UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN
FACULTAD DE CIENCIAS QUÍMICAS

EVALUATION OF THERMAL AND CHEMICAL TREATMENTS ON GRANULAR ACTIVATED CARBON TO REMOVE ORGANIC MOLECULES FROM WATER

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M. SC. CARINA AGJAETP SÁENZ ALANÍS

COMO REQUISITO PARA OBTENER EL GRADO DE DOCTOR
EN CIENCIAS CON ORIENTACIÓN EN
PROCESOS SUSTENTABLES

NOVEMBER, 2016

UNIVERSIDAD AUTÓNOMA DE NUEVO LEÓN
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THESIS

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AUTONOMOUS UNIVERSITY OF NEW LEON
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PRESENTED BY

M.SC. CARINA AGJAETP SÁENZ ALANÍS

TO OBTAIN THE DEGREE OF DOCTOR IN SCIENCES WITH ORIENTATION IN SUSTAINABLE PROCESSES

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CONTENT

Summary

The influence of three different treatments on the physical and chemical properties of activated carbon, as well as the adsorption capacity towards phenol, methylene blue and congo red was evaluated. After the heat treatment, surface area decreased and total pore volume diminished about 8.5%, and the total basic groups decreased 18% while the total acid groups increased 8% in comparison with the raw activated carbon. Equilibrium adsorption of phenol was described well with the Freundlich model, whereas methylene blue and congo red adsorption fitted the Langmuir isotherm model. Adsorption kinetics of all three was predicted adequately with the empirical pseudo--second order model, the intraparticle diffusion model and the homogeneous solid diffusion model, but mass transfer coefficients of the diffusion models help to better understand the adsorption phenomenon. Intraparticle diffusion seems to be the rate--controlling step in the adsorption process. In conclusion, physical and chemical features of the activated carbon are affected when the adsorbent is heated under inert atmosphere increasing the adsorption capacity of phenol, methylene blue and congo red.

1. INTRODUCTION

Nowadays water availability is one of the most important environmental problems in the world due to some factors as the population increment, the disappearance of some sources of fresh water, and the low quality in water from natural sources because of the presence of microorganisms and/or anthropogenic chemicals and compounds.

The concern about the potential harm of man-made organic compounds in water and the improvement of the analytical capabilities have led to an array of regulations designed to address these risks.

In order to eliminate these harmful substances from water before the human use, diverse treatments conforming what is now called "conventional water treatment" are carried out in water treatment plants. These treatments include filtration, sedimentation, coagulation/flocculation, and disinfection. However, in the disinfection step, the addition of certain substances, just as the chlorinated compounds used in many of the water treatment plants, may react with residues of organic matter present in water, forming disinfection byproducts (DBPs), which generally are toxic for the human beings, therefore it is important to completely remove all of the organic material before the disinfection step.

An alternative to remove these organic substances from water is adsorption, which has proven to be very efficient removing pollutants in concentration lower than 10 mg/L, situation where conventional techniques became expensive. In addition, adsorption may be carried out by using a wide variety of adsorbents depending on the system requirements, being the adsorbent chosen for this study activated carbon because of its high surface area, porous structure, mechanical resistance and its capacity to be submitted to different treatments in order to change its surface functional groups. (Ahmed & Dhedan, 2012; Ai, Li, & Li, 2011; Aksu & Kabasakal, 2004)

In this work, the adsorption of phenol, methylene blue and congo red with a commercial bituminous activated carbon was studied. The three organic molecules were chosen in order to analyze the effect of the molecular size and ionization in the adsorption process. Besides, the effect of different thermal and chemical treatments on the activated carbon surface and its adsorption capacity was studied.

1.1 ADSORPTION

Adsorption is a surface phenomenon occurring when a substance, called adsorbate, migrates from a liquid or gaseous matrix to a solid component, called adsorbent, adhering to its surface with chemical and physical bonds. (Ali & Gupta, 2006)

Usually, in the adsorption process there are different types of possible interactions between the adsorbent and the adsorbate, leading to a combination of physical and chemical adsorption mechanisms occurring simultaneously. (Aksu & Kabasakal, 2004)

Adsorption is affected by several factors as the surface chemistry of the adsorbent, the chemical characteristics of the adsorbate, and some properties of the solution, including pH, temperature, adsorbate concentration, and presence of other adsorbates. (Aksu & Kabasakal, 2004; Ali & Gupta, 2006)

A variety of materials can act as adsorbents, and they are usually classified as biosorbents and adsorbents. Biosorbents are raw materials obtained in nature from previously living organisms, such as seaweeds, wood, fruit seeds, agricultural wastes and yeasts. Adsorbents are all of the others materials obtained synthetically or that are not previously living organisms, such as clays or activated carbon.

In this work, a commercial bituminous activated carbon was selected as adsorbent due to its physical and chemical characteristics, such as high surface area, and the possibility to be submitted to a series of physical and chemical treatments in order to change its chemical surface and improve its adsorption capacity towards a certain adsorbate.

1.2 ACTIVATED CARBON

Activated carbon is often used as adsorbent in water treatment processes due to its high surface area and mechanical resistance.

There are many different materials that can be used as activated carbon precursors, such as wood, coconut shells, raw straw, and mineral charcoal. The properties of the final activated carbon depend on the type and morphology the of precursor, activation temperature (usually 500 °C-1000 °C), the pyrolysis time, the oxidizing gas used and the chemical substance used for impregnation.

(Ahmad, Loh, & Aziz, 2007; Ahmed & Dhedan, 2012; Bahri, Calvo, Gilarranz, & Rodriguez, 2012)

1.2.1 STRUCTURE AND CHARACTERISTICS OF ACTIVATED CARBON

The structure of activated carbon is formed with carbon atoms aligned in parallel piles of hexagonal layers linked tetrahedrally. The heteroatoms of the carbon surface contain mainly oxygen, nitrogen and hydrogen, being the former the one in more proportion. The activated carbon surface contain functional groups such as carboxylic, carbonyl, phenolic, enols, lactones and quinones, which have great influence in the adsorption proprieties and the carbon surface reactivity. Depending on the type and quantity of the functional groups present, the surface of activated carbon may have acid, basic or neutral characteristics. (Abe, Kawashima, Kozawa, Sakai, & Kaneko, 2000; Allwar, 2012; Green & Martin, 1967; Shaarani & Hameed, 2011)

Nevertheless, adsorption capacity of activated carbon depends mainly on its large surface area and pore distribution. The pore size of activated carbon is classified as micropore (less than 2 nm), mesopore (2-5 nm) and macropore (more than 5 nm). (Abe et al., 2000; Asadullah et al., 2013)

1.2.2 TREATMENTS ON ACTIVATED CARBON

Adsorption of a specific adsorbate on activated carbon may be improved by a surface modification that changes the physical structure and/or the types and quantities of the functional surface sites.

In this work, three treatments were carried out on activated carbon in order to analyze the effect on its physical and chemical surface properties and its performance as adsorbent of different organic molecules: a thermal treatment in nitrogen atmosphere, a chemical treatment with nitric acid, and a chemical treatment with ammonium hydroxide.

1.3 SELECTED POLLUTANTS

The usage of phenol, methylene blue and congo red was selected in order to obtain information about the role of surface functional groups in adsorption of both ionized and not ionized molecules, as well as the importance of the molecular size in the adsorption process.

1.3.1 PHENOL

Phenol is a toxic substance that may cause severe renal insufficiency, convulsions or even death. The presence of phenol on water causes an unpleasant taste and a change of odor during chlorination. Also, the chlorination of water containing phenol may produce chlorophenols, which are toxic and corrosive to eyes and skin. (Gundogdu et al., 2012)

Phenolic compounds may be present in wastewater of industries that produce paper, resins, pesticides, insecticides, plastics, paints and solvents, as well as in oil refineries and pharmaceutical industries, but they are also produced naturally by plants. (Beker, Ganbold, Dertli, & Duranog, 2010; Gundogdu et al., 2012)

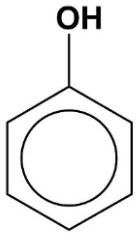

Figure 1. Molecular structure of phenol. The molecular weight is 94 g/mol, its diameter is 0.25 nm and its pKa is 9.9.

1.3.2 METHYLENE BLUE

Methylene blue may be present in wastewater of industries such as textiles, printing, food, cosmetic, paints and plastics. It is chemically stable and resistant to biodegradation sue to its complex aromatic molecular structure, and when it reacts with strong oxidant agents some of the products may be toxic, carcinogenic or mutagenic. (Ai et al., 2011; Sharma, Sinha, & Upadhyay, 2010)

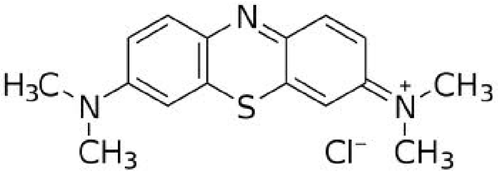

Figure 2. Molecular structure of methylene blue. The molecular weight is 319.85 g/mol, its diameter is 1.5 nm and its pKa is 2.4.

1.3.3 CONGO RED

Congo red may be present in effluents of industries as textiles, food, and printing, among others. Besides, congo red metabolizes benzidine, which is carcinogenic, its structural stability makes difficult its biodegradation. (Oladoja & Akinlabi, 2009)

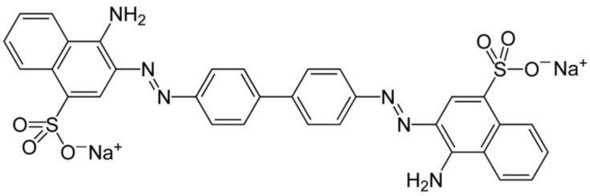

Figure 3. Molecular structure of congo red. The molecular weight is 696.66 g/mol, its diameter is 2.1 nm and its pKa is 0.2.

2. ANTECEDENTS

Adsorption processes had been studied for many years, as well as the effect of different treatments on adsorbents surface. Some of those studies are about activated carbon and its adsorption capacity towards a variety of adsorbates before and after chemical and thermal treatments.

2.1 ACTIVATED CARBON SURFACE MODIFICATION TREATMENTS

Adsorption capacity of activated carbon usually decreases with time when stored in a humid environment due to a gradual surface oxidation. Therefore, obtaining activated carbons with surface properties basics and/or hydrophobic is quite important, since these types of activated carbons have showed being more resistant to this effect. (Menendez, Phillips, Xia, & Radovic, 1996)

In order to modify the surface chemistry of activated carbon, different treatments can be carried out. Most of the treatments reported in literature consist of heating the activated carbon in presence of different gases, as well as oxidation, amination, and impregnation with different chemicals at room temperature. These treatments may change not only the chemical and structural characteristics of the carbon, but also the surface reactivity towards specific compounds of interest, such as ionized or neutral organic compounds. It has been reported that when activated carbon is treated at high temperatures under nitrogen atmosphere, the oxygen containing sites are removed and the carbon basicity increases, but this surface is not stable, and can re adsorb oxygen even at room temperature and rapidly become reacidified. Menéndez et al. proposed a model for explaining these reactions considering in particular the pyrone and lactone groups and assuming that all the others acidic oxygen surface groups suffer a similar fate. This model stablishes that after the activated carbon is thermally treated in a nitrogen atmosphere, isolated unpaired electrons (free radicals) edge sites are formed, as well as carbon atoms with a triple bond character, leaving highly reactive carbon atoms in the resultant surface. (Green & Martin, 1967; Menendez et al., 1996)

2.1 ADSORPTION ISOTHERMS

Adsorption capacity can be calculated by Equation 1, where q is the adsorption capacity, C_0 is the initial adsorbate concentration in the solution, C_e is the adsorbate concentration in solution at equilibrium, V is the volume of the solution, and m is the adsorbent mass quantity.

$$q = \frac{V(C_0 - C_e)}{m} \qquad \text{Equation 1}$$

Adsorption experiments at equilibrium allow relating the concentration of adsorbate that remains in the solution and the adsorption capacity of the adsorbent, in other words, the quantity of adsorbate removed per unit mass of adsorbent. In this work, Langmuir, Freundlich and Temkin isotherm models were used to describe the adsorption at equilibrium of phenol, methylene blue and congo red with raw and treated activated carbons.

