

# Adsorption of Phenolic Compounds on Activated Carbon DSAC36-24

Khaoula Hidouri, Ali Benhmidene, Bechir Chouachi, Dhananjay R. Mishra, Ammar Houas

**Abstract**—Activated carbon DSAC36-24 is an adsorbent material, characterized by a specific surface area of 548.13 m<sup>2</sup>g<sup>-1</sup>. Their manufacture uses the natural raw materials like the nucleus of dates. In this study the treatment is done in two stages: A chemical treatment by H<sub>3</sub>PO<sub>4</sub> followed by a physical treatment under nitrogen for 1 hour then under stream of CO<sub>2</sub> for 24 hours. A characterization of the various parameters was determined such as the measurement of the specific surface area, determination of pH<sub>PZC</sub>, bulk density, iodine value. The study of the adsorption of organic molecules (hydroquinone, paranitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol) indicates that the adsorption phenomena are essentially due to the van der Waals interaction. In the case of organic molecules carrying the polar substituents, the existence of hydrogen bonds is also proved by the donor-acceptor forces. The study of the pH effect was done with modeling by different models (Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson), a kinetic treatment is also followed by the application of Lagergren, Weber, Macky.

**Keyword**—DSAC36-24, organic molecule, adsorption isotherms, adsorption kinetics.

## I. INTRODUCTION

ADSORPTION is a very important method for the removal of contaminants, especially organic wastewater effluents. The most common adsorption is carried out on the activated carbon. The removal process is often carried out in static mode by contacting the contaminated water with powdered activated carbon with stirring for a sufficient period of time. The decontaminated water is recovered by filtration after deposition of the activated carbon. Phenolic compounds are everywhere released into the environment [1]. Several studies have examined wastewater [2], [3].

Pocurull et al. showed concentrations of nitrophenols (2-nitrophenol, 4-nitrophenol and 2,4-dinitrophenol) in Ebro river (Spain) ranging from 0.1 to 5.0 µg/l [3]. The other results indicated concentration of phenol over 40 mg/l in river water, which was receiver of wastewater from petrol industry [4]. Moreover, in the area fertilized by municipal sewage sludge, the concentration of 4-nonylphenol was 2.7 mg/kg of soil [4]. In view of the high cost of activated carbons, several experimental works are aimed at preparing them from different primary materials such as coconuts [5]-[9]. The present work has a dual purpose, which is to characterize an activated carbon prepared from date nuclei, to show its effectiveness in the removal of phenolic compounds and to test the validity of some models.

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## II. EXPERIMENTAL STUDY

### A. Preparation of Active Carbon DSAC36-24

In Tunisia, there is a natural, inexpensive and very abundant material. These are date palm which can, after a suitable treatment, give rise to an active carbon. The date palms are first washed with tap water to remove traces of the pulp from dates and then rinsed with distilled water. They are then dry in an oven (110 °C) for one day in order to remove traces of water and volatile matter. Once crushed to a size of 2 to 5 mm, they give rise to the useful precursor in the rest of the preparation.

The chemical activated by H<sub>3</sub>PO<sub>4</sub> (36%) is brought into contact with a mass *m* of precursor obtained, for 1 hour. Once filtered, this mass is washed with distilled water to pH=6 and dried in an oven (110 °C) for 24 hours. The purpose is to eliminate the volatile products trapped in the carbon skeleton. This pyrolysis takes place under a stream of nitrogen (3.6 l/h) with a heating rate of 7.5 °C/min at 400 °C for 1 hour. After cooling under CO<sub>2</sub>, the activated carbon is recovered, washed with distilled water to pH=6-7, dried, weighed and stored in hermetic bottles.

SEM analysis of DSA36-24 is presented on the micrographs (Fig. 1) at two different extensions respectively 497 and 2011, showing that it has a more or less uniform spongy structure.

