Water treatment by activated carbon resulting from the biomass: Application to the phenol (2.4DCP)

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Abstract – Water is a basic unit for the continuation of the life. But today it is seen that the ground and water pollution, accidentally or voluntarily by certain chemicals of industrial origin (hydrocarbons, phenols, dyes...) or agricultural (pesticides) became currently a crucial problem and great concern, since it constitutes a source of environmental pollution .The use of natural resources renewable of low cost and available in great quantities makes it possible to develop a product having an impact reduced on the environment. Among the natural resources most usually used the activated carbon which there remains the material of choice for its expensive effectiveness but what concretely causes a complementary research for the manufacture of new less expensive adsorbents   materials starting from matters which are not traditional, starting from the biomass. This exploratory study confirms the interest and the feasibility of the use of materials rich in carbon, prepared starting from the residues of agriculture and chemically activated by various agents (H_3PO_4, H_2SO_4 and HCl). We present, initially, the various procedures followed for the preparation and the modification of these materials used and then we will describe the various techniques used for their characterizations. These activated carbons prepared are used as adsorbents for the purification of phenol water in charge in particular the 2,4DCP. The influence of the various parameters such as the initial concentration, the time of contact, the pH and the temperature were studied.   The modeling of the kinetics obeys the model of pseudo-second order and the model of Langmuir describes correctly the isotherms of adsorption. The values of $\Delta G°$ and $\Delta H°$ show that the process of adsorption studied is spontaneous and endothermic.

 Key words: Elimination, residues of agriculture, activated carbon, activation, 2,4DCP

I. Introduction

The water pollution by the organic matter took the great part of the environmental concerns. Therefore, it matters that the concentrations of these pollutants are weakest possible to ensure a good quality of water and consequently to ensure the human wellbeing. Pollution by chlorophenols poses serious problems because of their remanence in the medium and of their toxicity. In particular the 2,4-dichlorophénol (2,4-DCP), pollutant chlorophenolic most frequently met in the hazardous waste sites, soils, wastewater and drinking water, and has now been designated by the Environmental Protection Agency (EPA) as a priority pollutant [1]–[2].

Different techniques from decontamination of polluted water were developed such as coagulation, flocculation, membrane filtration

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and adsorption [3]. The technique of adsorption is the method most favorable for elimination of chlorophenols. It became an analytical method of choice due to its high efficiency, simple and safe treating processes, versatility for different water systems and low cost [4], flexibility and simplicity [5] and the high-quality of the treated effluents [6].

Various solid materials (activated clays, zeolites, aluminas, mud, biomasses, residues agricultural, industrial products and activated carbon…) being able to be used in processes of water treatment. Adsorption by the synthesized activated carbon, starting from the residues of agriculture is the object of several recent studies because of their very significant porous structure, their great specific surface and their great capacity of adsorption [7].

The objective of our study with for goal to prepare activated carbons starting from waste of agriculture (lemon peels) in order to obtain an applicable product in the field of water treatment.

II. Experimental

A. Materiel and chemicals

The material gross used in this study is the peels of a vegetable material: lemon fruit. Lemon peels were collected locally, H_3PO_4, H_2SO_4, HCl and NaOH. 2,4 dichlorophenol (2,4 DCP) (MW=163.1g/mol, λmax = 284nm and pKa = 7.85) was obtained from Sigma–Aldrich.

B. Preparation of adsorbents

The lemon peels were washed several times with water distilled until obtaining clear flushing water. Then they were dried in a drying oven and they were crushed and filtered to obtain it from a rough material.

The activation of coals was quoted several times in literature [8]. In this study, the lemon peels were activated by the three acids (H_3PO_4, H_2SO_4 and HCl) with the same procedure. As an example 10 g of rough material were dispersed in 250 ml of a phosphoric acid solution (0.6M) under agitation during 30 min at ambient temperature and a stirring velocity

equalizes with 150tr/min. After centrifugation, the precipitate obtained is put at the drying oven during 24 hours with 50 °C, and then with 120°C during 1heure, then crushed, filtered until obtaining a powder homogeneous black.

The samples obtained were washed several times with cold distilled water and then dried to 50°C during 24 hours. To improve the structural properties, the samples activated with the three acids are put in a furnace at calcinations during one hour (1h) at 600°C. The samples obtained are noted: CA $_{cal}$ -H_3PO_4, CA $_{cal}$ - H_2SO_4 and CA $_{cal}$ -HCl.