2.1.1 LANGMUIR ISOTHERM

Langmuir isotherm model is represented considers that the adsorption process is carried out in a monolayer, where all of the adsorption sites are of the same type and they are all occupied at the end of the process.

Langmuir model is represented by Equation 2, where q_e is the adsorption capacity at equilibrium, C_e is the concentration of the adsorbate in the solution at equilibrium, q_{max} is the maximum adsorption capacity, b is the Langmuir constant.

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \qquad \text{Equation 2}$$

2.1.2 FREUNDLICH ISOTHERM

Freundlich isotherm model considers that active sites for adsorption are heterogeneous, and there is also a possibility that multilayers of adsorbate may be formed on the adsorbent surface.

Freundlich model is represented by equation 3, where q_e is the adsorption capacity at equilibrium, C_e is the concentration of the adsorbate in the solution at equilibrium, K_F is the Freundlich constant and n is the heterogeneity factor.

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$$q_e = K_F C_e^{1/n} \qquad \text{Equation 3}$$

2.1.3 TEMKIN ISOTHERM

Temkin isotherm considers the effect of some indirect adsorbent-adsorbate interactions. This equation considers that the heat adsorption of all molecules in the layers decreases linearly with coverage because of these interactions.

Temkin model is represented by equation 4, where q_e is the adsorption capacity at equilibrium, C_e is the concentration of the adsorbate in the solution at equilibrium, R is the gas constant, T is the absolute temperature, b_T is a Temkin constant and K_T is a Temkin parameter related to heat adsorption.

When K_T is lower than 10 kcal/mol, it is attributed to physical adsorption, and if its value is between 20-100 kcal/mol, it is related to chemical adsorption.

$$q_e = \frac{RT}{b_L} ln(K_T C_e) \quad \text{Equation 4}$$

2.2 Adsorption kinetics

Adsorption kinetics represent the behavior of the adsorption process along the time. It provides information about both the dominant step in the adsorption process and the affinity of the adsorbate with the adsorbent.

In this work, the obtained adsorption kinetic data were used to obtain the parameters of the pseudo second order model. Also, the effective diffusion coefficient was calculated by using the intraparticle diffusion model proposed by Weber and Morris and the homogeneous solid diffusion model (HSDM) with the mathematical solution proposed by Crank.

2.3.1 PSEUDOSECOND ORDER MODEL

The pseudo second order was proposed by Ho and McKay as shown in Equation 4: (11)

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad \text{Equation 4}$$

Where q_e and q (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively, and k_2 (g/mg.min) is the rate constant of the adsorption process.

Integrating Equation 4 from $t = 0$ to $t = t$ and from $q = 0$ to $q = q$, and reaccommodating terms, the Equation 5 is obtained:

$$\frac{1}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Equation 5}$$

The parameters k_2 and q_e in this model can be calculated by plotting t/q versus t. Moreover, with the estimated values of k_2 and q_e, the initial adsorption rate (h) can be obtained with Equation 6:

$$h = k_2 q_e^2 \quad \text{Equation 6}$$

Here h (mg/ g.min) represents the quantity of adsorbate adsorbed per unit of mass of the adsorbent and per unit of time, and it can be used as a comparative parameter for kinetic adsorption experiments conducted at similar conditions.

2.3.2 WEBER AND MORRIS MODEL

In the model proposed by Weber and Morris (12) (Equation 7), q_t represents the concentration of the adsorbate in the activated carbon at time t, k_p is associated with the intraparticle diffusion rate constant, which corresponds to the slope of the plot, and the intersection I is related with the thickness of the boundary layer.

$$q_t = k_p t^{0.5} + I \qquad \text{Equation 7}$$

After obtaining the k_p value, the effective diffusion coefficient D_i can be determined with Equation 8, where dp is the particle diameter.

$$k_p = \left(\frac{3q_e}{d_p}\right)\sqrt{\frac{D_i}{\pi}} \qquad \text{Equation 8}$$

2.3.3 HOMOGENEOUS SOLID DIFFUSION MODEL

In the homogeneous solid diffusion model and its solution firstly proposed by Crank (1956) (Equation 9), (13) $\bar{q}$ and q_∞ are the average concentration of solute in the solid at any time and at infinite time, respectively, t represents the time, R the particle radius, and D_s the effective diffusion coefficient.

$$\frac{\bar{q}}{q_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2} exp\left(\frac{-D_s n^2 \pi^2 t}{R^2}\right) \qquad \text{Equation 9}$$

It is noteworthy that Equation 9 is valid only by assuming an “infinite bath” situation, which occurs if the adsorbent is a solid sphere initially solute free and its surface concentration remains constant during the adsorption process. (13)

The mass transfer coefficient can be determined by using Equation 10, where C represents the concentration at any time, C_0 is the initial concentration, L is the length of the packed bed, ϵ is the packed bed porosity, v is the interstitial axial velocity, k_f is the global mass transfer coefficient in the liquid phase, and S_0 is the surface area of the adsorbent particle per unit of particle volume.

$$\frac{C}{C_0} = exp\left[-\frac{(1-\epsilon)k_f S_0 L}{\epsilon v}\right] \qquad \text{Equation 10}$$

If the values obtained of C/C_0 are plotted versus time for the first minutes of the process, it can be possible to extrapolate the data to the time when the first fraction of the fluid that entered the column goes out of it, that is, when $t = L/v$, and the value of C/C_0 can be determined. By using this value, k_f can be calculated if the rest of the parameters are known. (13)

3 HYPOTHESIS AND OBJECTIVES

According to revised bibliography a hypothesis was created for this project. This hypothesis and the objectives of this work are showed below.

3.1 HYPOTHESIS

When activated carbon is subjected to a thermal treatment in nitrogen atmosphere, or a treatment with ammonium hydroxide, the surface chemistry changes enhance the adsorption capacity of organic molecules negatively charged in solution.

3.2 GENERAL OBJECTIVE

To evaluate the effect of different thermal and chemical treatments on the commercial granular activated carbon structure and its behavior in the adsorption of dissolved organic molecules.

3.3 SPECIFIC OBJECTIVES

1. To modify the activated carbon with a thermal treatment in nitrogen atmosphere, a chemical treatment with nitric acid and a chemical treatment with ammonium hydroxide.

2. To characterize the materials obtained before and after the treatments by Boehm’s method, nitrogen physisorption (BET), infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

3. To determine the parameters of the Langmuir, Freundlich and Temkin models.

4. To determine the parameters for the pseudosecond order kinetic model and the diffusion coefficient with the Weber and Morris model and the homogeneous solid diffusion model.

4. METHODOLOGY

A bituminous commercial granular activated carbon acquired in CLARIMEX was used as starting material for this study. The physical and chemical changes on the surface of activated carbon after a thermal treatment, a treatment with nitric acid and a treatment with ammonium hydroxide on the carbon surface was evaluated, as well as the effect of these treatments on adsorption capacity of phenol, methylene blue and congo red. Besides, kinetic experiments were carried out and a global diffusion coefficient was calculated.

4.1 ACTIVATED CARBON TREATMENTS

A thermal treatment in nitrogen atmosphere, an oxidation treatment with nitric acid and a treatment to introduce nitrogen groups with ammonium hydroxide were carried out for a bituminous commercial granular activated carbon.

4.1.1 THERMAL TREATMENT

A carbon sample was placed in a quartz reactor with a constant nitrogen gas flow. The sample was heated at a rate of 10 °C/min until 800°C, and then the heating rate was reduced at 5 °C/min until a temperature of 900°C was reached. The carbon was kept at 900 °C for 4 h, and subsequently it was allowed to cool down at room temperature maintaining the same nitrogen gas flow rate. Finally, the heat treated carbon was sieved to a size of 1-2 mm and stored in a desiccator for future use. The resulting carbon was labeled as HGAC, and will be presented like that in the document.

4.1.2 NITRIC ACID OXIDATION

Activated carbon was added to HNO_3 at 40% volume with a relation of 50g/L. The solution was then heated to 60 °C and this temperature was kept for 4 h. After that, the activated carbon was filtered and dried at 100 °C for 12 h. After the drying step the activated carbon was washed with distillated water to remove the acid excess, dried again at 100 °C for 12 h, and stored in a desiccator for future use. The resulting carbon was labeled as OGAC, and will be presented like that in the document.

4.1.3 AMMONIUM HYDROXIDE TREATMENT

Activated carbon was put in contact with HNO3 at 40% volume with a relation of 50g/L. The solution was then heated to 60 °C for 4 h, filtered and put in contact with a 20% ammonium hydroxide solution maintaining a relation of 30 g/L for 2 days at 25 °C. After this the activated carbon was washed with distillated water, filtered and dried out at 100 °C for 12 h and saved in a desiccator for future use. The resulting carbon was labeled as AGAC, and will be presented like that in the document.

4.2 CHARACTERIZATION

The effects of the treatments on the activated carbon surface were studied by: infrared spectroscopy (FTIR) to verify the destruction or appearing of different functional groups on the carbon surface; nitrogen physisorption (BET) to evaluate the effect of the treatments on the surface area of the activated carbon as well as it pore size distribution; X-Ray diffraction (XRD) to analyze the carbon surface crystallinity; scanning electron microscopy (SEM) to determine structural changes on the activated carbon surface after the treatments; and the Boehm method to calculate the total acid and basic sites and identify the chemical surface changes caused for the different treatments carried out.

4.2.1 INFRARED SPECTROSCOPY

Functional groups on the carbon surface were determined with a Fourier Transform Infrared Spectrophotometer Shimadzu IRAffinity-1 scanning from a wave number from 400 to 4000 nm^{-1} before and after the treatments and before and after the adsorption process of phenol, methylene blue and congo red.

4.2.2 NITROGEN PHYSISORPTION

Specific surface area, total pore volume, and size distribution of the activated carbon before and after the heat treatment were determined from physical adsorption measurements with N_2 at 79 K on samples which were previously degasified at 363 K. The Autosorb 1 automated gas sorption system (Quantachrome Instruments) was used and the surface areas and pore size distribution were obtained with the BET (Branauer-Emmet-Teller) and the BJH (Barrer-Joyned-Halena) analysis, respectively.

4.2.3 X-RAY DIFFRACTION

Activated carbon before and after the heat-treatment was analyzed by X-Ray diffraction in a Siemens Ray-X Diffractometer scanning from 5 to 90 2-theta-degrees in order to evaluate any possible structural change occurred during the modifications.

4.2.4 SCANNING ELECTRON MICROSCOPY

Structural morphology of activated carbon was analyzed before and after the treatments with a Scaning Electron Microscope Jeol JSM-6510LV.

