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Chemical modification of activated carbons and its effect on the adsorption of phenolic compounds

INGENIERÍA QUÍMICA

Modificación química de carbones activados y su efecto en la adsorción de compuestos fenólicos

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Abstract

In this paper two commercial activated carbons, granular and pelletized, were impregnated with aqueous solutions of phosphoric acid (H_3PO_4), or potassium hydroxide (KOH) in 60% w/w concentrations under moderate temperature conditions (18 °C). It was observed that the impregnation with phosphoric acid increases the adsorption of 2,4-dinitrophenol regarding the starting activated carbon. The adpsorption was determined from isotherms in aqueous solution of phenol and 2,4-dinitrophenol, and experimental data were adjusted to the Freundlich, Langmuir, Toth and Prausnitz-Radke models. Langmuir was the model that best fitted for phenol adsorption, and Toth was the model that best fitted the for 2,4-dinitrophenol adsorption. The results showed that the impregnation of activated carbons without post further heating continued creating changes in surface chemistry and porous structure.

Keywords: *2,4-dinitrophenol, impregnation, isotherm adsorption, modification, phenol, phosphoric acid, sodium hydroxide.*

Resumen

En este trabajo se impregnaron dos carbones activados comerciales, uno granular y otro pelletizado, con soluciones acuosas de ácido fosfórico (H_3PO_4), e hidróxido de potasio (KOH) en concentraciones de 60% p/p en condiciones de temperatura moderada (18°C). Se observó que la impregnación con ácido fosfórico produce un aumento en la capacidad de adsorción de 2,4-dinitrofenol con respecto a los carbones de partida. La adsorción se determinó a partir de la elaboración de las isotermas desde solución acuosa de fenol y 2,4-dinitrofenol, y la posterior aplicación de los modelos de Freundlich, Langmuir, Prausnitz-Radke y Toth de los cuales se obtuvieron los mejores ajustes para Langmuir en el caso de adsorción de fenol, y Toth para la adsorción de 2,4-dinitrofenol. Los resultados permiten concluir que la impregnación de los carbones post activación sin un posterior calentamiento, sigue generando modificaciones en su química superficial y estructura porosa.

Palabras clave: *Ácido fosfórico, 2,4-dinitrofenol, fenol, hidróxido de sodio, impregnación, isoterma de adsorción, modicifación.*

1. Introduction

Industrial development entails the use of high technology products and the development of such products but it generates waste that affects significantly the environment. A product line that has been very successful in the industry is that one which uses phenolic compounds as raw materials, for example the cleaning products sector. These compounds are resistant to degradation, the coagulation and flocculation treatments commonly used in water purification.

One treatment used to clean water after primary separation of waste is the use of activated carbon as a final filter. Because of its porosity and surface chemistry, it provides good results in the adsorption of contaminants such as phenolic compounds, although in some cases these procedures do not reach the necessary purity required by the law nor the one required in order to use the treated water. The uses of activated carbon are conditioned to its surface chemistry and its heteroatoms content, elements such as nitrogen, oxygen and hydrogen, which give the material different acidic, basic or rust-reducing characteristics, and influence their properties, Briceño&Guzmán (2007), Figueredo& Pereira (1999), Ghingombe & Saha (2005), Pereira, et al. (2014), Xua, et al. (2014). Studies have reported that the chemical composition of activated carbons can be altered even more if it is impregnated with a chemical that allows that the adsorption may be accompanied by a reaction of the substance into the carbon, or that the impregnant product may act as a catalyst that promotes oxidation or transformation, Rodriguez-Reinoso& Molina-Sabio (2004), Molina-Sabio et al. (1996).

Impregnating activated carbon with chemicals is performed to change the adsorption capacity of organic contaminants found in water. In this paper the impregnationof activated carbon was used, activated carbons which have a porosity and surface chemistry already developed. The choosen agents were KOH and H_3PO_4. These compounds are used as activating agents when preparing activated carbons by chemical activation. Impregnation without further heating is intended to observe its influence on the adsorption of organic compounds. With this purpose two activated carbons, one granular and another pelletized, were impregnated with a phosphoric acidsolution, ora potassium hydroxide solution in 60% w/w concentrations ata temperature of 18.5 ° C. In order tomeasurethe adsorption capability of the modifiedcarbons, the adsorption isotherms were prepared from aqueous solution of phenol and 2,4-dinitrophenol, and the experimental results were adjusted to the Freundlich, Langmuir, Prausnitz - Radke and Toth models, from where the characteristic parameters were obtained.