TABLE I  
PHYSICO-CHEMICAL CHARACTERISTICS OF ACTIVATED CARBON DSAC36-24

First material	Date nuclei
Type Activation	Activation (Chemical+Physical)
Specific surface area (m <sup>2</sup> /g)	548.13
Average pore diameter (Å)	25.55
Pore volume (cm <sup>3</sup> /g)	0.35
Granulometry (µm)	< 50
Ash (%)	4.37
Iodine value (mg/g)	849.839
Bulk density (g/cm <sup>3</sup> )	0.37
Acid surface function (meq/g)	1.57
Acid surface function (meq/g)	0.25
pH <sub>PZC</sub>	8.37

The organic molecules selected in this work are all phenol compounds possessing a growing nitro group (NO<sub>2</sub>) given in Fig. 2.

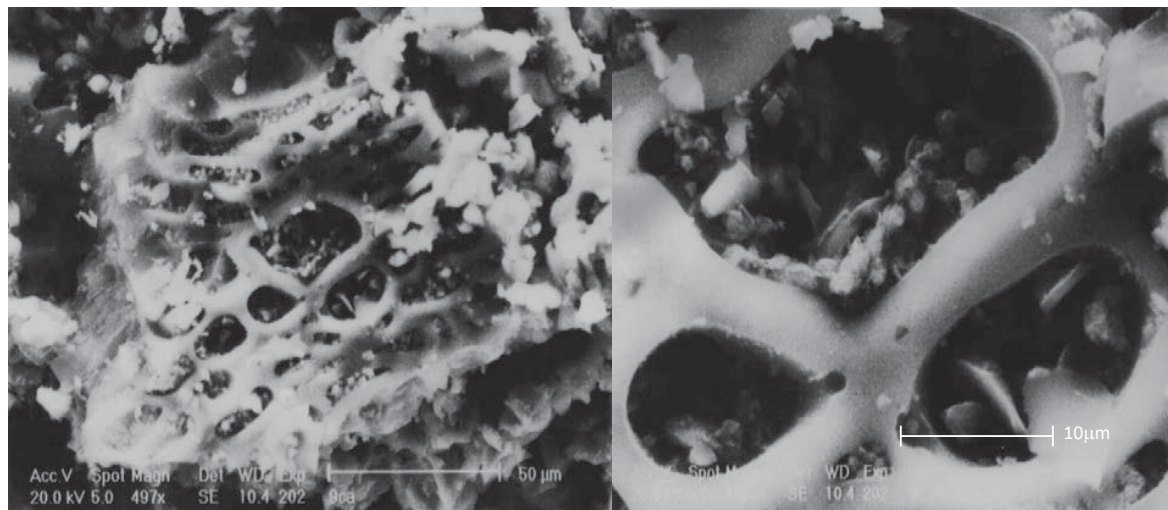


Fig. 1 Micrographs of activated carbon DSAC36-24 with an enlargement: (a) of 497 and (b) of 2011

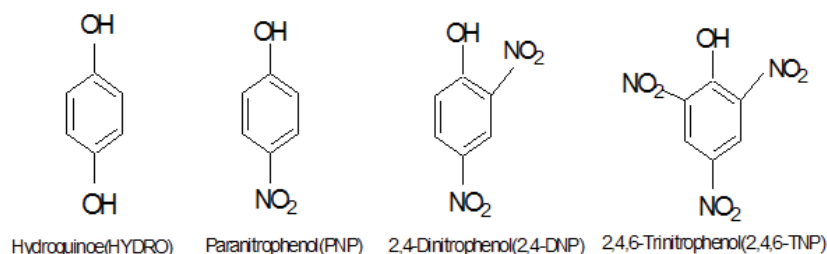


Fig. 2 Phenolic compounds

 TABLE II  
 MAIN PHYSICO-CHEMICAL CHARACTERISTICS OF THE ORGANIC COMPOUNDS USED

Phenolic compound	HYDO	PNP	2,4-DNP	2,4,6-TNP
pKa	9.69	7.16	4	0.8
Molar mass (g/mol)	110.11	139.1	184.11	239.11
Fusion temperature (°C)	173	114	113	122
Ebullition temperature (°C)	286	279	-	300
Dipolar moment (µdeby)	0	5.6	3.4	1.5
Natural pH	5.65	5.62	4.82	3.85
Chemical shift ( $\delta_{ortho}$ ppm)	0.74	-0.6	-1.57	-1.94