4.2.5 BOEHM METHOD

In order to evaluate the effect of the heat treatment on the surface chemistry of the activated carbon, basic and acid sites were determined before and after the treatments by Boehm titrations by adding 250 mg of the carbon to 25 mL of NaOH, Na_2CO_3, $NaHCO_3$ or HCl 0.1 N and stirring the suspensions in an orbital shaker at 150 rpm and a constant temperature of 25°C for one week. After that time, a 10 mL aliquot was taken for each sample and titrated with standardized NaOH 0.1 N for HCl and by retrotitration adding 10 ml of HCl 0.1 N and then titrating with NaOH 0.1 N for NaOH, Na_2CO_3, $NaHCO_3$ until the equivalent volume was obtained. Finally, the quantity of basic and acid sites was calculated.

4.3 ADSORPTION ISOTHERMS

Adsorption isotherms were carried out using a relation of 1 g of activated carbon/L of solution. For phenol, methylene blue and congo red the initial concentrations were from 10-200 mg/L. The pH was adjusted to 7 with NaOH and HCl 0.1 N and the solutions were stirred in an orbital shake at 100 rpm and

25 °C for 1 week in the case of phenol and 2 weeks for methylene blue and congo red. After the stirring time the concentrations of all samples were measured by a Thermo Scientific Genesys 10S spectrophotometer at 270, 666 and 500 nm for phenol, methylene blue and congo red, respectively.

4.4 ADSORPTION KINETICS

Adsorption kinetic experiments were performed in a differential column batch reactor with a 2 cm diamemter. A relation of 1 g of activated carbon/L of solution was used, and the pH was adjusted to 7 with NaOH and HCl 0.1 N. Experiments were carried out at room temperature (~25 °C) at an initial concentration of 200 mg/L for phenol, methylene blue and congo red. Aliquots were taken until equilibrium was reached and the concentrations of the samples were analyzed in a Thermo Scientific Genesys 10S spectrophotometer at 270, 666 and 500 nm for phenol, methylene blue and congo red, respectively until equilibrium was reached.

5. RESULTS AND DISCUSSION

The results obtained in this work are presented and compared with the information present in

5.1 ACTIVATED CARBON TREATMENTS

Figure 1 shows the percentage of pore volume distribution for activated carbon before and after the treatments. It can be noted that the treatments do not affect this distribution, even when the total quantity of every type of porous does change, as shown in Table 1.

In addition, Table 1 shows that the activated carbon surface area increases after the thermal treatment, but decreases after the chemical treatments. This can be explained due to the fact that the objective of the thermal treatment in an inert atmosphere was to clean up the surface by making all of the chemically unstable sites to volatilize. On the contrary, chemical treatments usually are aggressive against the carbon surface, destroying part of it and making some walls of the pores to collapse, which may be the reason for the surface area decrease for both OGAC and AGAC. Besides, AGAC presents the lowest surface area, and it is also the activated carbon submitted to the most destructive treatment out of the three used for this work.

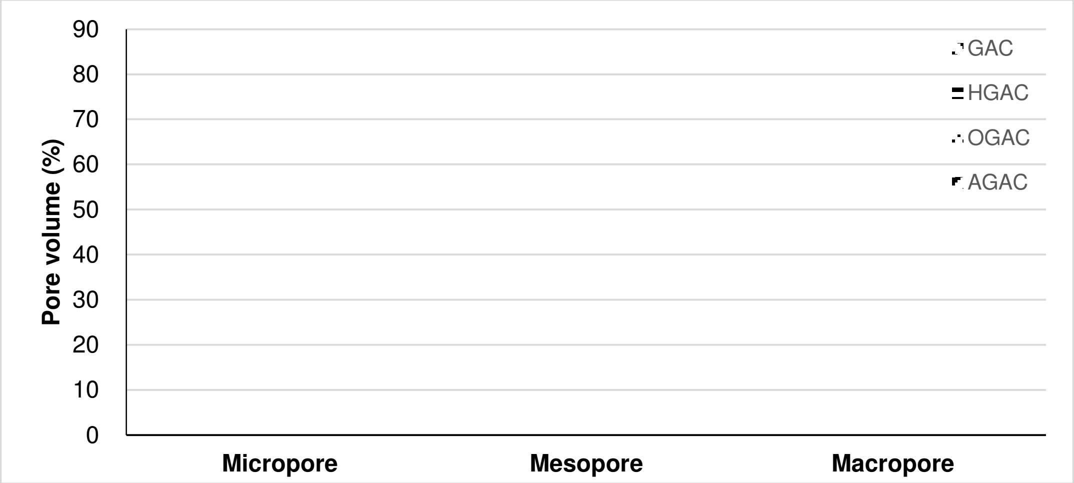

Figure 1. Pore volume distribution for GAC, HGAC, OGAC and AGAC.

Table 1. Surface properties of activated carbon before and after the treatments.

Property	Activated carbon			
	GAC	HGAC	OGAC	AGAC
Surface area (m^2/g)	676.7	819.4	621.0	604.3
Micropore volume (cm^3/g)	4.90E-02	8.10E-02	4.75E-02	4.08E-02
Mesopore volume (cm^3/g)	7.16E-01	1.23E+00	6.84E-01	6.42E-01
Macropore volume (cm^3/g)	1.36E-01	2.22E-01	1.25E-01	1.21E-01
Packed bed density (g/cm^3)	0.4891	0.4775	0.5621	0.5410
Packed bed porosity	0.7171	0.7549	0.8493	0.7926
Total basic sites (meq/g)	0.33	0.23	0.00	0.00
Total acid sites (meq/g)	0.00	0.00	0.07	0.87
Phenolic sites (meq/g)	0.00	0.00	0.00	0.00
Lactonic sites (meq/g)	0.00	0.00	0.57	1.16
Carboxilic sites (meq/g)	0.00	0.00	0.16	0.43

Similar results were obtained by Menéndez et al., who submitted a commercial granular activated carbon, which precursor was wood, to a treatment with N_2 at 950 °C, and observed that this treatment did not affect drastically the physical properties of activated carbon. (Menendez et al., 1996)

The effect of chemical treatments with nitric acid on activated carbon was evaluated by Vinke et al., Biniak et al. and Rios et al., who found that this treatment change slightly the surface area and the pore volume by decreasing them, but increases the quantity of oxygen containing surface functional groups, particularly hydroxyl and carbonyl, making the chemical surface of activated carbon acidic. These results agree with the ones obtained in this work. (Biniak, Pakuła, Szymański, & Świątkowski, 1999; Rios et al., 2003; Vinke, van der Eijk, Verbree, Voskamp, & van Bekkum, 1994)

FTIR results, showed from Figure 2 to Figure 6, present the characteristic peaks for common functional groups of activated carbon, such as C-C, C-O, C-N, C-H, etc., and it can be noted also that the signal changes in the form of noise to signal ratio after the adsorption process, which may be due to the presence of phenol, methylene blue and congo red, on the surface, although the characteristic signals for these compounds (C-C, C-O, C-H, O-H for phenol;

C-C, C-H, C-N for methylene blue; and C-C, C-H, C-N, C-S, S-O, N-N, N-H for congo red) probably became melted with the ones of the activated carbon, and therefore it is impossible to note them.

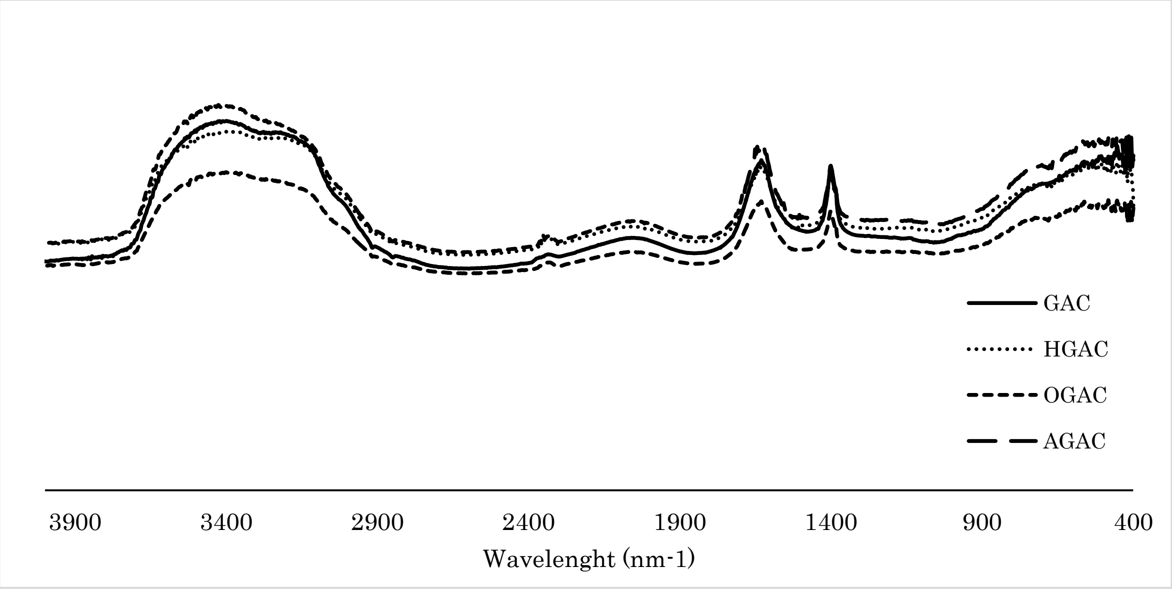

Figure 2. Infrared spectra for GAC, HGAC, OGAC and AGAC.

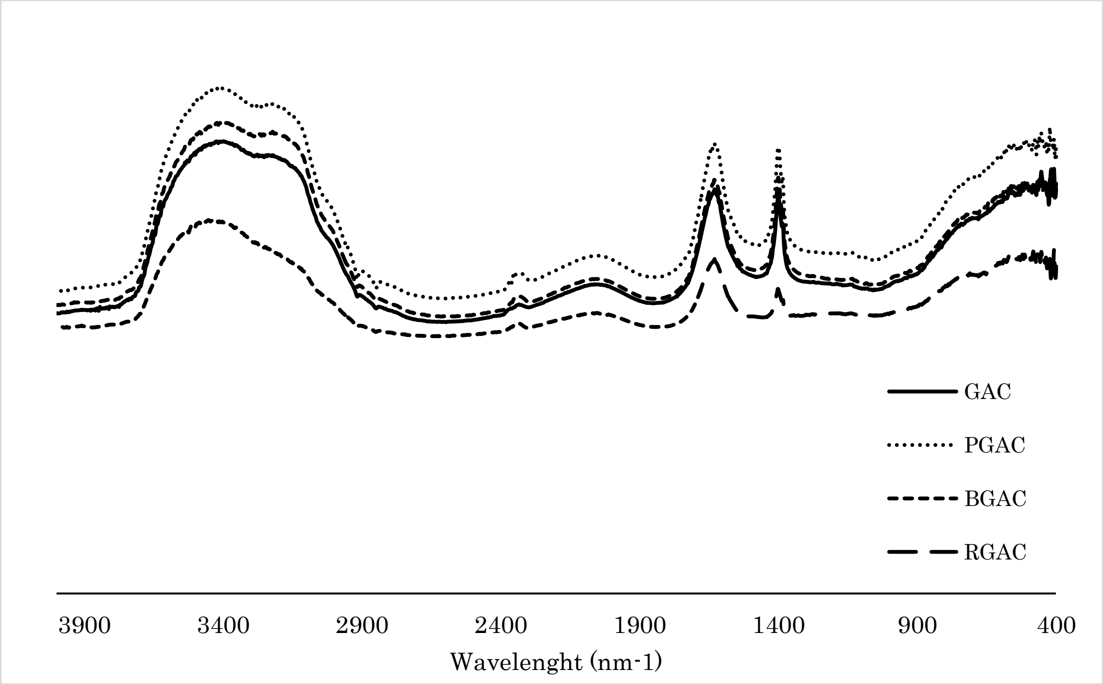

Figure 3. Infrared spectra for GAC before and after the adsorption process of phenol, methylene blue and congo red.