2. Materials and methods

2.1 Sample preparation

Two commercial activated carbons, one granular (G) and another pelletized (P) were used as starting materials. Modification of these carbons was carried out using as impregnating agents: H_3PO_4 (GP samples and PP) and KOH (GK and PK sampling) solutions at concentrations of 60% w/w; the ratio of activated carbon to impregnating agent was 1:3 w/w. The impregnation was made at a temperature of 18.5 ° C and the samples were kept at this temperature for 72 hours. After this time, the samples were washed with deionized water until getting a constant pH and then were dried in an oven at 150° C for 72 hours. Some properties of the phenols and the equilibrium pH of each solid are summarized in Table 1.

2.2 Adsorption from aqueous solution of phenol and 2,4-dinitrophenol

The adsorption isotherms from aqueous solution were made by adding 50 mL of phenol solution in the range of 20 to 1000 mg / L and 2.4 -dinitrophenol (2.4-DNP) from 20 to 400 mg / L, into different vials containing 0.1000 g of each of the modified carbon. The pH of the solutions was not adjusted. Samples were storedduring 20 days at a temperature of 18 ° C to guaranteethe equilibrium conditions (storage time was determined by measuring phenol's concentrations in samples every five days, using a UV spectroscopy until getting constant values); then, the samples were filtered and concentrations of phenol and 2,4-dinitrophenol were measured

Table 1. *Physical properties of the phenols in this study andpH balance for activated carbons*

Samples	Equilibrium pH	Molecular weigt (g/mol)	Molecular size (Å)	Solubility (g/L)	pKa
G	6.83				
GK	10.2				
GP	3.15				
P	5.07				
PK	9.6				
PP	3.03				
Phenol		94.1	5.76X4.17	93	9.89
2,4-dinitrophenol		184.1	6.84X5.76	0.6	4.09

by using an UV spectroscopy equipment Thermo Spectronic Genesys 5, at λ_{max} = 271nm for phenol and λ_{max} = 358 nm for 2,4-dinitrophenol.

2.3 Sample identification

The samples identification were performed using a three-letter code: the first corresponding to the type of carbon: granular (G) and pelletized (P); the second corresponds to the substance used for impregnation, in each case: phosphoric acid (P) and potassium hydroxide (K)

To identify the adsorption process at the end of a letter identifying the corresponding sample used as adsorbate: phenol (F) and 2,4-dinitrophenol (D).

Adsorption of phenol and 2,4-dinitrophenol in equilibrium, qe (mmol / g), was calculated through a mass balance is summarized in the following equation:

$$q_e = V\frac{C_o - C_e}{m} \quad (1)$$

Where Co and Ce are the initial and equilibrium concentrations respectively of the phenolic compound in solution (mmol / L); V is the volume of the solution (L) and m is the mass of adsorbent (g).

2.4.Samples characterization

The surface physical properties of the modified activated carbons were determined by measuring the adsorption of nitrogen at 77K on a Quantachrome AS-Au Qwin device. The surface area (S) was calculated using the BET model and the micropore volume, Vo, was obtained by applying the Dubinin-Radushkevich model to the adsorption data; the total pore volume and mesopore volume, Vmeso were also calculated. Vargas (2012).

3. Results and discussion

3.1 Textural parameters

Figure 1 shows the nitrogen adsorption isotherms at 77K corresponding to the original and modified carbons. The isotherms correspond to type I according to IUPAC, Sing et al. (1985), which is characterized by a steep curve with a more closed curvature at low relatively pressures (P/P0 < 0.1), and a plateau in the high pressure range, characteristic of highly microporous materials. As observed, the modification of both carbons do not change the microporosity significantly.

Table 2 summarizes the textural properties of all the samples. The surface area was calculated using the Brunauer, Emmet and Teller model, Brunauer, et al. (1938) which have surface area values in the range of 856–1147 $m^2 \cdot g^{-1}$ and pore volume values of 0.36–0.58 $cm^3 \cdot g^{-1}$ calculated by the Dubinin–Raduchkevich model [17]. The IUPAC classification of porosity was used, Sing et al. (1985).