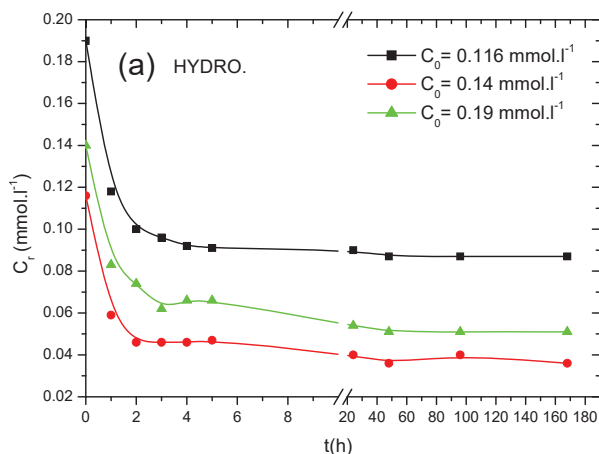
TABLE III $\lambda_{max}$ (NM) AND $\epsilon$ L (L/MMOL) OF DIFFERENT COMPOUNDS STUDIED				
compounds	HYDO	PNP	2,4-DNP	2,4,6-TNP
$\lambda_{max}$ (nm)	246	317	264	356
$\epsilon$ l (l/mmol)	4.89	7.54	5.84	6.65

Tables II and III give physicochemical characteristics and wavelengths for the phenolic compounds studied.

### III. ISOTHERMS OF ADSORPTION

Knowledge of the physicochemical characteristics of a solute-liquid-solid adsorbent system makes it possible to better understand the phenomena of adsorption. Several isothermal modellings (Langmuir, Freundlich, Redlich-Peterson, Langmuir-Freundlich) will be used in this work. It is therefore necessary to determine the adsorption equilibrium conditions.

The residual concentration as a function of time, Figs. 3 (a)-(d), gives these results. Figs. 4 (a)-(d) give there's results which is very largely sufficient to obtain in each case the equilibrium of the adsorption.