C. Characterization of adsorbents

The morphology and the surface chemistry of the prepared adsorbents were investigated by the Fourier transform infrared spectroscopy (FTIR), the surface acidity/basicity and the point of zero charge (pHpzc).

The FTIR study was carried out using FTIR 8400S Shimadzu having a standard mid-IR DTGS detector and FTIR spectra were recorded in the range of 400–4000 cm^{-1} with KBr pellet technique.

Surface acidity and basicity are important criteria describing the surface chemistry of the adsorbents, the surface acidity was estimated by mixing 0.1g of the adsorbents (LP, CA$_{cal}$-H_3PO_4, CA$_{cal}$ - H_2SO_4 and CA$_{cal}$ -HCl) with 50 ml of 0.1M NaOH solution in a closed flask, and agitating for 48 h at room temperature. The suspension was decanted, and the remaining NaOH was titrated with 0.1M HCl. The surface basicity was measured by titration with 0.1M NaOH after incubation 0.1g of witch adsorbents with 0.1M HCl.

The pHpzc was determinate according to the method described by Benhouria et al [9]. In brief, the initial pH (pHi) of aqueous solutions of distilled water (10mL) was adjusted in the pH range of 2–12 using 0.1MHCl or NaOH. Then, 10 mg of adsorbent (CA $_{cal}$-H_3PO_4, CA $_{cal}$ - H_2SO_4 and CA $_{cal}$ -HCl.) was added to each solution. The dispersions were stirred for 24 h at ambient temperature and the final pH of the solutions (pHf) was determined. The point of

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zero charge (pHpzc) was obtained from the plot of (pHf-pHi) versus pHi.

D. Adsorption studies

To study the effect of contact time on the removal of 2,4 dichlorophenol (2,4 DCP), batch experiments were conducted at T=23 ± 2°C and a solution pH(pH=5.4). For each experimental run, 10mL of a 2,4 DCP solutions with initial concentration (C_0=100mg/l) containing an adsorbent dose (m=10mg) was agitated in a rotary shaker at a constant speed (V_{acts}=250tr/min).

The effect of the initial dichlorophenol concentration study was carried out by changing the initial concentration from 50 to 150 mg/L at pH 5.4, with 10 mg of sorbent dose.

The experiments of effect of the pH and the temperature were performed using just the best adsorbent among the samples tested, the pHi was varied from 2 to 10 by adding a few drops of HCl and NaOH (0.1 mol/L) and the temperature was varied from 10 to 40°C. The adsorption experiments were investigated at a fixed 2,4DCP solution volume of 10mL, initial 2,4DCP concentration of 100 mg/L, 10mg adsorbent dose and shaking speed of 250tr/min.

The isotherm adsorption experiments were evaluated at different initial concentrations of dichlorophenol ranging from 10 to 800 mg/L at an initial solution pH. The amounts of 2,4 DCP adsorbed onto the adsorbents, at equilibrium qe (mg/g) and at any time qt (mg/g), were calculated using the following relationship:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad \text{Eq.1}$$

Where C_0 is the initial chlorophenol concentration (mg/L), C_t is the concentration of chlorophenol at any time t, V the volume of solution (L) and m is the mass of adsorbent (g).

III. Results and discussion

A. Characterization of adsorbents

Representative FTIR spectra of LP, CA_{cal}-H_3PO_4, CA_{cal}-H_2SO_4 and CA_{cal}-HCl are presented in **Fig.1**. The broad band at 3308-3248 cm^{-1} is related to the stretching vibration of the hydroxyl group (-OH), the signal at 2841-2882 cm^{-1} is identical to the symmetric and asymmetric stretching vibrations of methyl and methylene groups [10]–[11].