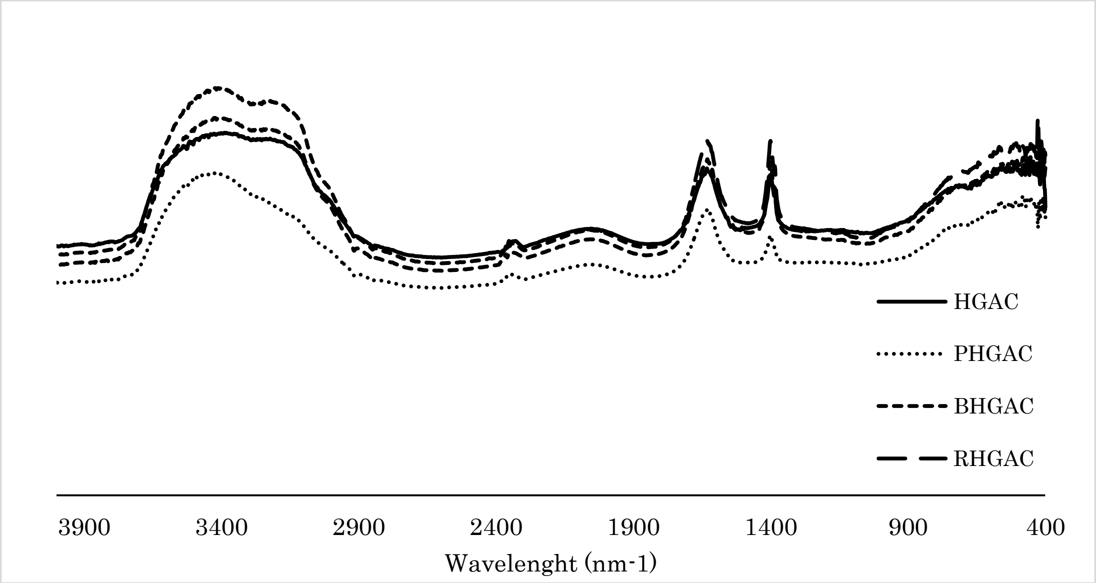

Figure 4. Infrared spectra for HGAC before and after the adsorption process of phenol, methylene blue and congo red.

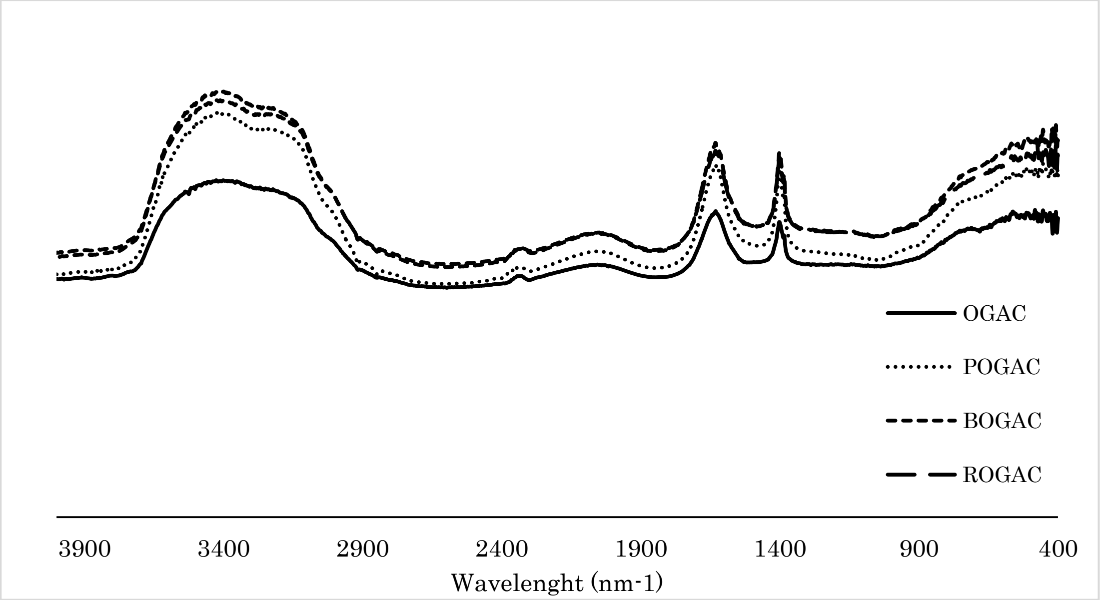

Figure 5. Infrared spectra for OGAC before and after the adsorption process of phenol, methylene blue and congo red.

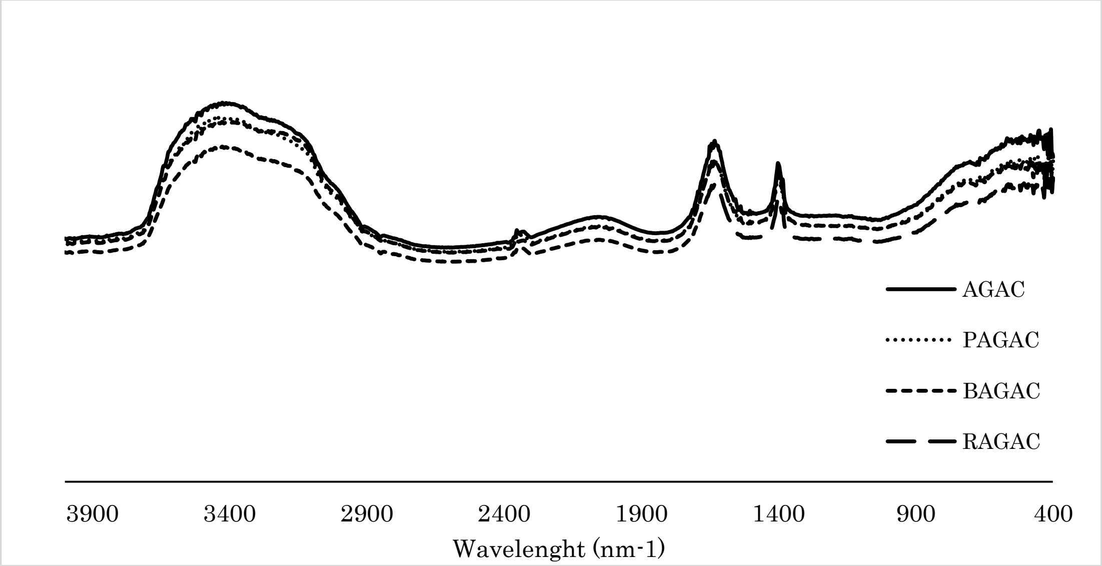

Figure 6. Infrared spectra for AGAC before and after the adsorption process of phenol, methylene blue and congo red.

The results obtained with SEM Figure 7 showed that after the heat treatment the carbon surface became more planar and several pores got blocked. These results agree with the diminution in the surface area obtained by nitrogen physisorption and with the proposed adsorption mechanism that includes pi-pi interactions with the carbon surface, which enhances both phenol and methylene blue adsorption by leaving a more approachable surface.

Chemical treatments also made a more planar and approachable surface, but these treatments blocked more pores on the carbon surface that the heat treatment, being the treatment with nitric acid the most aggressive, which explains both the difference on the surface area and the decrement on the adsorption capacity for phenol, methylene blue and congo red.

Additionally, an EDAX study was performed, revealing the presence of Al and Si in the activated carbon surface, which can be explained considering that a mineral activated carbon was used in this study, and aluminosilicates are usually present in the natural sources of these types of materials. The presence of Si on the activated carbon surface was corroborated with DRX, presented in Figure 8, where it can be noted also that activated carbon is essentially amorphous.

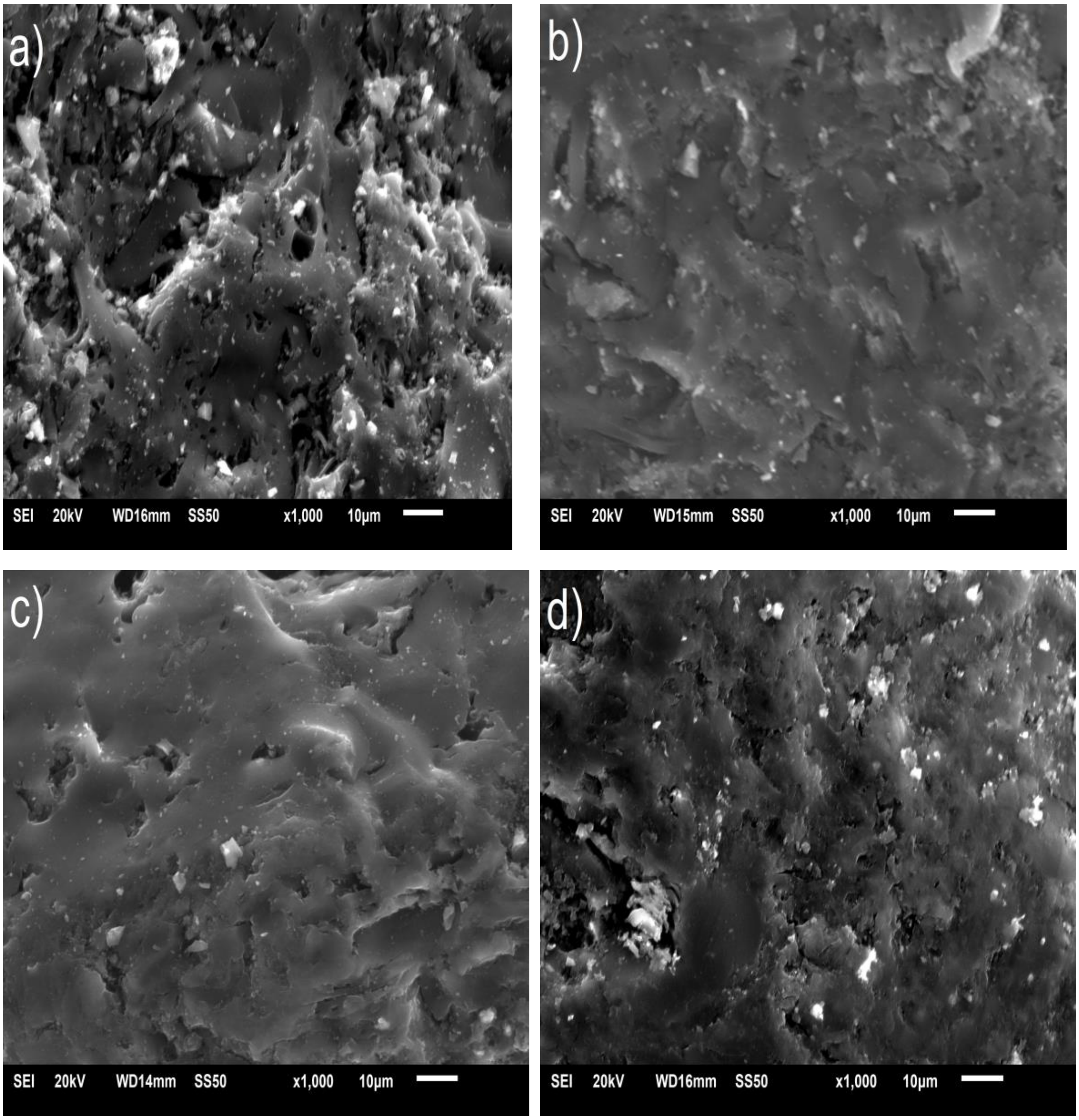

Figure 7. SEM for GAC (a), HGAC (b), OGAC (c) and AGAC (d).

