

Kinetic Models of Adsorption on Active Carbon DSAC36-24

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Abstract

Activated carbon is one of the highly adsorbent materials, characterized by a specific surface area of $548.13 \text{ m}^2 \text{ g}^{-1}$. Their manufacture uses the natural raw material such as date cores. Several models have been used to monitor the adsorption kinetics. Lagergren model, for the determination of the apparent velocity constant (k_{ad}) and the order of the reaction. Model of Weber and Morris to approximate the kinetic constant of intraparticle diffusion (k_{id}). McKay model, to determine the external mass transfer coefficient (k_f). The interpolation by the three models above is carried out for each compound for the different initial concentrations and different pH. That all the models used well describe the experimental results of diffusion adsorption. All the models used describe well the experimental results of the adsorption and that of Langmuir-Freundlich (with three constants) gives a more precise description. A classification of the adsorption of four phenolic compounds according to the maximum adsorption capacity at different of solution (pHs), and according to the pH for each compound.

Index terms—

1 Introduction

Phenols are aromatic organic compounds of great environmental interest; their determination has increased over the last few years because of their toxicity. Phenolic compounds are often derived from various manufacturing processes such as pharmaceuticals, petroleum refineries, coke plants, and phenolic resin plants [1,2]. They emit an unpleasant odor and taste at a concentration of 5 mg/L and are toxic to aquatic life, plants and humans. [3] Kumar et al gives the ingestion of phenols whose concentration varies between 10 and 240 mg/L for long periods causes irritation of the mouth, impaired vision, and diarrhea [3]. They are considered one of the priority pollutants by the US Environmental Protection Agency [4]. The maximum permissible concentration of phenol in drinking water is 1 mg/L (World Health Organization [5]) as a result; various studies have been carried out for the removal of phenolic compounds before being released to the receiving medium.

In Tunisia the dates for centuries have been the staple food of the desert populations. With its dietary properties, it is now on the way to becoming a strategic agricultural product for export, as much as olive oil. In Tunisia, the production of dates continues to increase. It is estimated annually at 105 thousand tons of which 70 thousand tons of Degletnour (finger of light), variety considered the best. This product is very successful in the domestic and foreign markets. The major production of dates involve the existence of large quantities of date waste among them their nuclei. In this way, the idea to produce activated carbon (by chemical and physical activation) was found from dates nuclei characterized by a high surface area.

The aim of this study was to investigate kinetics and equilibrium aspects of the adsorption of phenol onto date cores activated carbon. Three kinetics models including pseudo-first order, pseudo second order and intra-particle diffusion models were used to discuss adsorption mechanisms. Lagergren [6] model, for the determination of the apparent velocity constant (k_{ad}) and the order of the reaction. Model of Weber and Morris [7] to approximate the kinetic constant of intra particle diffusion (k_{id}). McKay [8], determine the external mass transfer coefficient (k_f)

2 II. Materials And Experimental Methods

In Tunisia there is a natural, inexpensive and very abundant material. These are dates nuclei which can, after a suitable treatment, give rise to an active charcoal. The date nuclei are first washed with tap water to remove traces of the pulp from dates and then rinsed with distilled water. They are then dried 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.

3 a) Chemical Activation

A well-determined quantity of H₃PO₄ (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.

4 b) Pyrolysis and gasification

The next step is carbonization. The purpose is to eliminate the volatile products trapped in the carbon skeleton. The organic matter is removed, and is preserved in addition to the mineral matter, only the carbon skeleton. Thus, this pyrolysis takes place under Year 2017 C a stream of nitrogen (3.6L/h) with a heating rate of 7.5°C/min to 400°C. and maintained for 1 hour at this temperature. Finally, gasification (physical activation) by carbon dioxide for 24 hours at 900 °C. Allows the internal surface of the carbonized material to be developed by eliminating the residues of the pyrolysis responsible for the clogging of the pores. After cooling under CO₂, the activated carbon is recovered, washed with distilled water to pH = 6-7, dried, weighed and stored in hermetic bottles.

5 III.

Determination of the Physico-Chemical Characteristics of Active Coal DSAC36-24 a) Measurement of the specific surface area and porous distribution Among the essential characteristics of an activated carbon, the specific surface and the pore volume greatly influence the adsorption capacities and condition the mechanisms of the adsorption.