The signal at 2283-2323 cm^{-1} is identical to the C≡N stretch of alkynes. The band at 1000-1500 cm^{-1} is assigned to asymmetric and symmetric stretching of carboxylic acid and the peak observed at 952 cm^{-1} is attributed to C–H in plane.
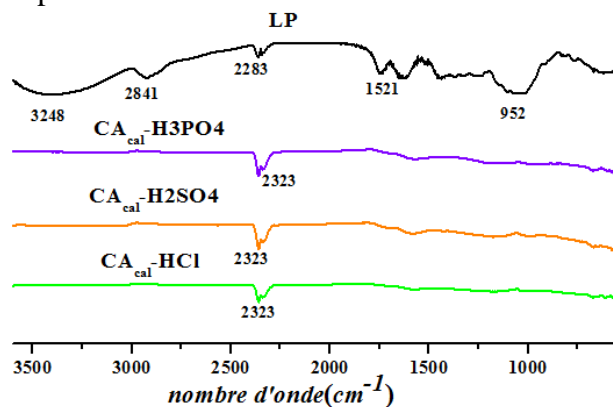

Fig.1: FTIR spectrum of: LP, CA $_{cal}$-H_3PO_4, CA $_{cal}$-H_2SO_4 and CA $_{cal}$−HCl.

Analysis of the data from **Table 1** shows that all the samples exhibited an acidic character of the surface with a surface acidity of 1.14, 1.05, 1.06 and 1.08 mmol/g of LP, CA $_{cal}$-H_3PO_4, CA_{cal}-H_2SO_4 and CA_{cal}-HCl respectively. It can be postulated that the acidic nature of theses samples was derived primarily from carboxylic, anhydrides, lactones and phenol containing groups. However, the surface basicity was associated with the presence of oxygen-free Lewis sites, carbonyls, pyrone and chromene type structures [12].

Table1: Acidity and Basicity of: LP, CA $_{cal}$-H_3PO_4, CA_{cal}-H_2SO_4 and CA_{cal}-HCl

|	LP	CA_{cal}-H_3PO_4	CA_{cal}-H_2SO_4	CA_{cal}-HCl
Acidity (mmol/g)	1.14	1.05	1.06	1.08
Basicity (mmol/g)	1.10	1.03	1.04	1.05
Total content of surface oxides (mmol/g)	2.24	2.08	2.10	2.13

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The zero point of charge (pHpzc) an index of the propensity of the surface charge as a function of pH. The values of pHpzc of LP, CA cal-H_3PO_4, CA cal -H_2SO_4 and CA cal -HCl were found as 5.47, 2.65, 3.43 and 3.94 respectively (**Fig.2**) the surface of these adsorbents is highly acid. For pHs of solution lower than these values, adsorbents are anion attractors and for pHs greater they are cation attractors.
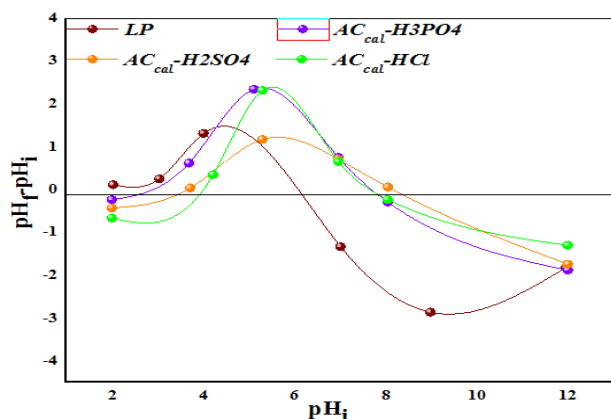
Fig.2: Points of zero charge of: LP, CA cal-H_3PO_4, CA cal -H_2SO_4 and CA cal –HCl.

B. Adsorption studies
B.1 Effect of time of contact
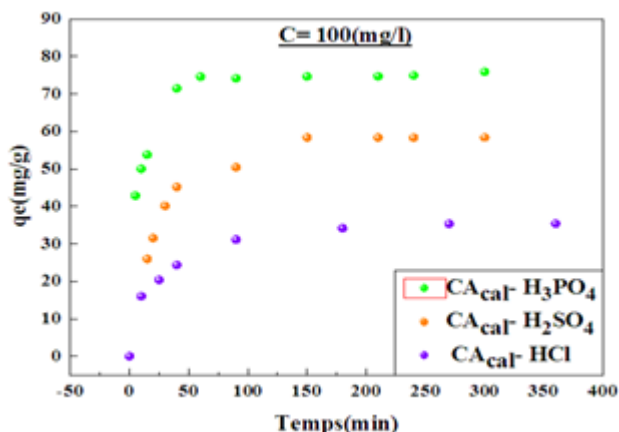
Fig.3: The kinetic of adsorption of 2,4DCP according to time of contact on the various prepared adsorbents (m=10mg, T=23 ± 2°C, V=10ml, pH=5.4, V_{acts}=250tr/min, C_0= 100mg/l).