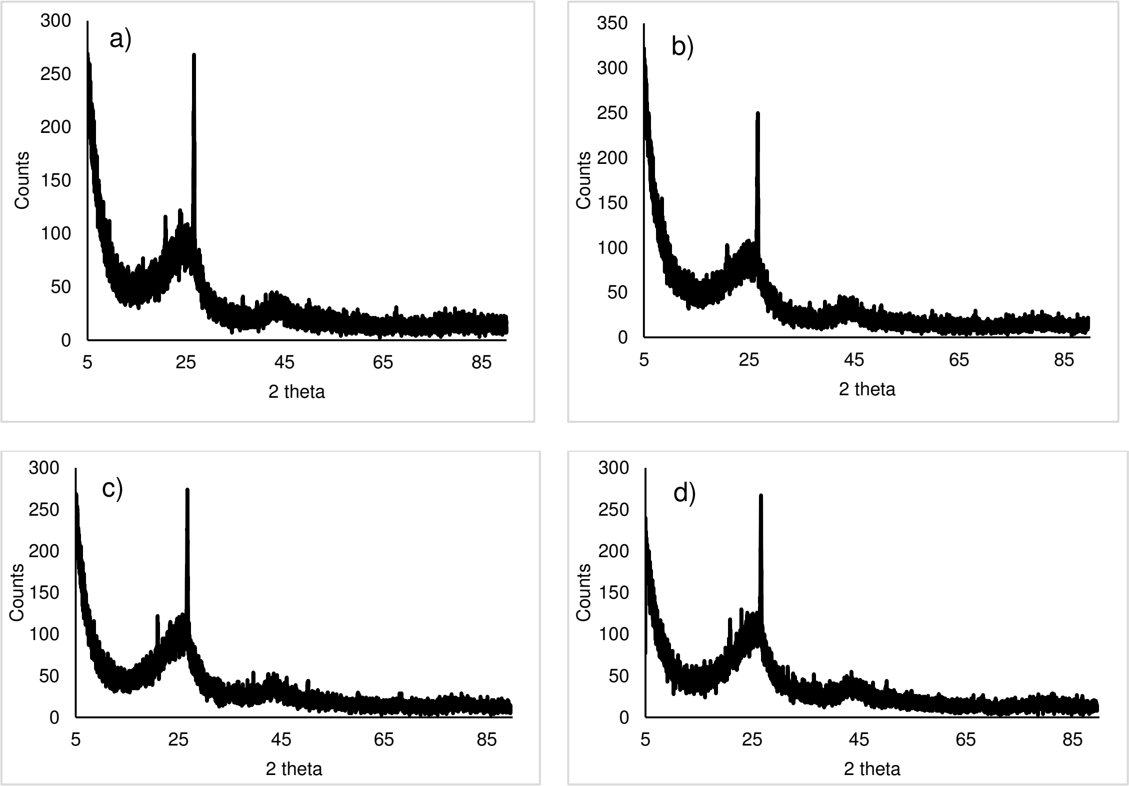

Figure 8. DRX for GAC (a), HGAC (b), OGAC (c) and AGAC (d).

Table 4. EDAX for GAC

Element	Percentage
C	97.1
Si	1.5
Ca	0.6
P	0.5
Al	0.3

5.2 ADSORPTION ISOTHERMS

The parameters obtained for Langmuir, Freundlich and Temkin models for adsorption isotherms of phenol, methylene blue and congo red are presented in

Table 2.

Table 2. Isotherm parameters for phenol, methylene blue and congo red adsorption

Adsorbate	Model	Parameter	Carbon			
			GAC	HGAC	OGAC	AGAC
Phenol	Langmuir	b	0.68	1.13	0.44	0.34
		q_{max}	169.90	189.38	71.08	102.62
		Error	702.45	3208.29	191.02	1224.50
	Freundlich	K	68.22	86.91	30.48	38.00
		1/n	0.29	0.28	0.19	0.24
		Error	2561.89	5782.81	643.47	1787.99
	Temkin	A	8.44	13.99	12.16	5.55
		b	76.87	70.16	241.35	141.25
		Error	842.20	3864.46	439.65	1446.50
Methylene blue	Langmuir	b	22.30	26.09	5.69	10.35
		q_{max}	138.28	133.63	82.99	96.41
		Error	4175.70	4146.50	985.97	1423.25
	Freundlich	K	103.21	98.05	47.98	58.75
		1/n	0.15	0.12	0.16	0.15
		Error	2236.82	3349.23	147.23	848.04
	Temkin	A	3726.77	7508.17	876.57	1120.71
		b	179.78	207.09	308.69	262.48
		Error	2276.92	2954.74	169.29	790.48
Congo red	Langmuir	b	0.01	0.01	2.20.E-03	3.12.E-06
		q_{max}	38.01	41.12	58.46	24608.41
		Error	107.48	131.53	361.21	111.57

	K	1.55	3.35	0.24	0.01
Freundlich	**1/n**	0.51	0.41	0.76	1.45
	Error	89.20	102.29	71.88	80.14
	A	0.27	1.54	0.12	0.06
Temkin	**b**	479.55	578.18	595.30	546.64
	Error	138.02	197.16	393.25	149.00

For phenol adsorption, experimental data are better represented with Langmuir model for the four activated carbons used in this work: GAC, HGAC, OGAC and AGAC, as presented in Table 2 and from Figure 5 to Figure 7. These results suggest that phenol adsorption is carried out in the form of single or multilayers due to the pi-pi interactions between the graphene of the activated carbon and the aromatic ring of phenol. Besides, at pH 7, phenol is not ionized, therefore electrostatic attraction contribution to adsorption, if exists, should be minimal.

Other authors have reported that the adsorption of phenol is well described by Langmuir and Freundlich models. In 2012, Gundogdu et al. (Gundogdu et al., 2012) studied the adsorption of phenol with activated carbon produced from tea industry wastes, and concluded that the Langmuir model described the process well according to the tendency of the curves and the fitting of the data (visually). Miao et al. (Miao et al., 2013) remarked that the best model to describe the adsorption of phenol on activated carbon prepared from soybean straw was Freundlich based on the determination coefficient values (R^2). Mohd Din et al. (Mohd Din, Hameed, & Ahmad, 2009) proposed that there was a possibility of mono and heterolayer phenol formation on the adsorbent surface due to the surface chemistry of the activated carbon, since active functional groups with high energy level tend to form heterolayers, while active sites with lower energy level will induce monolayer coverage due to electrostatic forces.

It can be noted also that the maximum adsorption capacity is higher for HGAC, then GAC, AGAC, and finally OGAC. These results agree with the effects of the treatments on the carbon surface and the proposed attraction mechanism, being the carbon with the highest surface area and cleanest surface, HGAC, the one with the highest adsorption capacity at equilibrium, and the carbon with the lowest surface area, OGAC, the one with the lowest adsorption capacity at equilibrium.

These differences in adsorption capacity are also caused by the pore volume diminution and the addition of surface functional groups, because adsorption by pi-pi interactions requires a planar carbon surface, and the presence of functional groups makes difficult the arrangement of the phenol molecule on the carbon surface and, therefore, the adsorption process.

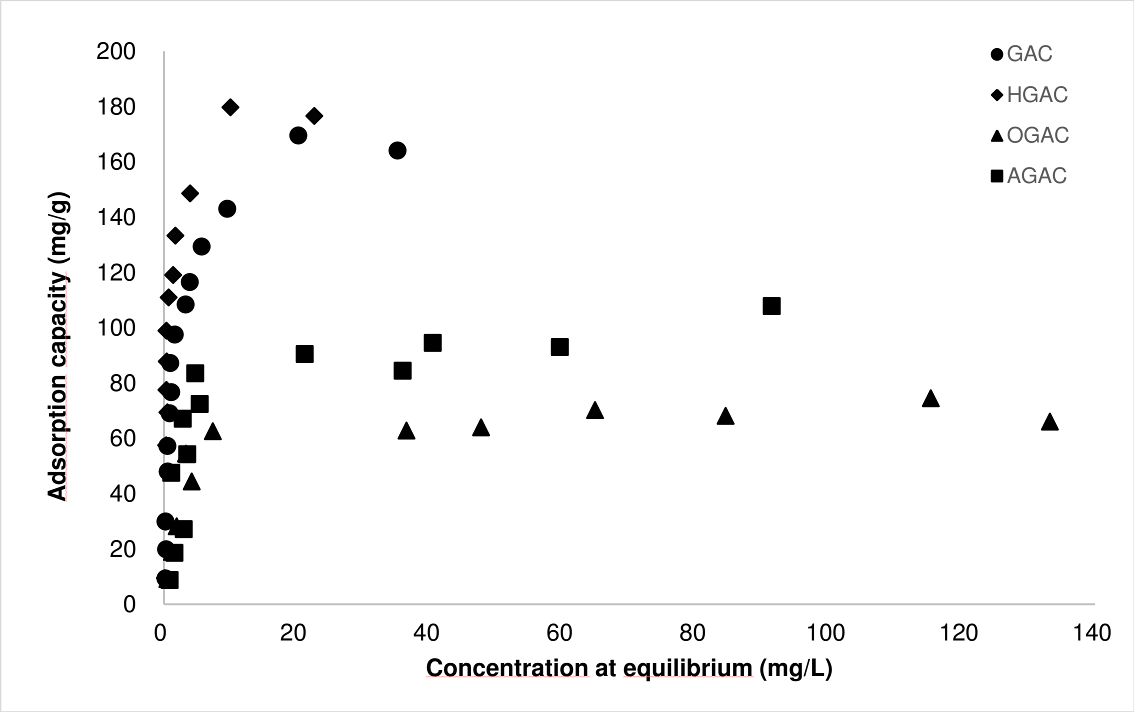

Figure 5. Adsorption isotherms for phenol with GAC, HGAC, OGAC and AGAC.