Modifications with potassium hydroxide, and phosphoric acid generated changes in surface area, micropore volume, and the volume of mesopores,

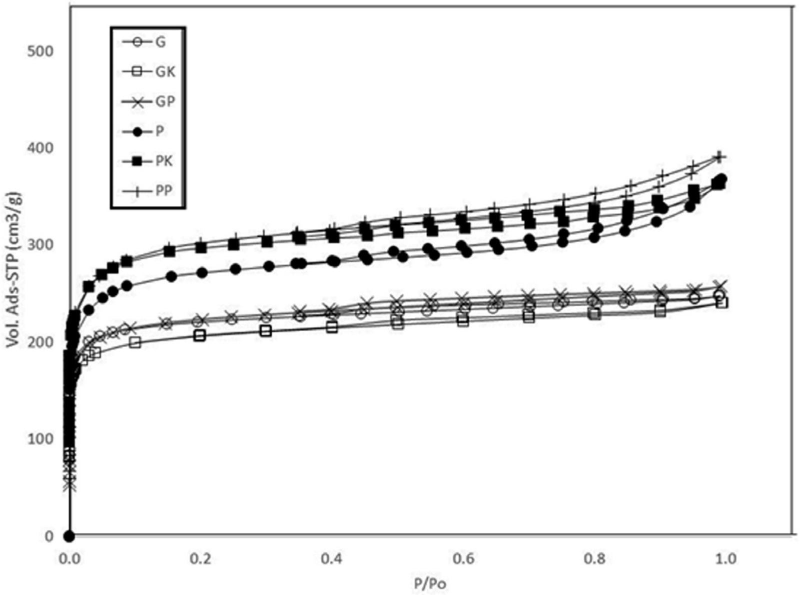

Figure 1. *Nitrogen adsorption isotherm at 77K*

Table 2.*Textural parameters for activated carbons, obtained from N2 adsorption isotherms at 77 K..*

Sample	***SBET***	***Voa***	***Vmesob***	***V0.99c***
	m^2/g	cm^3/g	cm^3/g	cm^3/g
G	*856*	*0.34*	*0.04*	*0.38*
GK	*784*	*0.3*	*0.06*	*0.36*
GP	*857*	*0.32*	*0.07*	*0.39*
P	*1040*	*0.37*	*0.15*	*0.52*
PK	*1142*	*0.41*	*0.13*	*0.54*
PP	*1147*	*0.44*	*0.14*	*0.58*

[a]Micropore Volume; [b]Mesopore Volume; [c]Total Volume.(values calculated from Dubinin-Raduchkevich model)

showing that both the potassium hydroxide and phosphoric acid interact with the surface groups in the activated carbon.

The results show that impregnation of the activated carbons with these chemicals at 18°C causes them to react with superficial oxygen groups, initiating a surface modification that is accompanied by a change in the surface area and volume of micropores in the activated carbons.

3.2 Adsorption isotherms

To study the effect of the changes produced by impregnating the activated carbons, in the adsorption of phenol and 2,4 dinitrophenol, the experimental data was adjusted to the Freundlich, Fierro et al. (2008), Langmuir, Murillo et al. (2011), Quing-Song et al. (2010), Praustitz-Radke , Foo & Hammed (2010), Leyva-Ramos et al (2007), and Toth , Foo & Hammed (2010), models.

Figures 2 and 3, show the isotherms from aqueous solution for the samples of granular activated carbon modified with H_3PO_4 and KOH respectively, compared to granular carbon with no a subsecuent change. To compare the isotherms, it shows that the impregnation of granular carbon with phosphoric acid generates an increased adsorption of 2,4-DNP, indicating that the post activation impregnation