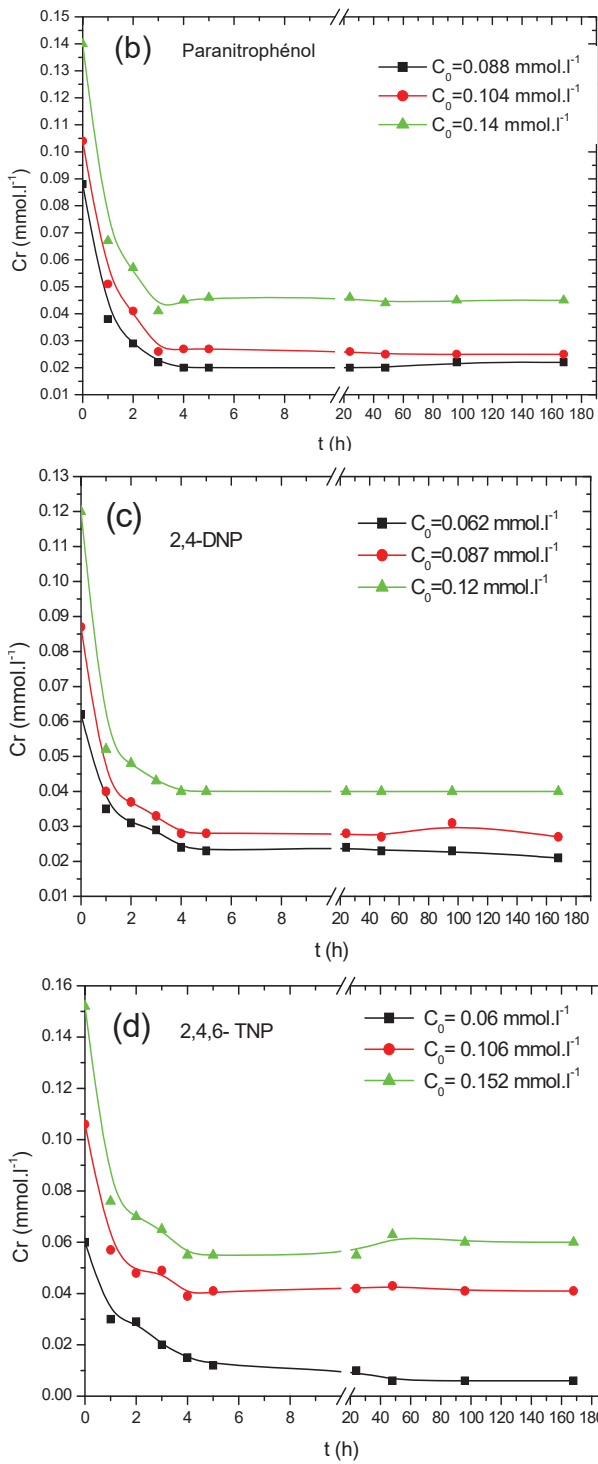
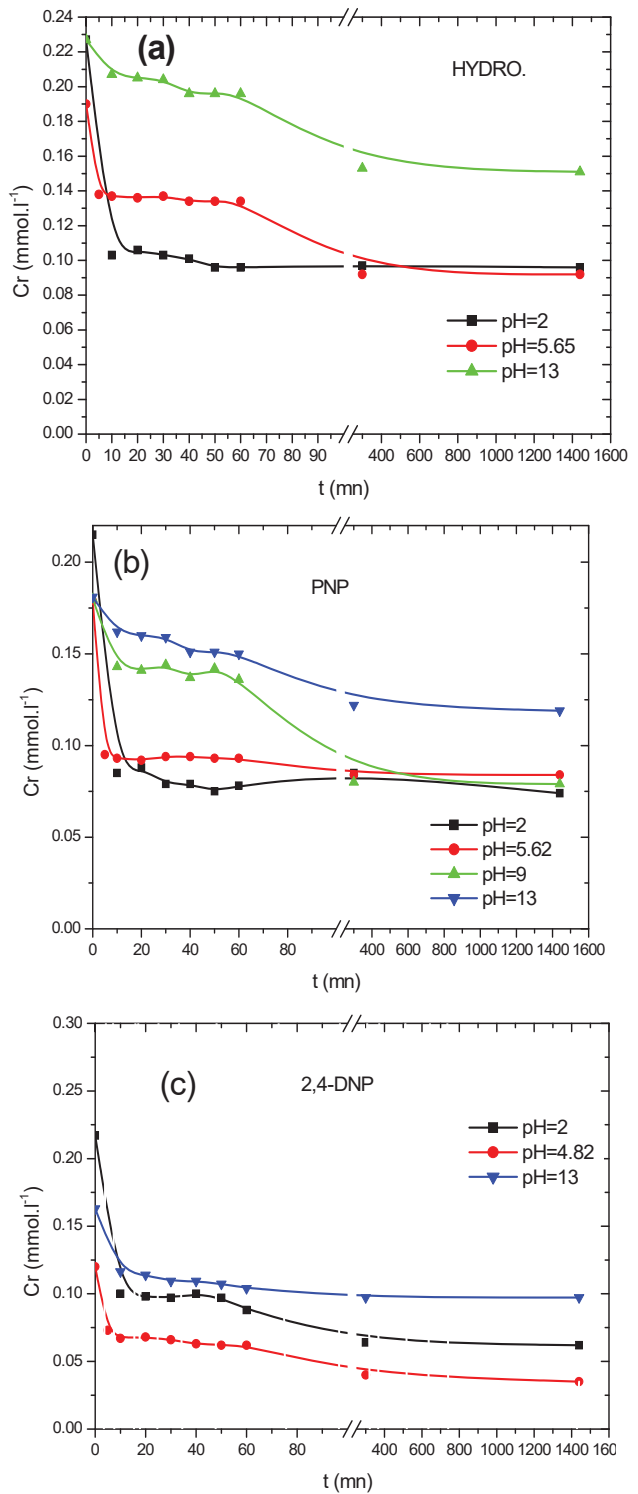


Fig. 3 Evolution of residual concentration ( $c_r$ ) of the solution in the liquid phase of contact time ( $t$ ) at natural pH

*A. Langmuir Model*

The adsorption isotherms shown in Figs. 5 (a)-(d) respectively for HYDRO, PNP, 2,4-DNP and 2,4,6-TNP show that the adsorption phenomenon obeys well Model of

Langmuir. The interpolation software determines the values of the theoretical maximum adsorption capacities and the values of the adsorption equilibrium constants.