The study of the specific surface and of the pore distribution is carried out from the nitrogen gas adsorption isotherm. The gas adsorption isotherm of nitrogen (molecular surface area equal to 16.2 10⁻²⁰ m²) is carried out for a range of relative pressures between 0 and 1 ?m. The isothermal adsorption desorption curve of N₂ (Figure (1)) can allow us to derive two information by its form:

6 ?

The type of solid by the type of isotherm ?

The shape of the pores by the shape of the hysteresis It is there fore a coal which can present both micropores and mesopores and the hysteresis obtained shows that the pores are open slit. The specific surface area is calculated from the linear BET transform shown in Figure (2). The slope of the line is the essential parameter that makes it possible to calculate the specific surface area.

7 C

The ash rate, bulk density and iodine value found for DSAC36-24 activated carbon are summarized in the summary table of its physico-chemical characteristics (Tab (1)). These results show that the DSAC36-24 coal has a low ash content indicating that it consists essentially of organic matter. Its iodine value and apparent density are comparable to those of commercial activated carbon F400 [9]. The concentrations of functional groups (Table 1, lines 10 and 11) correspond to the neutralization with 0.1N concentration for NaOH acid groups and the neutralization with 0.1N HCl for the basic groups. As can be seen from the values found, the activated carbon DSAC36-24 contains mainly basic functions

(1.57meq/g). It is therefore a coal with a rather basic character. This is confirmed by the found value of pH PZC (8.37). SEM analysis of DSA36-24 is presented on the micrographs (Figure 3) at two different extensions respectively 497 and 2011, showing that it has a more or less uniform spongy structure. In Table [2], the main characteristics of the molecules studied are grouped together. Other more conventional characteristics such as melting and boiling temperatures are also given in this table. These give information about the strength of the bonds that exist between the molecules. The dipole moment makes it possible to account for the polarity of the molecule and therefore the most active sites electrically. The choice of these chemical compounds also makes it possible to obtain molecules in solution in distilled water with electrically different chemical forms (acids, conjugated mesomeric forms, etc.). The isotherms and kinetics of adsorption of these molecules are carried out at different pHs. The choice of the pH value depends on the pKa of these different molecules (figure 4). It allows us to have solutions in which one or the other or both forms, molecular (nondissociated) form and ionized (dissociated) form exists.

The pH is adjusted by adding a few drops of concentrated sulfuric acid or soda. The adsorption capacity, the rate constant and the external mass transfer coefficient of a solute on an adsorbent material can be calculated from the adsorption kinetics. For activated carbon, it is assumed that the solute is transferred from the solution

to the liquid film and then a transfer of the solute to the solid. After these steps, the phenomena of adsorption and diffusion in the material will take place. Thus, Thomas [10] shows that the rate of adsorption of a solute on a porous solid support can be written:

The equation can be exploited using adsorption kinetics: when equilibrium is established Bohart and Adams [11] estimate that in the rapid phase of adsorption kinetics the desorption of the solute is very small, we obtain:

The slope of the line, which makes it possible to have an estimate of the maximum capacity of adsorption. From the kinetic equation used by McKay et al [12] we obtain: V .

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9 Relation Of Lagergreen

The Lagergreen relation allows us to study the adsorption kinetics as a whole. It therefore makes it possible to determine an apparent kinetic constant k_{ad} . The rate of adsorption therefore depends in this case on: The concentration of absorbable solute, The surface area of the adsorbent and its surface functions, The conditions of transfer of the molecules to be adsorbed to the liquid from the liquid to the surface of the adsorbent: the diffusion rate of the molecule and the conditions of turbulence prevailing in the medium. This relation is of the form:

10 Relation By Weber And Morris

In static reactors, transport of the adsorbate within the pores of the adsorbent may be the limiting stage of the adsorption rate. This has been observed for several adsorption processes. In order to verify the intervention of this phenomenon, Weber and Morris studied the evolution of the quantity adsorbed in the solid phase or the conversion rates as a function of the square root of time.