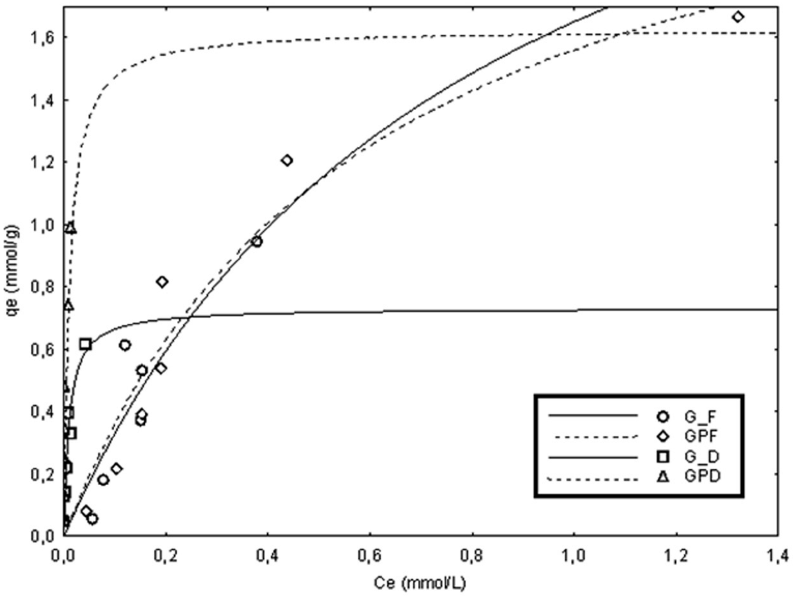

***Figure 2**.Granular Carbon H_3PO_4 modified for phenol adsorption (GPF) and 2,4-DNP (GPD) compared to granular activated carbon with no a subsequent change in phenol adsorption(G_F) or 2,4-DNP (G_D). The lines represent the fit to the Langmuir model.*

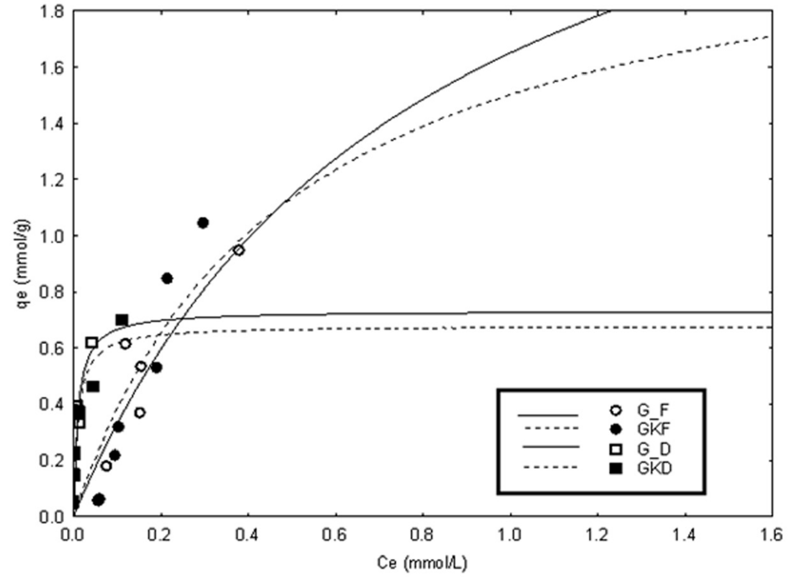

***Figure 3**. Granular Carbon KOH modified for phenol adsorption (GKF) and 2,4-DNP (GKD) compared to granular activated carbon with no a subsequent change in phenol adsorption(G_F) or 2,4-DNP (G_D). The lines represent the fit to the Langmuir model.*

without temperature increase, generates a change occurs in the solid which favors the adsorption of the phenolic compound. This modification is associated with the chemistry surface since phosphoric acid can interact with oxygen groups present on it and remain there to facilitate retention of the 2,4-DNP or also it carries out polymerization of phosphoric acid whose species is deposited on the surface and promote the adsorption of the adsorbate, Nahil&Williams (2012), Yavuz, (2010).

Regarding the impregnation hydroxide (Figure 3), it can be observed a slight decrease in the adsorption of 2,4-DNP reference to the nonimpregnated activated carbon, indicating that under the conditions of this study the impregnation of activated carbons with KOH has not effect on 2,4 DNP adsorption. The samples impregnated with sodium hydroxide, KOH shows a slight decrease in the adsorption of phenol, and the modification with phosphoric acid, H_3PO_4, appears to have no influence on the adsorption of phenol.

In Figures 2 and 3, can be seen that the isotherms behavior is not ideal. This may be due to lateral interactions between the adsorbed molecules or interactions with the surrounding water.