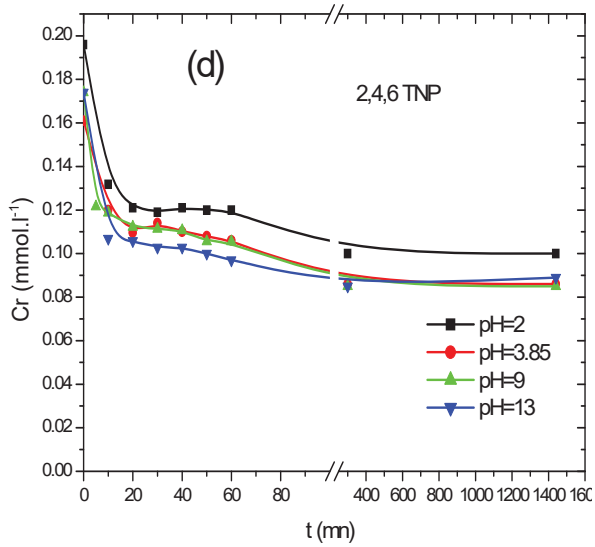


Fig. 4 Evolution of residual concentration ( $c_r$ ) of the solution in the liquid phase of contact time at different pHs

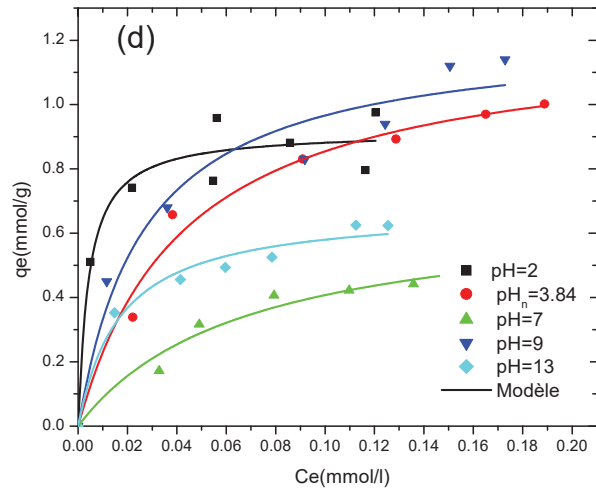
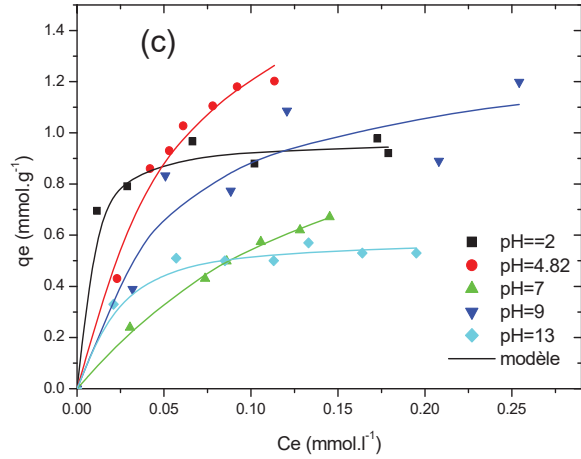
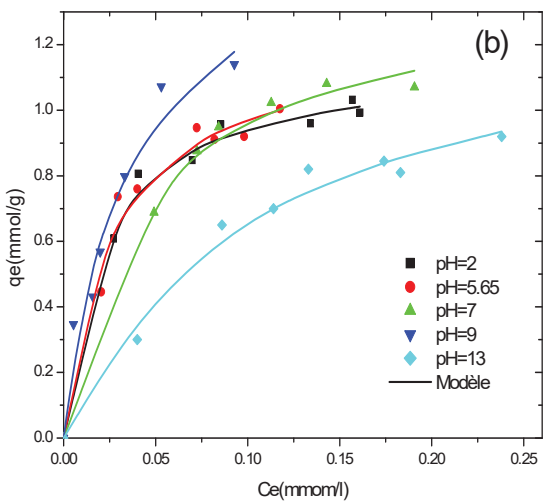
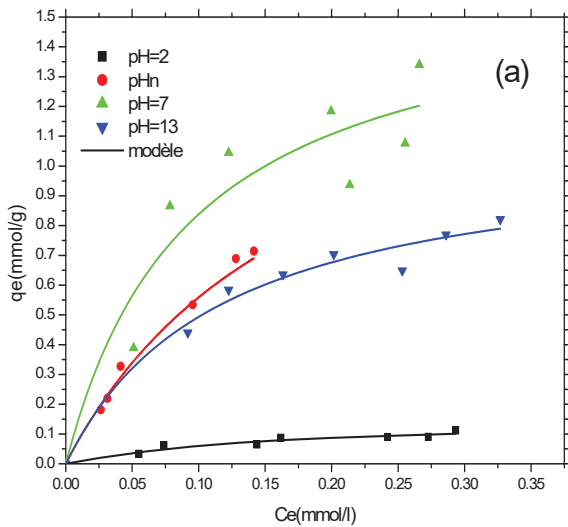