According to **Fig.3**, we can note that the curves of fixing of 2,4DCP can be divided into two parts: the first part of the kinetic corresponding to a short phase, where the fixing of the 2,4DCP is fast and of a second phase of average speed where the adsorbed quantity evolves more slowly and the rate of adsorption is relatively weak. The latter is well represented by a stage of saturation. This phenomenon can be explained by the existence of a first stage of adsorption of 2,4DCP on the sites easily accessible probably localized on external surfaces from the solid supports, followed by a molecular diffusion of 2,4DCP towards the less accessible sites of adsorption.

We also notice that the adsorbents which were calcined and activated by H_3PO_4 and H_2SO_4 present kinetics of adsorption faster that of the adsorbent which at summer calcined and activated by HCl, balance is reached at the end of 2 hours for CA$_{cal}$-H_3PO_4, and CA cal - H_2SO_4. The adsorbed quantities obtained are respectively of **75.88 mg/g and 58.40 mg/g**. For the adsorbent calcined and activated by HCl, the balance of adsorption is obtained at the end of 3 hours and the adsorbed quantity is equal to **50.39 mg/g**. It should be noted that these variations are due to the mode of conditioning of materials. That shows well that the functions of surface and the properties texturales play a significant role in the phenomena of adsorption.

B.2 Effect of the initial concentration

The study of the kinetic of adsorption according to the initial concentration which is presented on the **Fig.4** shows that the increase in the initial concentration involves an increase in the adsorption of 2,4DCP. We also note that the adsorbed quantity is better for the strong concentration (150 mg/l) for all the adsorbents (CA$_{cal}$-H_3PO_4, CA$_{cal}$-H_2SO_4, and CAcal-HCl). The results obtained seem to also state that if the initial concentration of 2,4DCP in the solution is weak, they are only adsorbed in the surface to form full-course during a very short time [13] and when the initial concentration is raised, there will be consequently more

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molecules which will diffuse towards surface, therefore towards the sites of adsorption, consequently the retention becomes more significant.

degree of the dissociation of the functional groups of the active sites of the adsorbent [14]. The results are represented on the **Fig.5**.
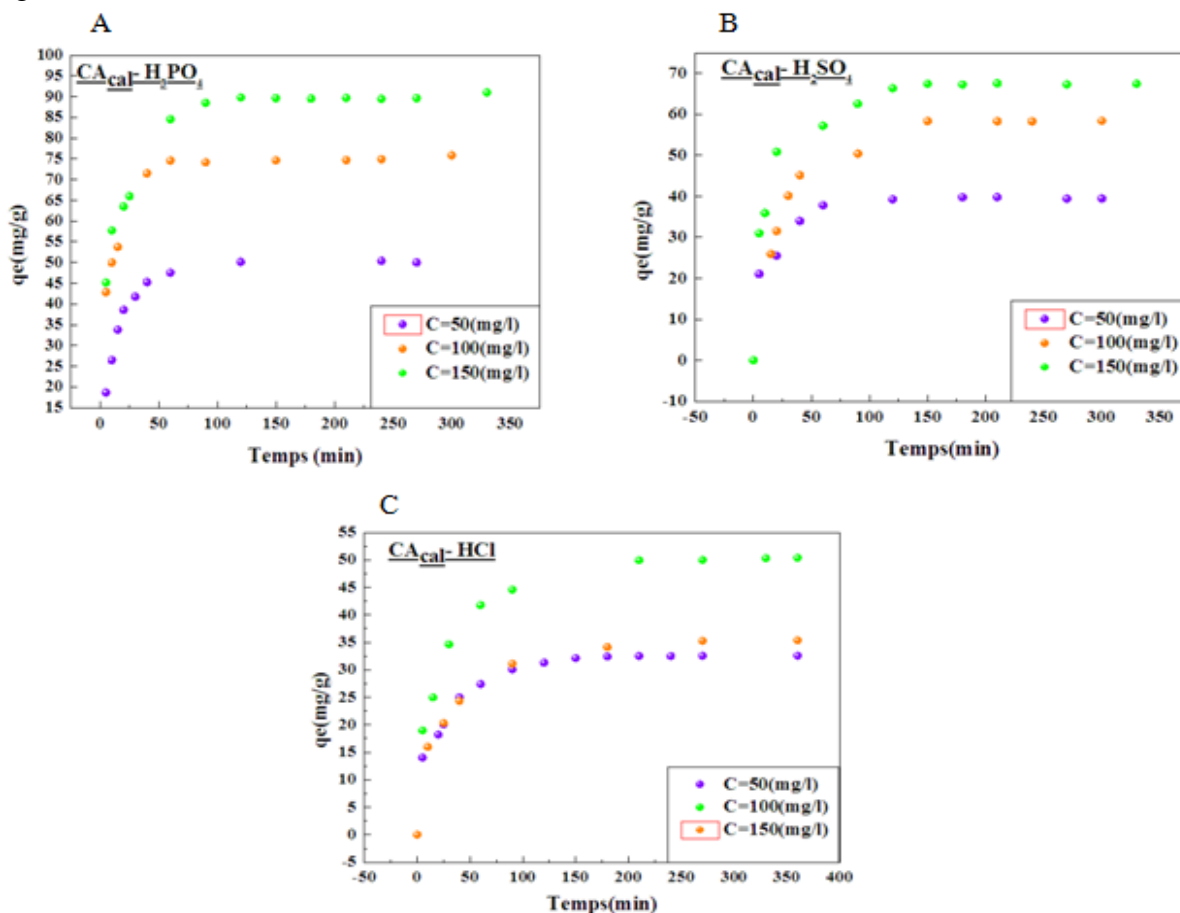