In studies of adsorption of phenol and nitrophenols on carbonaceous materials, it was found that the adsorption of phenolics followed the sequence 2,4-DNP >2-NP > phenol, and this behavior is associated to pH from the solution and the content of surface groups on the activated carbon. The pH influences the ionization state of the phenols and the solid surface, and the amount of phenolic compound adsorbed decreases with the increased amount of anionic species in solution. This behavior may be attributed to the presence of electronic repulsion forces between the formal charge of the anions and the carbon surface which would make it more difficult to the fenolate anions to approach to the appropriate spatial orientation: parallel to the graphene plane. At the same time, it is possible that the phenolic compounds have lower electron affinity towards carbon spheres in the shape of phenolate, it is because the donoric nature of the anionic oxygen counteracts the presence of nitro attractor groups. In an alkaline environment, phenolics are predominantly in the protonated form and the oxygen anion stabilizes its own negative charges through the resonance aromatic ring by increasing the repulsion forces between molecules of phenol and the carbon surface, Lazo-Cannata (2011).

This adsorption sequence matches the results of this study and it allows the observation that the adsorption of phenol on the surface of the activated carbon is favored by the presence of the nitro group (NO_2) on the structure of the phenols; the latter produce a decrease in the electronic density around the aromatic rings.

Regarding the size of the molecule adsorbate, this is a factor that determines its adsorption on the pore structure of activated carbon, and for it to occur in the case of water treatment, it is required a wide distribution of micropores able to level the mesopore range taking into account that in this case substances with different molecular dimensions have to be adsorbed. Another aspect to consider is that the adsorption in aqueous phase is essentially an exchange process, Moreno-Castilla (2004), so many molecules are adsorbed not only because they are attracted by the solid but because they are rejected by the aqueous medium due to its polarity, which is consistent with the fact that the maximum adsorption of the compound 2-4 DNP of a less polar character, compared with that obtained for phenol, one of a more polar character.

About the effect of the solvent, Qing Song et al (2010), reports that the water molecules can be adsorbed on the surface oxygenated groups through hydrogen bonds, which is not favorable for the adsorption of phenol and some active sites that may be occupied. Moreno-Castilla et al (2000), also describe the effect of the hydrophobic interactions in the adsorption of phenol; as on an aqueous solution the hydrophobicity adsorbate, such as 2.4-DNP, would have a higher tendency to be adsorbed and retained on the carbon surface, as long as the surface of the activated carbon has low content of oxygen groups.

Table 3 shows the summary of the results obtained for the parameters of Langmuir and Freundlich models, qe is the amount per unit mass of carbon (mmol / g), KF Freundlich constant (mmol/g (mmol/L)n), Ce is the concentration of adsorbate in the solution at equilibrium (mmol /L), n is an empirical parameter. Adsorption is considered satisfactory when the Freundlich constant n takes values in the 1-10 range. q0 is the maximum adsorption capacity per unit mass of carbon (mmol/g), KL is a constant that is related to the free energy of adsorption (L/mmol). RL is a dimensionless constant called separation factor, the adsorption is: irreversible when RL = 0, favorable when 0 <RL<1, linear when RL = 1, and unfavorable when RL> 1. In the table it can be seen that for the Freundlich model the value of n, which represents the energy heterogeneity of

Table 3. *Parameters of the Langmuir and Freundlich models.*

Samples	Freundlich			Langmuir			
	$q_e = K_F C_e^{1/n}$			$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$			
	K_F	N	R^2	q_o	K_L	R_L	R^2
	mmol/ g(mmol/L) n			mmol/g	(L/mmol)		
G_F	2.161	1.215	0.900	2.968	1.254	0.200	0.907
GKF	1.338	1.976	0.927	2.226	2.077	0.083	0.965
GPF	1.502	1.743	0.941	2.470	1.717	0.099	0.968
G_D	2.672	2.174	0.962	0.732	99.258	0.006	0.968
GKD	1.582	2.659	0.975	0.678	100.556	0.006	0.966
GPD	16.685	1.489	0.953	1.628	95.018	0.005	0.955
P_F	2.084	1.267	0.951	3.933	0.920	0.170	0.959
PKF	1.164	1.896	0.919	1.789	2.161	0.080	0.930
PPF	1.914	1.447	0.939	3.150	1.343	0.123	0.958
P_D	4.264	1.953	0.952	0.843	113.941	0.005	0.966
PKD	5.508	1.749	0.964	0.879	101.132	0.006	0.953
PPD	4.903	2.495	0.938	1.103	390.046	0.001	0.970

the adsorption sites for the samples, is between 1.215 and 2.659. This indicates that the adsorption of both phenol and 2,4-dinitrophenol, according to this model, can be considered satisfactory. The high settings of the different samples to the Freundlich model may be an indication of the heterogeneity of the surface of each of the solids.