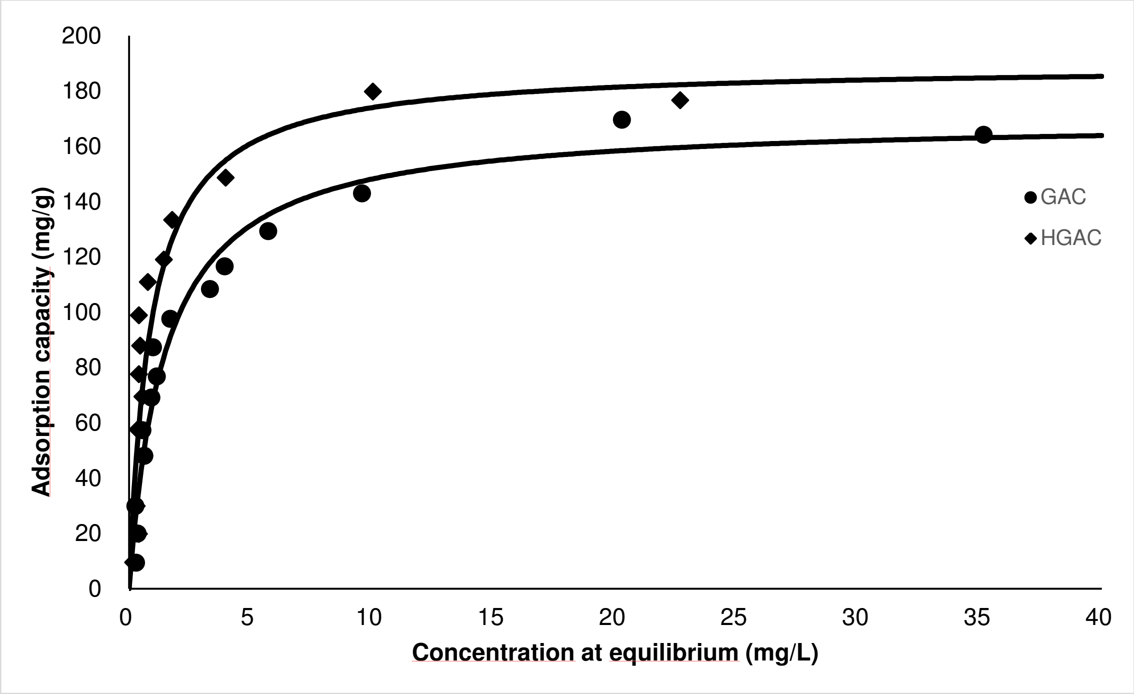

Figure 6. Adsorption isotherms for phenol with GAC and HGAC with the adjust for Langmuir model.

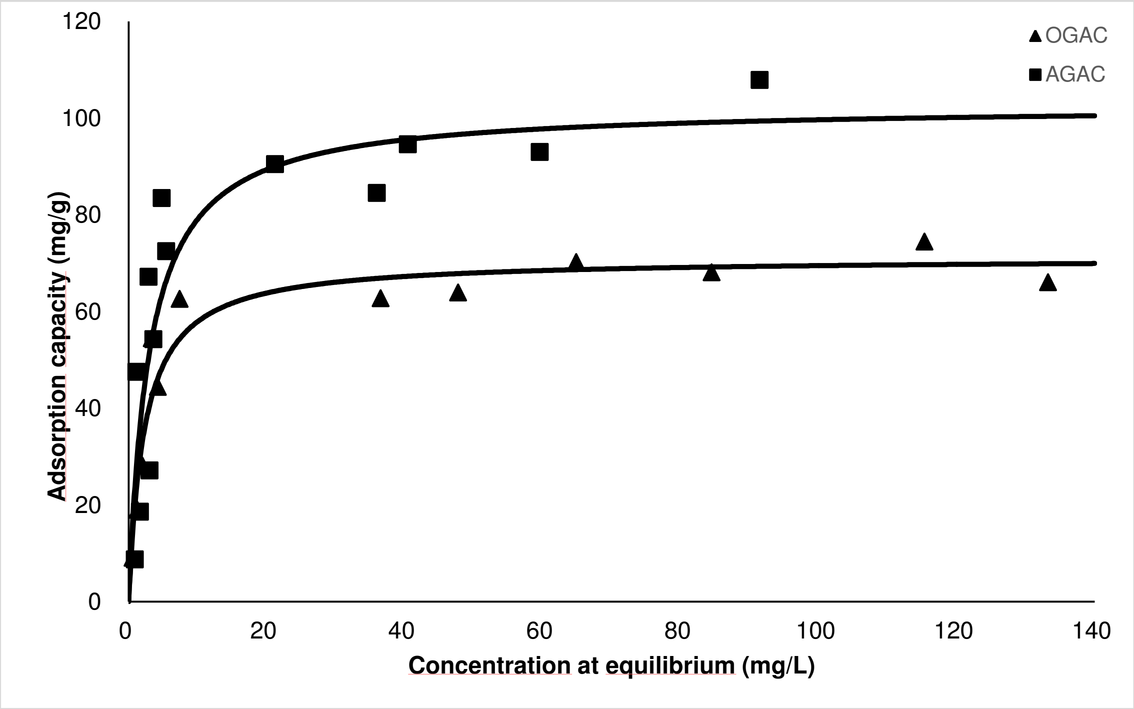

Figure 7. Adsorption isotherms for phenol with OGAC and AGAC with the adjust for Langmuir

model.

For methylene blue, the adsorption process was better described with Freundlich model than with Langmuir model, suggesting a combination of adsorption mechanisms occurring simultaneously, including electrostatic attraction between the dissociated acid functional groups on activated carbon and the positively charged molecule of methylene blue, as well as interactions similar to the ones presented by phenol, such as pi-pi interactions. The adsorption isotherms for methylene blue are presented from figure 8 to figure 10.

By analyzing the information in Table 1 and the Figure 8, it can be inferred that the available surface area is key for this particular case, being GAC and HGAC the carbons that presented higher adsorption capacities for methylene blue, achieving similar results. Additionally to this, by observing the behavior of OGAC and AGAC in methylene blue adsorption, it can be noted that the presence of acid surface functional groups is also important, particularly lactonic and carboxylic sites, as AGAC presented a higher adsorption capacity than OGAC.

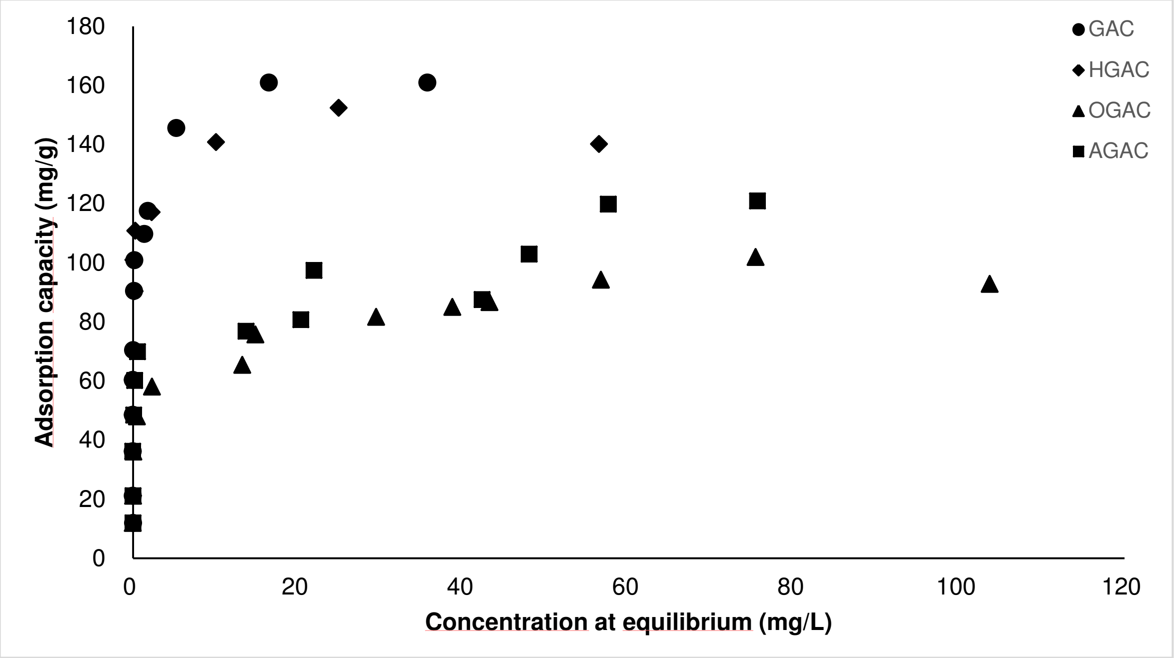

Figure 8. Adsorption isotherms for methylene blue with GAC, HGAC, OGAC and AGAC.

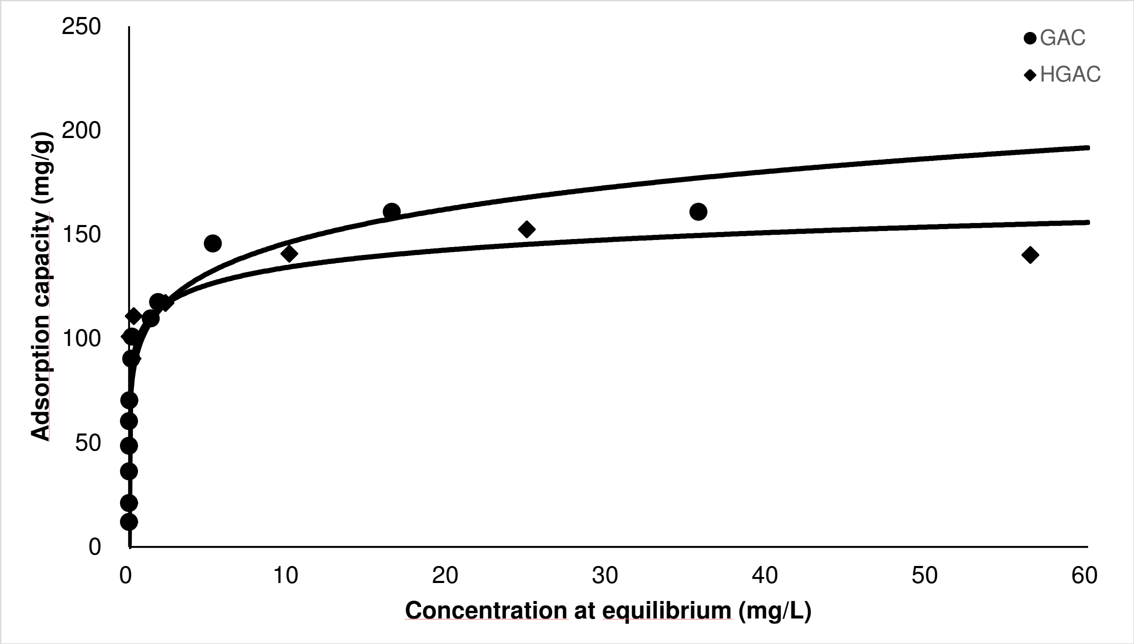

Figure 9. Adsorption isotherms for methylene blue with GAC with the adjust for Freundlich model and HGAC with the adjust for Temkin model.