It often happens to find curves in the form of two portions, which can be explained by the fact that the first portion of the curve is attributed to the effect of diffusion in the boundary layer, whereas the final portion, which is linear, is attributed to the effect of intraparticle scattering. The slope of the linear portion of such curves has been defined as a kinetic parameter k_{id} note, characterizing the rate of adsorption in the region where intraparticle diffusion is the limiting factor of the kinetics of adsorption.

11 Adsorption Kinetics

The kinetic study is carried out for duration of one hour for each compound, at different initial concentrations or different pHs.

12 a) Influence of initial concentration

The adsorption kinetics were carried out by introducing 100 mL of an adsorbate solution to a concentration and 0.1 g of activated carbon in several stirred reactors controlled at $25 \pm 0.2^\circ \text{C}$. The adsorbent is separated from the solution by filtration (0.45 μm).

The analyzes of solutions are carried out by HPLC. The equipment used is a Hewlett-Packard 1050 series. Consisting of a Shimadzu SPD-6A UV detector (268 nm) and a Supelcosil C18 column (250 mm $\times$ 4 mm d.i. ; Particle size 5 μm). All analyzes were carried out in isocratic mode with a phase mobile composition: methanol: water (1% acetic acid) (20:80) at a flow rate of 1 mL.min⁻¹.

For adsorption kinetics and adsorption isotherms studies, adsorption capacities (q_t) at time t (q_t (g/g)) are calculated by the following relation:

Where C_0 , C_t represents the concentration of the phenolic compound in the initial solution and at time t , m is the mass of activated carbon (g) and V is the volume of the solution in the reactor (L).

By analogy, equilibrium adsorption capacities (q_e (g/g)) are calculated from this same Relationship. The lines obtained with the Lager green model show that whatever the initial concentration or the pH, the kinetics of adsorption of the various compounds is of order 1.

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The values of the various kinetic constants determined, the errors on the values and the coefficients of correlations are grouped, for the different initial concentrations, in the Table 3. The apparent rate constant k_{ad} varies with the initial concentration, it decreases for Hydroquinone, paranitrophenol and 2,4,6-trinitrophenol when the initial concentration increases. On the other hand, it increases with 2,4-dinitrophenol. Decay is exponential for HYDRO, but linear for PNP. In the case of 2,4, -DNP, k_{ad} grows exponentially with the initial concentration.

14 Table 3: Values of the various kinetic constants pH naturel

Co(mol/l) k_{ad} (mn⁻¹) k_{id} (mn^{-1/2}) k_f (m.mn⁻¹) $k_{f.S}$ (mn⁻¹)

15 C

These equations of k_{ad} in function of C_0 it show in this figure ???. From these equations obtained and for an identical initial concentration (0.15 mmol /l), the k_{ad} classification of the four compounds studied is as follows: 2,4-DNP > PNP > HYDRO > 2,4,6-TNP. This classification appears to be related to the shape of the molecule in solution (non-dissociated or dissociated). Indeed 2,4-DNP is in solution in both forms, which would increase the rate of adsorption, due to the presence of all types of interactions. Moreover, the natural pHs of the different compounds, being different and more or less remote from the pH PZC of the coal, the proportions of the acidic and basic surface functions will therefore vary, which would influence the rate of adsorption.

In conclusion, the form of the compound considered in solution, its natural pH (more or less distant from the pH PZC of the coal) and the nature of the surface functions of the coal, induce the presence of the different types of interaction and therefore adsorption rates Different.

Moreover, all the straight lines obtained, giving the variation of C / C_0 as a function of $t^{1/2}$ not exceed 1, thus showing that the intraparticle diffusion is not the only process that controls the kinetics.

The intraparticle diffusion constant (k_{id}) also depends on the initial concentration. Its variation as a function of this is shown in figure (7). The k_{id} constant appears to decrease when the initial concentration increases. In fact, the more it increases, the greater the thickness of liquid film surrounding the particles of the coal, the lower the rate of diffusion in the pores.

16 b) Effect of pH

The values of the mass transfer coefficient k_f grouped in Table (4) appear to be very complex to discuss. Indeed, k_f depends mainly on the hydrodynamic conditions, which have not been considered in our work. The products $k_f \cdot S$ presented in Table (4) have the same unit as the apparent constant k_{ad} (mn⁻¹) and are generally of the same order of magnitude as this, indicating that the adsorption rate is controlled By diffusion. The effect of pH is shown in Table (4), the variation as a function of the pH respectively of the initial velocity v and the intraparticle diffusion constant k_{id} . It is found that the adsorption rate of hydroquinone and 2,4-DNP is faster at alkaline pH.