Fig.4: The kinetic of adsorption of 2,4DCP according to the initial concentration on: A) CAcal-H_3PO_4, B) CAcal-H_2SO_4, C) CA_{cal}-HCL (m=10mg, T=23 ± 2°C, V=10ml, pH=5.4, V_{acts} =250tr/min).

Based on the preliminary assessment of the different adsorbents in terms of the maximum quantities adsorbed of 2,4DCP, CA_{cal}-H_3PO_4 was the best adsorbent among the samples tested. Therefore, the experiments of effect of the pH and the temperature were performed using the CA_{cal}-H_3PO_4.

B.3 Effect of the pH

The pH is a very significant parameter to control the process of adsorption [4], it has an effect on the adsorbed quantity. It can change: the load of the surface of the adsorbent, the
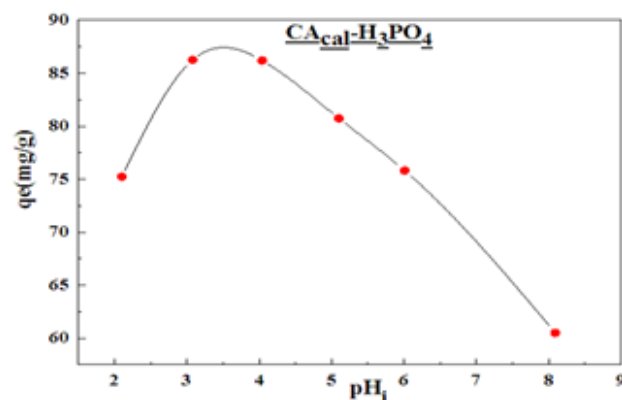
Fig.5: Effect of the pH on the adsorption of the 2,4DCP by CA_{cal}-H_3PO_4 (m=10mg, V=10ml, T=23 ± 2°C, C=100mg/l and V_{acts}= 250 tr/min).

Fig.5 shows that for the adsorbent (CA_{cal}-H_3PO_4) used, there is a variation in the adsorbed quantities. This variation is related to the nature of 2,4DCP and its chemical

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composition. From this figure, one observes that the values of pH ≤ 5, most of 2,4DCP is in molecular form. There is thus adsorption by dispersive interactions of Van Der Walls. The adsorbed quantity of 2,4DCP increases until a maximum then it decreases when the pH of the solution increases due to the competions of the OH⁻ solution and phenolates.