For the Langmuir model, in the same table, it is noteworthy that the values of the constant related to the free energy of adsorption KL for all carbon samples which adsorb 2,4-DNP are between 95.018 and 113.941, while for the samples that adsorbed phenol it is significantly lower and these values fluctuate between 0.920 and 1.343. This indicates differences in the adsorption process. On the subject of the maximum adsorption capacity, higher values were observed for the adsorption of phenol on activated with respect to the values obtained for the 2.4 DNP carbons. On the other hand, the values of RL of the Langmuir model in this study are in the range 0.005 to 0.200 for the granular carbons and 0.005 to 0.17 for pelletized carbons, indicating that the adsorption of both phenol and 2,,4-DNP is favorable. It is remarkable that when comparing the same parameters in function of the adsorbate, the RL values for carbons with phenol are in the range from 0.08 to 0.17 while the values of this parameter for carbons that adsorb 2-4 dinitrophenol are among 0.005 and 0.006. These values are closer to zero than the values corresponding to phenol adsorbing carbons, suggesting that the adsorption process of a larger molecule such as 2,4-DNP is closer to irreversibility.

In Figure 4, it is observed the relationship between parameter n and KL of the Freundlich and Langmuir models; where one can see the difference in adsorption energy for all samples where adosrbate is the phenol compared to those where the adsorbate is the 2,4 DNP. By analyzing the values of maximum adsorption

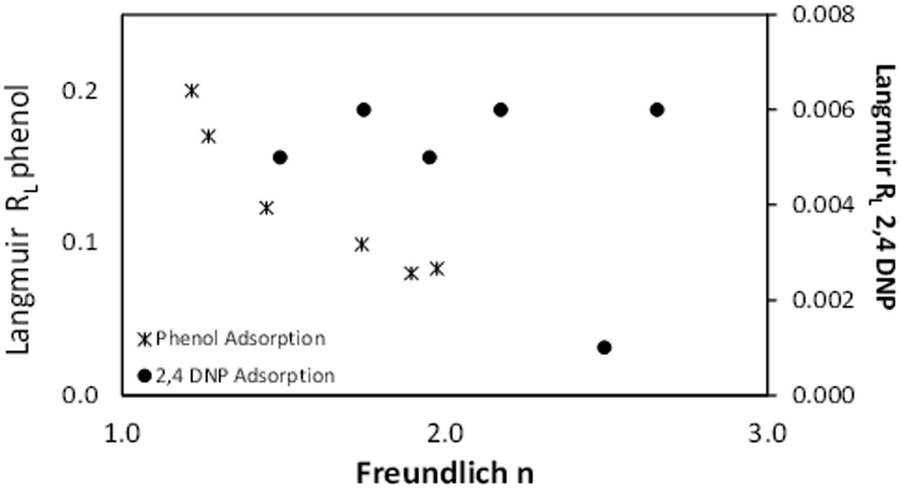

Figure 4. *Relationship between n and R_L*

capacity per unit mass of carbón, qo of the Langmuir model for the samples, it can be seen that this value is between 2.226 and 2.968 for granular carbon which adsorbed phenol, while for the same granular carbons when they adsorbed 2,4-DNP,the values are between 0.678 and 1.628. This suggests a greater adsorption capacity for a smaller molecule such as the case of phenol whose size has a better ability to reach the micropores where adsorption takes place.