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On the other hand, that of PNP and 2,4,6-TNP are faster at acid pH. The classification of different compounds according to the initial rate At pH = 2 is as follows: PNP>2,4,6-NPT>HYDRO>2,4-DNP At pH=13 it is as follows HYDRO > 2,4-DNP > PNP > 2,4,6-TNP Intraparticle scattering is generally faster at acid pH, indicating that the undissociated form will diffuse more rapidly than the dissociated one. Indeed, the undissociated molecule seems to be less hampered by electrostatic attraction-repulsions on the surface of the particle.

18 VIII.

19 Conclusion

The adsorption kinetics studied at various initial concentrations or different pHs showed that: The adsorption reaction is first order for all compounds regardless of the initial concentration or pH. The apparent rate constant k_{ad} decreases when the initial concentration increases exponentially in the case of HYDRO and 2,4,6-TNP and linearly in the PNP case, but increases exponentially with the initial concentration in the case of 2,4,6-TNP -DNP. From the equations obtained, giving the variation of k_{ad} as a function of the initial concentration, a classification following k_{ad} is deduced for an identical initial concentration. This ranking is as follows: 2,4-DNP > PNP > HYDRO > 2,4,6-NPT. Intraparticle scattering is not the only process that controls kinetics. Its k_{id} coefficient appears to decrease when the initial concentration increases.

Adsorption kinetics depend on pH; It is faster at alkaline pH for HYDRO. And 2,4-DNP and at acid pH in the case of PNP and 2,4,6-TNP. All the results obtained demonstrate the simultaneous presence of all or only certain types of interactions: nonlocalised (Van Der Waals-London ?-dispers dispersive forces), donoracceptor, by electrostatic attraction-repulsion and hydrogen bonding. The nature of the interactions responsible for adsorption depends essentially on the pH of the solution, the nature of the surface functions of the coal and the physico-chemical characteristics of the phenolic compounds to be adsorbed.

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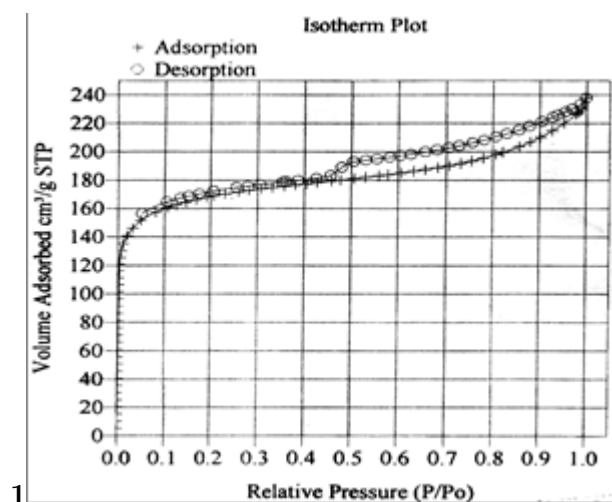
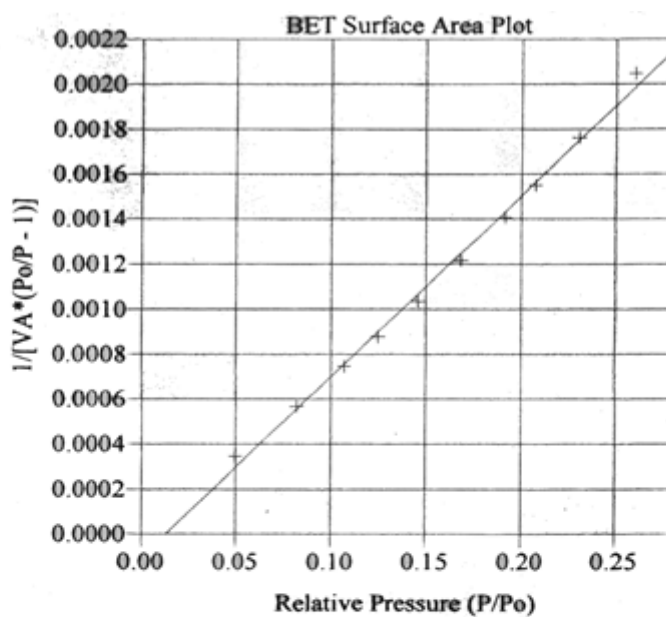