B.4 Effect of the temperature

The results obtained represented in **Fig.6**
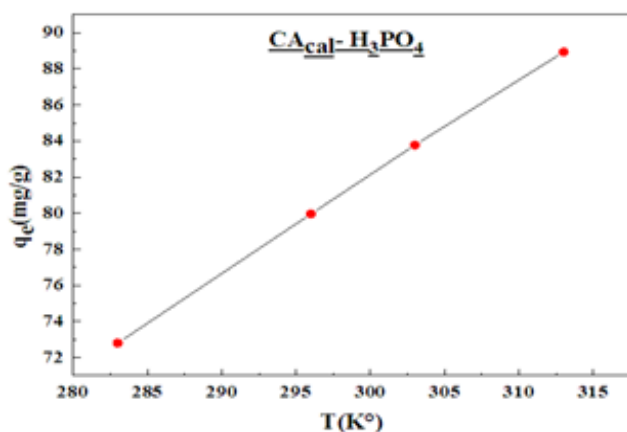
Fig.6: Effect of the temperature on the adsorption of the *2,4*DCP by CA$_{cal}$-H$_3$PO$_4$ (m=10mg, V=10ml, pH=5.4, C=100mg/l and V$_{acts}$ = 250 tr/min).

The increase in the temperature is known to increase the speed of the diffusion of the molecules of adsorbate through the external boundary layer and inside the particles of adsorbent, because of the reduction in the viscosity of the solution [15]. To leave **Fig.6**, it is noted that there is a light increase in the quantity adsorbed with the increase in the temperature.

The parameters thermodynamics, free energy of Gibbs (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) of the adsorption of 2,4DCP on the support (CA$_{cal}$-H$_3$PO$_4$) were given, by using the following equations:

$$\Delta G^0_{ads} = \Delta H^0_{ads} - \Delta S^0_{ads} \qquad (1)$$

$$\log\left(\frac{q_e \times m}{C_e}\right) = \frac{\Delta S^0}{2.303 \times R} + \frac{-\Delta H^0}{2.303 \times R} \qquad (2)$$

Were:
ΔH°: the enthalpy (kJ/mol), ΔS°: entropy in (J/mol. K), T: the temperature in Kelvin. R: the constant of perfect gases (R = 8.314 J/mol.K), qe: adsorbed quantity (mg/g) and Ce: the concentration with balance (mg/l). The results of the thermodynamic parameters obtained are gathered in Table1

Table2: Thermodynamic parameters ΔG°, ΔH° and ΔS°.

T (°C)	ΔG° (kJ/mole)	ΔH° (kJ/mole)	ΔS° (J/mole.K)
283	-0.46		
296	-0.48		
303	-0.49	20.85	163.29
313	-0.51		

According to these results, we observe that the values of ΔG° at different temperatures are negatives this indicates that the adsorption of 2,4DCP on the support (CA$_{cal}$ - H$_3$PO$_4$) is spontaneous [16] some is the temperature, the process of adsorption of 2,4DCP is a physical absorption since values of ΔG° is lower than 20 KJ/mol [17]–[18]. The free enthalpy is positive, which implies that the process of adsorption is endothermic. ΔS° is positive, that wants to say that the molecules of 2,4DCP remain less ordered on the solid interface/solution during the process of adsorption [19].

B.5 Modeling of the kinetic of adsorption

We adopted two models of kinetic, these models are: models of pseudo-first-order (PPO), pseudo-second-order (PSO). We carried in **Table3** and **Table4** the results of modeling by using the linear regressions and not linear.

Table3: Results of model of kinetic of adsorption of 2,4DCP: model of pseudo-first-order

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		Pseudo-premier-ordre					
		Fit non linéaire			Fit linéaire		
	C_0	K_1	$q_{e, cal}$	R^2	K_1	$q_{e, cal}$	R^2
CA$_{cal}$-H$_3$PO$_4$	50	0.07	48.98	0.977	0.01	15.25	0.753
	100	0.12	73.89	0.869	0.01	15.34	0.752
	150	0.08	89.44	0.812	0.009	15.82	0.474
CA$_{cal}$-H$_2$SO$_4$	50	0.07	38.57	0.884	0.01	38.45	0.645
	100	0.04	59.06	0.983	0.01	50.49	0.907
	150	67.58	0.934	0.007	63	84	0.825
CA$_{cal}$-HCl	50	0.04	31.83	0.935	0.01	43.76	0.845
	100	0.04	48.43	0.949	0.01	29.98	0.976
	150	0.04	34.04	0.956	0.01	23.18	0.975

Table4: Results of model of kinetic of adsorption of 2,4DCP: model of pseudo-second-order.