The very same tendency can be observed for the pelleted carbons which have qo values between 1.789 and 3.933 for the ones adsorbing phenol and values between 0.843 and 1.103 for the ones adsorbing 2,4-DNP. The qo value showed the effect on the adsorption capacity caused by the modifications made. In the case of granular carbon, when phenol is adsorbed, it is observed that the value of qo is higher for the activated carbon without further impregnation (G_F: 2.968) while the lowest value is for the carbon impregnated with KOH (GKF: 2.226). This suggests that the impregnation performed has no major effect on the adsorption of phenol. Regarding the adsorption of 2,4-DNP, the situation is extremely different, because while for carbon impregnated adsorbent 2,4-DNP (G_D) the value of qo is 0.732, this same value is twice as high for phosphoric acid impregnated carbon (GPD: 1.628). This shows that the impregnation with phosphoric acid activated carbon generates a change in the surface which increases the capacity of selectively adsorbing to a compound of lower polarity such as the 2,4-DNP. The behavior observed for granular carbons is also present for the pelletized carbon. Regarding granular and pelletized carbons impregnated with KOH, the qo values are lower than the respective unmodified carbon, suggesting that the impregnation with KOH is not advisable if one wants to use the carbon to adsorb phenol because it lowers the adsorption capacity of the activated carbons toward such contaminants.

Table 4 summarizes the results obtained for the parameters of the models Radke-Prausnitz and Toth, with KT (mmol/g) and aT (L/mmol) are constants and t is the exponent of the model, arp y rR are constants that relate with carbon adsorption capacity and β is a constant related to the heterogeneity of the surface.

It shows that for the Prausnitz-Radke model the aRP constant value related to the adsorption capacity, has high values for both granular and pelletized activated carbons adsorbing 2,4- DNP, while carbons that adsorbed phenol have low values for this constant. This behavior is similar to that observed for the Langmuir model described above.

For the Toth model, it can be seen that the KT constant associated with the adsorption capacity show a great difference between the samples in which phenol was

Table 4. *Parameters of Prausnitz-Radke and Toth Models*

Samples	***Prausnitz-Radke***				***Toth***			
	$q_e = K_F C_e^{1/n}$				$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$			
	a_{RP}	r_R	β	R^2	K_T (mmol/g)	a_T (L/ mmol)	T	R^2
G_F	3.273	0.374	-2.435	0.911	904.954	3.869	0.246	0.907
GKF	3.336	184.120	-7.663	0.985	3542.534	4.614	0.226	0.975
GPF	3.121	3.974	-1.274	0.980	13491.810	5.273	0.204	0.975
G_D	105.954	1.319	0.201	0.973	0.213	0.793	0.043	0.944
GKD	142.858	1.188	0.241	0.982	1.231	0.002	1.370	0.983
GPD	72.829	72.460	-13.916	0.899	5.158	0.005	1.556	0.956
P_F	2.974	0.046	-13.538	0.963	1449.332	5.035	0.269	0.960
PKF	4.152	1.716	0.079	0.930	1.444	0.258	1.273	0.931
PPF	3.417	0.430	-15.428	0.977	339924	6.583	0.166	0.963
P_D	103.412	1.033	0.061	0.966	14.776	0.961	0.025	0.961
PKD	30.228	7.931	-4.667	0.866	4.799	0.001	2.146	0.964
PPD	322.531	0.245	-0.385	0.975	0.002	0.024	0.305	0.975

adsorbed and those in which 2,4-DNP was adsorbed. This behavior is similar to that one reported for the constant qo and aRP of the Langmuir and Radke-Prausnitz models respectively.

4. Conclusions

Impregnation of activated carbons, granular and pelletized, with phosphoric acid without subsequent heating, promotes the adsorption of 2,4-DNP; which indicates a change in the surface chemistry of carbon associated to the interaction between phosphoric acid and oxygen groups presents on the surface, this causes the acid to stay there and probably to get polymerized, and thus it facilitates the retention of 2,4-DNP.

The equilibrium pH found for activated carbon modified with phosphoric acid was about 3, a condition which favors the adsorption of phenolics.

Modifying activated carbon with potassium hydroxide has not influence on the adsorption of phenolic compounds, indicating that under the conditions of this study the impregnation of activated carbons with KOH solution does not modify the surface of the solid. The modification with phosphoric acid appears to have no influence on phenol adsorption.

In terms of higher adsorption capacity, high values for the adsorption of phenol on activated carbons were observed with respect to the values obtained for 2,4 DNP, considering that the maximum adsorption capacities are obtained between 0.68 and 1.63 mmol / g for 2,4-DNP while phenol adsorption is higher at levels between 1.79 and 3.93 mmol / g.

5. Acknowledgements

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