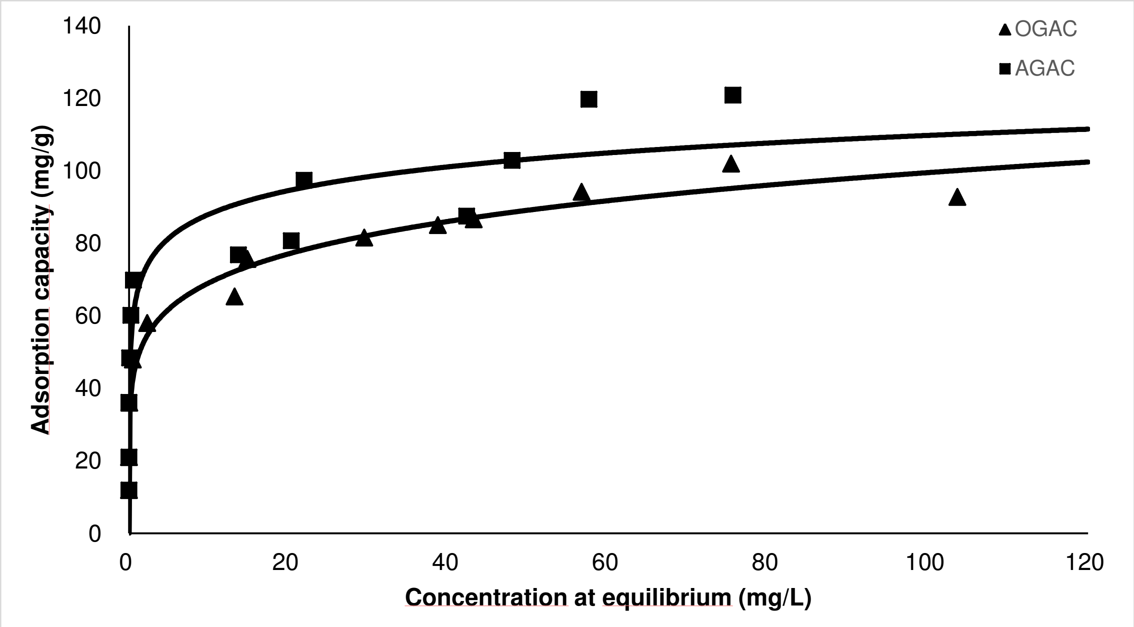

Figure 10. Adsorption isotherms for methylene blue with OGAC with the adjust for Freundlich model and AGAC with the adjust for Temkin model.

Adsorption isotherms for congo red are showed from figure 11 to figure 15. Congo red adsorption does not follow a clear tendency for any particular model, and the achieved adsorption capacities are very low compared to those for phenol and methylene blue. In the case of congo red, the big size of this molecule may be the main reason of this low adsorption capacity because, as presented in Table 1, the activated carbon used in this work is predominantly mesoporous, making difficult the diffusion process of the congo red inside the carbon particle.

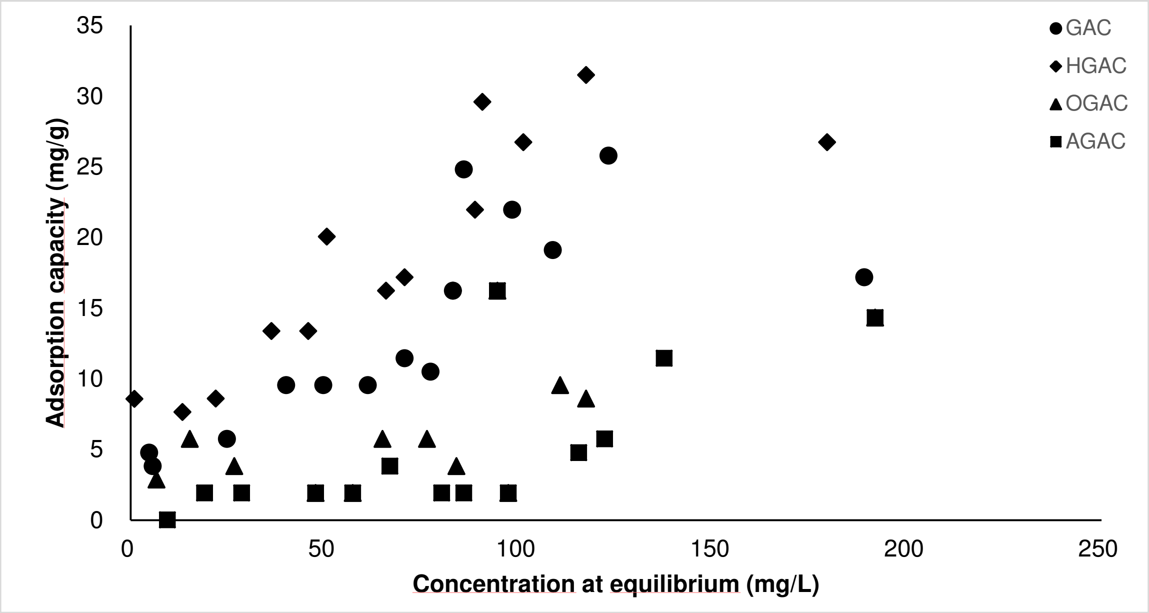

Figure 11. Adsorption isotherms for congo red with GAC, HGAC, OGAC and AGAC.

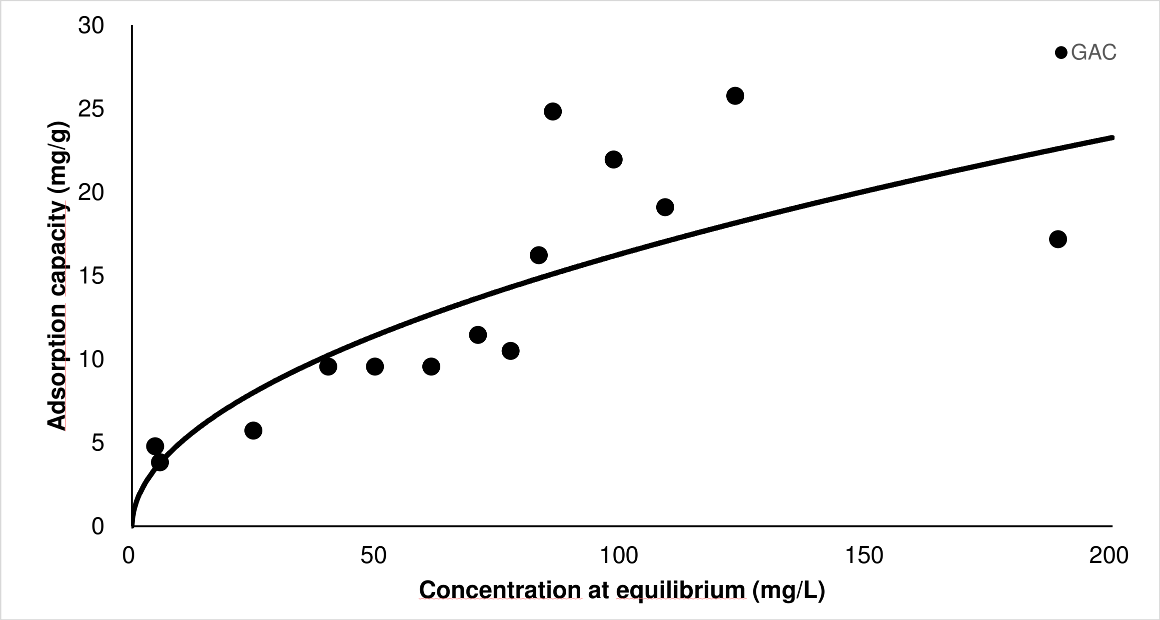

Figure 12. Adsorption isotherms for congo red with GAC with the adjust for Freundlich model.

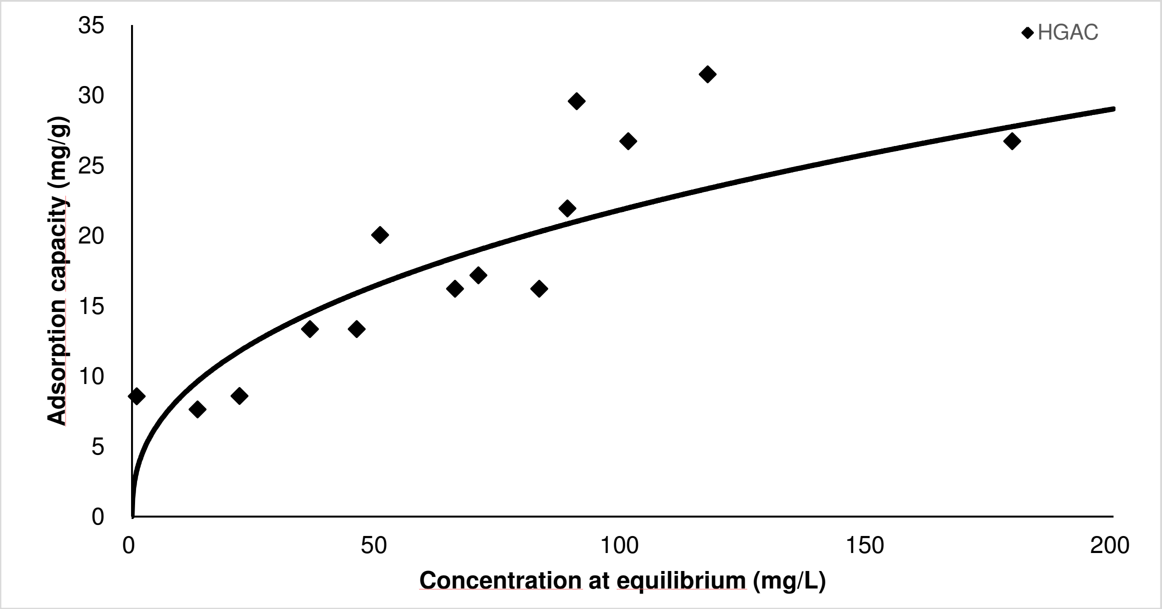

Figure 13. Adsorption isotherms for congo red with HGAC and the adjust for Freundlich model.

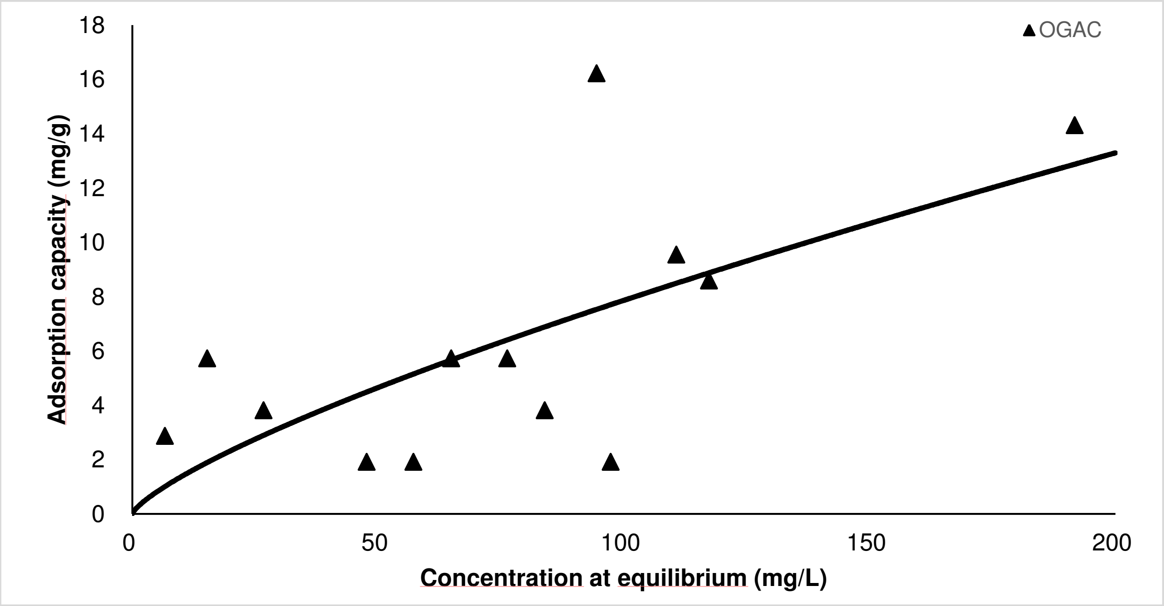

Figure 14. Adsorption isotherms for congo red with OGAC and the adjust for Freundlich model.