		Pseudo-second-ordre					
		Fit non linéaire			Fit linéaire		
	C_0	$K2$	$q_{e, cal}$	R^2	$K2$	$q_{e, cal}$	R^2
CA$_{cal}$-H$_3$PO$_4$	50	0.002	53.30	0.985	$2.69.10^{-5}$	51.79	0.992
	100	0.002	77.40	0.955	$3.17.10^{-5}$	76.63	0.985
	150	0.001	92.42	0.950	$1.68.10^{-5}$	92.50	0.996
CA$_{cal}$-H$_2$SO$_4$	50	0.003	40.45	0.969	$3.84.10^{-5}$	40.62	0.998
	100	0.008	63.45	0.992	$8.83.10^{-5}$	62.69	0.991
	150	0.001	69.19	0.988	$1.80.10^{-5}$	69.54	0.994
CA$_{cal}$-HCl	50	0.002	34.24	0.969	$2.30.10^{-5}$	34.12	0.989
	100	0.001	52	0.985	$1.37.10^{-5}$	52.99	0.995
	150	0.001	37.05	0.988	$1.49.10^{-5}$	37.34	0.994

From the results of **Table3** and **Table4**, we can deduce that the model of pseudo-second-order is that which describes better the process of adsorption of the 2,4DCP on the activated carbons synthesized (CA$_{cal}$-H$_3$PO$_4$, CA$_{cal}$-H$_2$SO$_4$ and CA$_{cal}$-HCl). This model presents the highest factor of correlation for all the concentrations. The analysis of the kinetic data by other researchers also showed that the equation the speed of pseudo-second-order makes it possible to simulate with a good agreement the adsorption of 2,4DCP [9]. We also see that the adsorbed quantities calculated by this model are closer with in experiments adsorbed quantities. Speeds of adsorption (K_2) decrease when the concentration of 2,4DCP increases this returns to the increase in the competition on the sites of adsorption on the other hand the competition decreases on the active sites of the adsorbent for the weak concentrations [20].

B. 6 Isotherms of adsorption

The results obtained are represented in **Fig.7**, according to this figure, the maximum values of the capacity of adsorption on CA$_{cal}$-H$_3$PO$_4$, CA$_{cal}$-H$_2$SO$_4$, and CA$_{cal}$-HCl are **236.2 mg/g, 160.03 mg/g** and **148.39 mg/g** respectively. It is noticed that the affinity of adsorption of 2,4DCP on the adsorbents is very large as of the first concentrations. It is clear that the activated carbons prepared starting from the lemon peels by chemical activation are more powerful than the natural lemon peels, then one can say that activation for a great purpose on the capacity of adsorption, also on the specific surface of the adsorbent.

The two models most usually employed are the models of Langmuir and Freundlich. In **Table5** and **Table6**, we carried the models of the isotherms and the results of modeling by using the linear regressions and not linear (constants speed, maximum quantities adsorbed and coefficients of correlation R^2).

Table5: Results of the modeling of the isotherms of adsorption of 2,4DCP on the various adsorbents: model of Langmuir.

	Langmuir					
	Fit non linéaire			Fit linéaire		
	q_{max}	K_1	R^2	q_{max}	K_1	R^2
CA$_{cal}$-H$_3$PO$_4$	292.90	0.005	0.975	269.54	0.008	0.975
CA$_{cal}$-H$_2$SO$_4$	167.76	0.003	0.939	165.56	0.045	0.994
CA$_{cal}$-HCl	200.49	0.006	0.984	179.21	0.009	0.962

Table6: Results of the modeling of the isotherms of adsorption of 2,4DCP on the various adsorbents: model of Freundlich.