Fig. 5 Equilibrium adsorbed quantity ( $q_e$ ) in the solid phase in function of residual concentration ( $c_r$ ) at different pHs

To better explain the adsorption phenomenon and the influence of both the nature of the solute and that of the pH on it, it is interesting to recall some characteristics of the carbon used. The process of preparing and activating our carbon produces an "H-type" activated carbon: hydrophobic carbon which is positively charged into water by adsorption of  $H^+$  ions, which makes the solution alkaline. Ishisaki and Martin [10] have determined that for an H-type carbon, the predominant surface oxides are lactones, quinones, phenolic hydroxides and carboxylates. Moreover, ignoring the oxides or metallic impurities that may be present on the carbon used, because of the lack of analyzes, there could be two major types of surfaces: The plane surfaces are almost uniform and have some functional groups, since the electrons of the carbon atoms have covalent bonds with those that are adjacent to them. However, the microcrystallites faces are not uniform and contain various functional groups. It is known that the adsorption of organic compounds can be strongly affected by the nature and proportion of surface oxide groups. For example, the phenol forms strong donor-acceptor complexes with the oxygens of these groups and thus its adsorption takes place via an acceptor-donor mechanism involving the oxygen

atoms of the surface carbonyl groups acting as an electron donor and the aromatic ring of the phenol as acceptor. The adsorption isotherms of the various compounds shown in Figs. 3-5 are of the L type according to the Giles classification [11]. The Langmuir type means that the aromatic ring is adsorbed parallel to the graphitic surface and that there is no strong competition between the solute and the solvent to occupy the surface sites. In general, and considering the importance of the nature of the surface functional groups and the molecular or dissociated form of the phenolic compounds on the adsorption, the possible interaction between the surface of the carbon and the phenolic compounds is:

1. Non-localized interaction (Van Der Waals-London dispersive forces) between the aromatic ring and the  $\Pi$  electrons of the graphitic structure ( $\Pi$ - $\Pi$ ).
2. Electron donor-acceptor interaction between the aromatic ring and the oxygens of the basic surface functions.
3. Electrostatic repulsion and attraction when ions are present.
4. Hydrogen bonds. In the case where the solute molecules' Van Der Waals-London interactions between the molecules and the surface of the carbon increase with the number of these bonds [3].

In general, for all pHs < pHPZC, the acid functions predominate by neutralization or by transformation of the basic functions. On the other hand, for pHs > pHPZC, the basic functions predominate.

- Hydroquinone (HYDRO): For the adsorption of hydroquinone, the order obtained for the various pHs is as:  $\text{PH} = 7 > \text{pHn} = 5.62 > \text{pH} = 13 > \text{pH} = 2$

At pH = 7, the basic surface functions as well as the charcoal acids are not affected in a very significant way ( $\text{pH}_{\text{PZC}} = 8.37$ ). All types of interactions:  $\Pi$ - $\Pi$ , acceptor-donor and hydrogen bonds can therefore take place, which explains the better adsorption, obtained for this pH. At pH = 5.65, the proportion of basic surface functions decreases, decreasing the interactions (b).