Figure 1: Figure 1 :



BET Surface Area Report

BET Surface Area: $548.1326 \pm 12.1639 \text{ m}^2/\text{g}$
 Slope: 0.008048 ± 0.000174
 Y-Intercept: -0.000106 ± 0.000029
 C: -74.860066
 VM: $125.914910 \text{ cm}^3/\text{g STP}$
 Correlation Coefficient: $9.981403\text{e-}01$
 Molecular Cross-section: 0.1620 nm^2

2

Figure 2: Figure 2 :

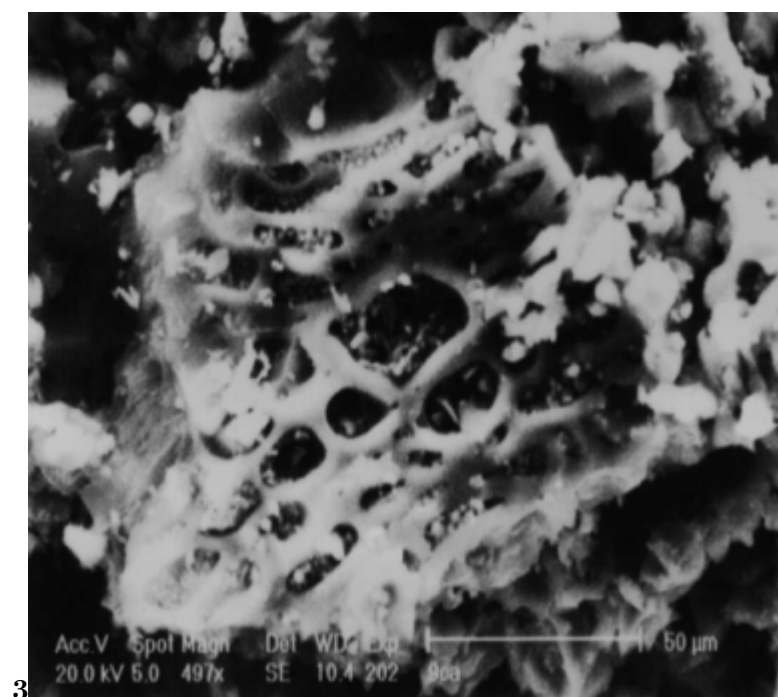


Figure 3: Figure 3 :



Figure 4: Figure 4 :

1

Origine	Date nuclei
Type Activation	Activation (Chemical+Physical)
Specific surface area (m ² /g)	548.13
Average pore diameter (Å)	25.55
Pore volume (cm ³ /g)	0.35
Granulometry (µm)	< 50
Iodine value (mg/g)	849.839
Bulk density (g/cm ³)	0.37
Acid surface function (meq/g)	1.57
Fonctions de surface acides (meq/g)	0.25
pH PZC	8.37

Figure 5: Table 1 :

2

	() Volume XVII Issue III Version I of Researches in Engineering Global Journal			
pKa	Phenol	Hydroquinone	2,4-DNP	2,4,6-TNP
	9.69	7.16	4	0.8
Molar mass (g/mol)	110.11	139.1	184.11	239. 11
Solubility in water (g/l)	80	17	6	1.23
Solubility in water (mmol/l)	0.72	0.122	0.032	0.0053
Fusion temperature (°C)	173	114	113	122
boiling temperature (°C)	286	279	-	300
Dipolar momentµ (deby)	0	5.6	3.4	1.5
Naturel pH	5.65	5.62	4.82	3.85
Chemical displacement? ortho (ppm)	0.74	-0.6	-1.57	-1.94

Figure 6: Table 2 :

Table 4 5. Santana CM, Ferrera ZS, Torres Padrón ME,
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Extraction
Environmental
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of Phenolic Compounds from
Sample New Approaches.

[Note: 6]

Figure 7:

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