	0.920
MAPZC4	22.82	2.38	9.57	0.996	0.789	0.0111	0.995
MAPZC5	36.62	17.90	2.16	0.999	0.522	0.0040	0.956
OA00	184.2	145.25	0.92	0.997	0.451	0.0041	0.923
Adsorbent	Temkin			Dubinin-Radushkevitch			
	b_T (J.g/mol ²).10 ⁶	A_T L/mol	R^2	B_D (mol ² /J ²).10 ⁹	Q_D (mmol/L)	E kJ/mol	R^2
M10-60-100	1.78	58.64	0.949	23.28	5.47	4.64	0.976
M10-24-100	1.46	19.30	0.980	41.98	5.20	3.45	0.985
MAPZC3	1.48	28.87	0.947	34.78	5.47	3.79	0.996
MAPZC4	1.74	33.30	0.982	30.98	5.81	4.02	0.990
MAPZC5	5.62	212.86	0.991	14.57	2.29	5.86	0.998
OA00	9.75	1765.08	0.979	6.71	1.85	7.75	0.998

The adsorption constants of a given isotherm allows, not only to evaluate the adsorbent properties of a sample, but also to determine if adsorption is favourable or not. The constant of

Langmuir K_L measures the intensity of adsorption. Infact, the higher the K_L value, the stronger the affinity between the acetic acid and the activated carbon. It thus comes out from this that

commercial sample OA00 has the strongest affinity for the acetic acid (184.20 mL/g) and the sample M10-24-100 the weakest (13.20 mL/g) in the range of considered concentrations. The origin of the precursor used for the preparation of the various samples could explain these differences, the nature of the surfaces obtained by SEM studies can also explain these differences: maize cobs activated carbons surfaces are heterogeneous with a great amount of macropores whereas a commercial sample surface is homogeneous in which some microporosities are observed. In addition, the linear correlation coefficients R^2 for this model are all higher than 0.96 making the Langmuir model suitable to explain the adsorption of acetic acid onto activated carbon from maize cobs²².

The values of the Freundlich constants, b_F determines if the adsorption of the acetic acid on the studied activated carbon is favourable or not. If the exponent $n = 1/b_F$ lies between 1 and 10, the adsorption is favorable²³. All the values of n lie between 1 and 10 and vary in the interval 1.107 - 4.098 on the basis of which it appears that the adsorption of the acetic acid on the activated carbon from maize cobs is favourable. The functional groups (showed by FTIR results in table-1) present at the surfaces of these materials particularly the carbonyl (CO) and the hydroxyl (OH) explained why the sorption is favorable in the maize cobs activated carbon particularly. However, Freundlich model has values of correlation coefficient lower than 0.96, in the samples OA00, MAPZC5, M10-24-100, M10-60-100 and MAPZC3 which restricts the utility of the model to describe acetic acid adsorption in these samples²².

The Temkin adsorption model explains the nature of adsorbents-adsorbate interactions while giving energetic information of the sorption process. If Temkin's constant, b_T , is positive, then the adsorbent-adsorbate interactions are gravitational and in the contrary case, they are repulsive^{24,25}. For all the studied samples, these constants are all positive; thus, the acetic acid-carbon interactions are gravitational. Attraction is much stronger for commercial sample OA00 with a value $b_T = 9.7 \times 10^6 \text{ J.g/mol}^2$, confirming the result obtained by the Langmuir model. In addition, the activated carbon from maize cobs with strongest attraction onto acetic acid is MAPZC5 sample with a value of $b_T = 5.62 \times 10^6 \text{ J.g/mol}^2$. These results further explain why these two samples (OA00 and MAPZC5) have values of R^2 higher than 0.96²². This strong attraction can also be explained by the values of specific surface area of these two samples (81.36 m²/g and 701.68 m²/g respectively) which are by far the greatest for all the coals studied.

The Dubinin-Radushkevich model gives information on the binding energies. The calculation of the average free energy, E , of a molecule of adsorbent, expresses the energy released when a molecule of adsorbate passes from the solution into the adsorbent²⁶. The energy was calculated from the equation 7 below:

$$E = \frac{1}{\sqrt{2B_{D-R}}} \quad (7)$$

These energies for the activated carbons studied vary between 3.451 kJ/mol for M10-24-100 sample and 7.753 kJ/mol for sample OA00 (see table-3) and are all characteristics of the Van der Waals forces²⁷. It appears that just like in the cases of the Temkin adsorption isotherm, samples OA00 and MAPZC5 are strongly related to the acetic acid. It is important to note that the Dubinin-Radushkevich model seems to be more general, so it is very suitable to explain the adsorption of acetic acid on various materials. That is why all the values of R^2 are higher than 0.96 for this model²².

The values of the adsorption capacities determined by the Langmuir and Dubinin-Radushkevich models (table-3) show that the higher the pH of coals the higher these values are for all the activated carbon samples from maize cobs. This is because acetic acid has a high propensity to react more with compounds tending to be basic. In other hand there are very great differences between the capacities of adsorption in the two models (except the samples OA00 and MAPZC5) due the fact that the Dubinin-Radushkevich model is more general, and then takes into account a greater number of active sites than the Langmuir model.

The material OA00 crystallizes as observed from the XRD results (table-1). This carbon has the greatest affinity for the acetic acid. This strong affinity is due to minerals present in this material mainly the hydroxyl-apatite although the SEM results (table-1) of this sample indicated that it is not very porous. The absence of minerals in the maize cobs activated carbons may explain why the adsorption capacities are lower than that from the animal origin. But for the sample MAPZC5 obtained from the hard part of the cobs, the high value of specific surface area explains the great affinity of this sample *Vis a Vis* acetic acid.

Conclusion

The adsorption of acetic acid on five samples of activated carbons of vegetal origin (maize cobs) and a commercial activated carbon of animal origin were studied. The ACs from maize cobs was obtained by various preparation methods by chemical activation with zinc chloride ZnCl_2 . The adsorption isotherms of samples M10-60-100, MAPZC5, OA00, MAPZC4 and MAPZC3 appear to be of type I and that of the M10-24-100 appears initially to be of type III but also presents the characteristics of a type V isotherm. Generally, the porosity and the method of preparation of various samples are responsible for different types of adsorption isotherms with respect to acetic acid. The application of the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich adsorption models, helps to highlight the adsorption properties of each sample. It shows that some activated carbon sample like MAPZC5 obtained from the hard part of the maize cobs had better adsorption properties than the studied industrial carbon of animal origin. Thus, the maize cobs activated carbon can be used to purify water and waste water. Sorption technology can be a feasible alternative for removing acetic acid in solutions and characterizing activated carbons.

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