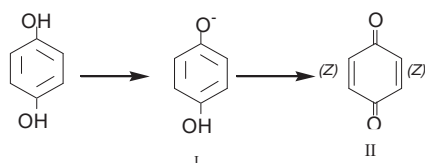


Fig. 6 Rearrangement of hydroquinone molecule

In addition to the quinone, the dissociated (ionized) form (I) also exists which improves the adsorption with respect to pH = 2. At pH = 2, the surface becomes more acidic by neutralizing the basic functions. As for the Langmuir (b) adsorption equilibrium constant, it is as follows:  $\text{PH} = 7 > \text{pH} = 13 > \text{pH} = 5.65 > \text{pH} = 2$ . This classification could be explained by the fact that the oxygen atoms of the non-dissociated basic groups make it possible to have donor-acceptor interactions (b), which are stronger than those  $\Pi$ - $\Pi$  (a), which necessitates the presence simultaneously of a maximum of non-dissociated

forms and a maximum of basic functions.

- Paranitrophenol (PNP): The adsorption of PNP on DSAC36-24 decreases in the following order:  $\text{PH} = 9 > \text{pH} = 7 \cong \text{pH} = 13 > \text{pHn} = 5.62 > \text{pH} = 2$ . The decrease in pH leads 7 at pH = 9. This would explain the greater amount of 2,4,6-TNP adsorbed at this pH. Indeed, this mesmeric would make it possible to have hydrogen bonds (d) in addition to the other 2 types of bond (b) and (c). At  $\text{pHn} = 3.85$ , the mesmeric (I) could be the majority or the further possibility of having (a) ( $\Pi$ - $\Pi$ ) bonds (benzene ring unchanged). The values obtained at pH = 2, 7 and 13 seem complicated to explain and to be correlated with the different types of binding.

#### IV. CONCLUSION

In this work, we studied the phenomenon of adsorption of four phenolic compounds (hydroquinone, paranitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol) on the activated carbon prepared from nuclei of dates DSAC36-24. This activated carbon is prepared by a chemical activation at room temperature with 36% orthophosphoric acid and a thermal activation at 900 °C. for 24 hours under  $\text{CO}_2$ . Its physicochemical characterization showed that:

- Its BET surface area is  $543.13 \text{ m}^2\text{g}^{-1}$ ,
- It has both micropores and mesopores with a total pore volume of  $0.35 \text{ cm}^3\text{g}^{-1}$  and an average porediameter of  $25.55 \text{ \AA}$ ,
- It has a rather basic character with a concentration of basic surface functions of  $1.57 \text{ meq.g}^{-1}$  while that of acid functions is worth  $0.25 \text{ meq.g}^{-1}$ . This basic characteristic is confirmed by its pHPZC equal to 8.37.
- Its iodine value is  $849.84 \text{ mg.g}^{-1}$  comparable to that of certain activated carbons widely used for the depollution of aqueous media.

The adsorption is studied in closed static reactor; the results obtained have shown that:

- The equilibrium time of adsorption is 5 hours for all the compounds whatever the initial concentration or the pH, The maximum adsorption capacity, determined by the Langmuir model, decreases to pH = 2 in the following order:  $\text{PNP} > 2,4\text{-DNP} \cong 2,4,6\text{-TNP} > \text{HYDRO}$ , at natural pH, as follows  $2,4\text{-DNP} > \text{HYDRO} > \text{PNP} \cong 2,4,6\text{-TNP}$ , for pH = 7. It decreases in the following order:  $2,4\text{-DNP} > \text{HYDRO} > \text{PNP} > 2,4,6\text{-TNP}$ , for pH = 9 and 13 its decay is respectively in the following order  $\text{PNP} > 2,4,6\text{-TNP} > 2,4\text{-DNP}$  and in the order  $\text{PNP} > \text{HYDRO} > 2,4,6\text{-TNP} > 2,4\text{-DNP}$ .
- All the models tested, with two or three constants, give a very satisfactory description of the experimental results of the adsorption isotherms, with the lowest mean quadratic deviations in the case of the three-constant Langmuir-Freundlich model.

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