	Freundlich					
	Fit non linéaire			Fit linéaire		
	n_F	K_F	R^2	n_F	K_F	R^2
CA$_{cal}$-H$_3$PO$_4$	0.39	18.5	0.980	1.60	0.05	0.989
CA$_{cal}$-H$_2$SO$_4$	0.26	23.81	0.970	1.35	0.03	0.998
CA$_{cal}$-HCl	0.42	11.52	0.977	1.80	0.10	0.990
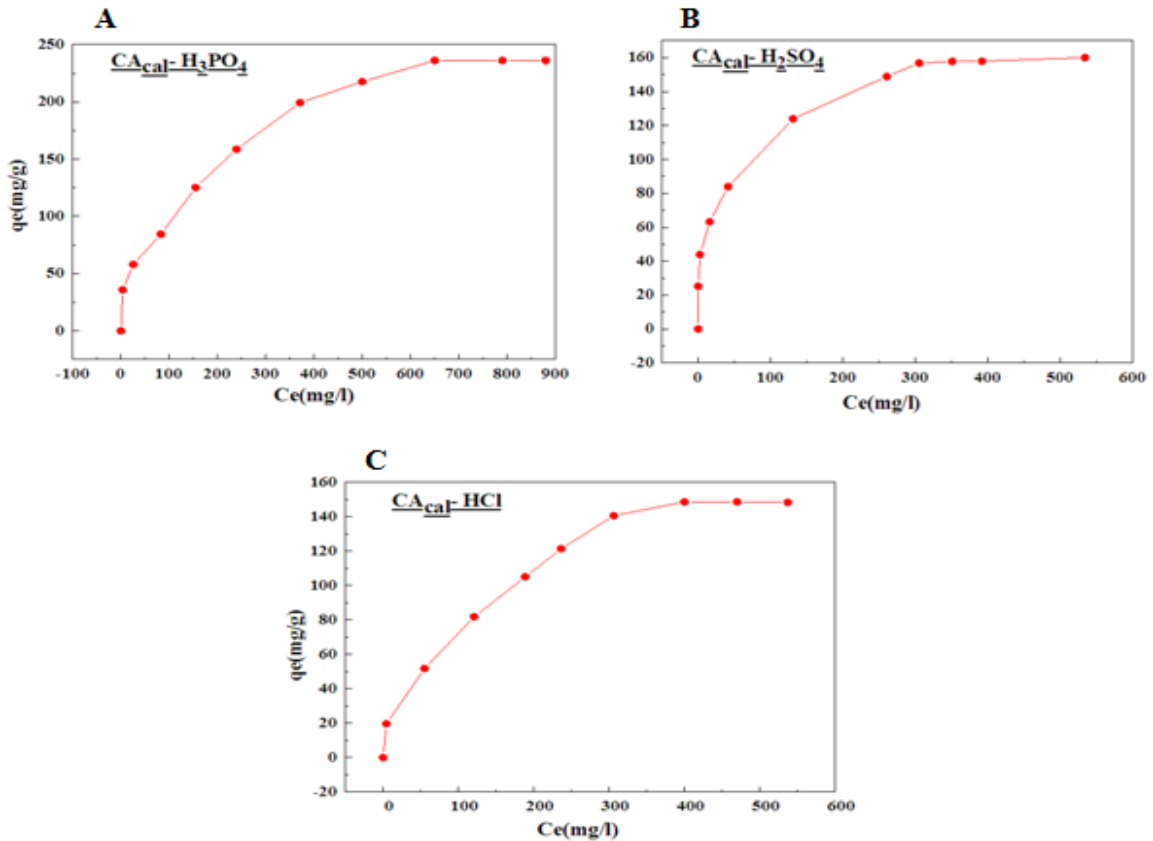
Fig.7: Isotherms of adsorption of 2,4DCP on: A) CA_{cal} -H_3PO_4, B) CAcal -H_2SO_4, C) CAcal -HCl.

It is observed that the model of Langmuir is the most credible model which describes our experimental results better, we also observe that there is a good correlation between the experimental data and the model of Langmuir with maximum quantities absorbed **292.90 mg/g**, **167.76 mg/g** and **200.49 mg/g** respectively for the synthesized activated carbons (CA_{cal}-H_3PO_4, CAcal- H_2SO_4 and CA_{cal} -HCl). The model of Langmuir shows that surfaces of our samples are homogeneous on the energy level and a monomolecular adsorption of 2,4DCP on our activated carbons. The values of n_F of the model of Freundlich are higher than 1 ($n_F > 1.3$) in all the cases show that adsorption is favorable and physical [20].

C. Conclusion

The objective of this study consists of the preparation of the activated carbon starting from waste of agriculture in order to obtain an applicable product in the water treatment, the agents activating used are acids (H_3PO_4, H_2SO_4 and HCl). The study related to the elimination of 2,4DCP by the various synthesized activated carbons.

The experimental data of the kinetic were tested by using the model of pseudo-first order and the model the pseudo one-second-order. The results obtained show that the model of pseudo-second order is the best model with a coefficient of correlation equalizes to 0.998. The experimental data of the isotherm show that the carbon calcined and activated with the phosphoric acid is the best adsorbing. According to results' obtained starting from modeling, the model of Langmuir is most plausible to describe the process of adsorption ($R^2 = 0.99$).

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D. References

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