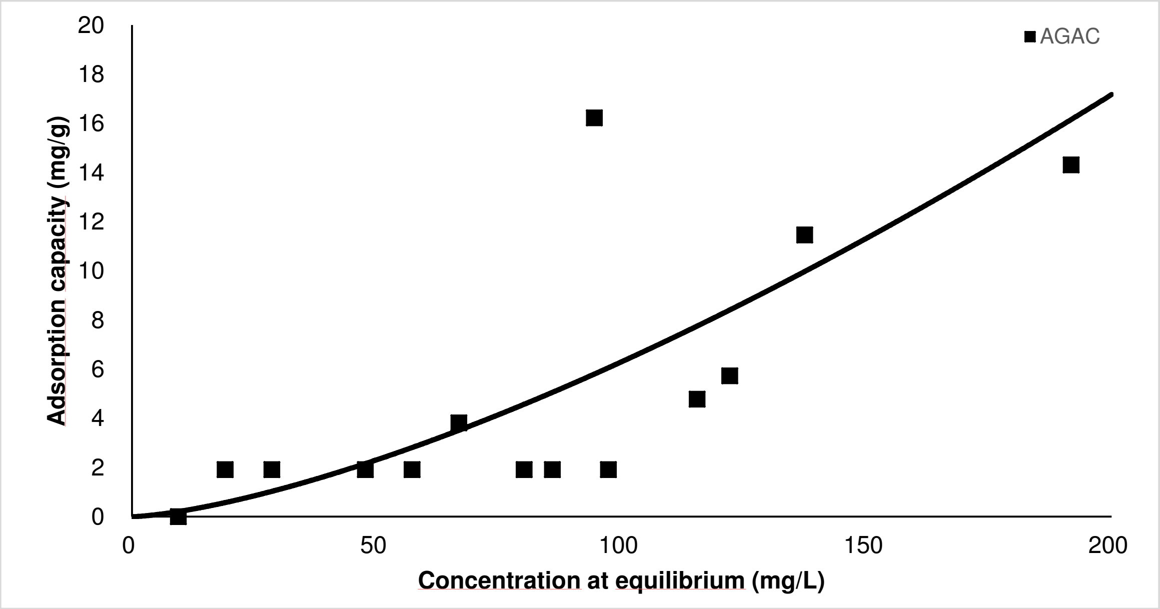

Figure 15. Adsorption isotherms for congo red with AGAC and the adjust for Freundlich model.

5.3 ADSORPTION KINETICS

Adsorption kinetic parameters for phenol, methylene blue and congo red are presented in Table 5.

Table 5. Kinetic parameters for phenol, methylene blue and congo red adsorption

Adsorbate	Model	Parameter	Carbon			
			GAC	HGAC	OGAC	AGAC
Phenol	PSO	k_2	1.98.E-04	1.44.E-04	1.91.E-04	2.51.E-04
		h	3.25	2.78	0.75	2.03
		Error	86.52	142.52	133.65	803.29
	Weber and Morris	k_{p1}	10.83	10.51	3.11	5.52
		I_1	-5.21	-5.76	4.1.E-02	5.89
		D_{i1}	1.09.E-02	1.69.E-02	3.83.E-03	7.37.E-03
		Error	75.27	84.53	81.04	56.26
	HSDM	k_f	2.22.E-04	1.50.E-01	2.11.E-01	8.40.E-01
		D_s	4.48.E-06	3.66.E-06	1.83.E-06	3.14.E-06

		Error	268.99	294.00	153.49	421.85
Methylene blue	**PSO**	**k_2**	1.97.E-05	3.12.E-05	7.19.E-05	2.59.E-05
		h	0.21	0.43	0.26	0.11
		Error	2010.56	1266.62	676.89	405.42
	Weber and Morris	**k_p**	1.23	2.11	0.92	0.98
		I_1	7.37	5.78	6.57	0.07
		D_i	1.10.E-04	3.79.E-04	1.46.E-04	1.80.E-04
		Error	198.70	268.95	306.87	119.78
	HSDM	**k_f**	2.91.E-02	3.62.E-04	3.10.E-04	1.13.E-03
		D_s	1.81.E-07	3.66.E-07	2.72.E-07	2.19.E-07
		Error	452.74	203.14	366.62	228.43
Congo red	**PSO**	**k_2**	3.82.E-04	2.22.E-04	2.43.E-02	8.44.E-02
		h	0.02	0.02	0.55	0.86
		Error	161.23	69.62	258.59	168.97
	Weber and Morris	**k_p**	0.07	0.16	0.70	9.20.E-03
		I_1	2.45	1.09	4.22	6.08
		D_i	3.67.E-05	2.40.E-04	6.72.E-03	2.02.E-06
		Error	106.64	64.54	4629.95	163.99
	HSDM	**k_f**	5.89.E-04	2.57.E-04	8.88.E-04	8.95.E-04
		D_s	1.09.E-07	6.73.E-07	1.61.E+05	6.60.E-04
		Error	146.10	67.05	198.48	179.81

k2[=]g/mgmin

h[=]mg/gmin

kp[=]g/mg/min

Di[=]cm2/min

kf[=]cm/min

Ds[=]cm2/min

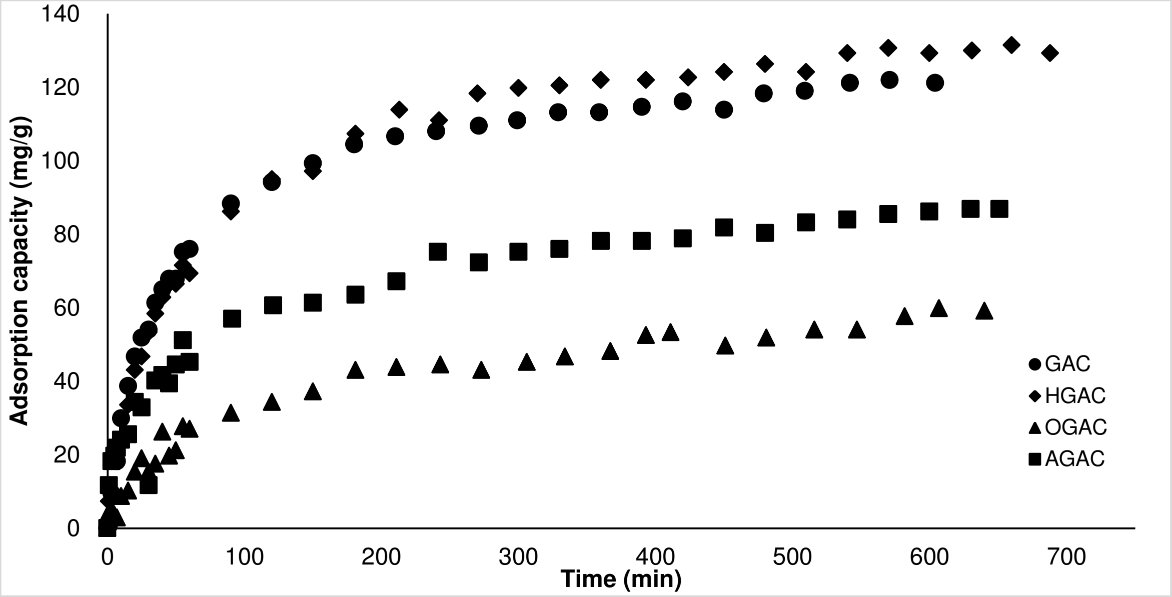

Figure 16. Adsorption kinetics for phenol with GAC, HGAC, OGAC and AGAC.

For phenol, adsorption kinetics reached equilibrium in about 700 min, as showed in Figure 16. The adsorption capacity reached at equilibrium was higher for HGAC, then GAC, AGAC and OGAC, which agree with the adsorption isotherms results.

According with the initial adsorption rate h of the pseudo-second order model, for short times adsorption is faster in GAC, then HGAC, AGAC and OGAC. These results agree with the k_p parameters of the Weber and Morris model and the diffusion coefficient D_s obtained by HSDM, indicating that adsorption process is more favorable in both GAC and HGAC, as showed previously in the isotherms studies. This may be due to the lack of surface functional groups on the surface of these carbons, which makes easier for the phenol to approach the surface and accommodate itself so the pi-pi interactions may occur. On the contrary, OGAC and AGAC present different surface functional groups and lower surface area, therefore the available graphene structures on the surface are less than in GAC and HGAC, therefore the adsorption capacity in equilibrium at the end of the kinetics was lower too.

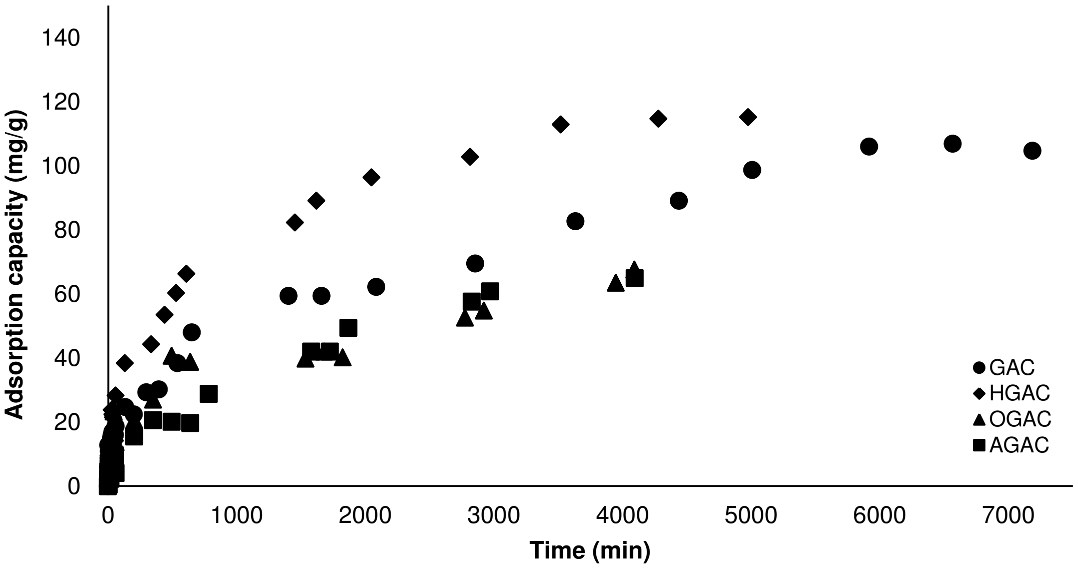

Figure 17. Adsorption kinetics for methylene blue with GAC, HGAC, OGAC and AGAC.

Adsorption kinetics for methylene blue with GAC, HGAC, OGAC and AGAC are presented in Figure 17. Time for reach equilibrium was about 6000 min, and the highest adsorption capacity was for HGAC, then GAC, AGAC and OGAC.

The mechanism proposed for methylene blue adsorption is electrostatic attraction with the functional groups present on the carbon surface, but results indicate that the surface area availability is more important for methylene blue adsorption, since adsorption capacity at equilibrium was higher in HGAC and GAC, that have more basic surface sites, and lower in OGAC and AGAC, which have more acid sites but lower surface area.

For both phenol and methylene blue the best model to explain the process is HSDM, since it considers the time when the whole process is carried out, while the PSO model and the Weber and Morris model consider only the first minutes of the process to make the mathematical fit.

Congo red adsorption kinetics do not present a clear tendency, therefore results obtained by all of the three models are not reliable for this compound.

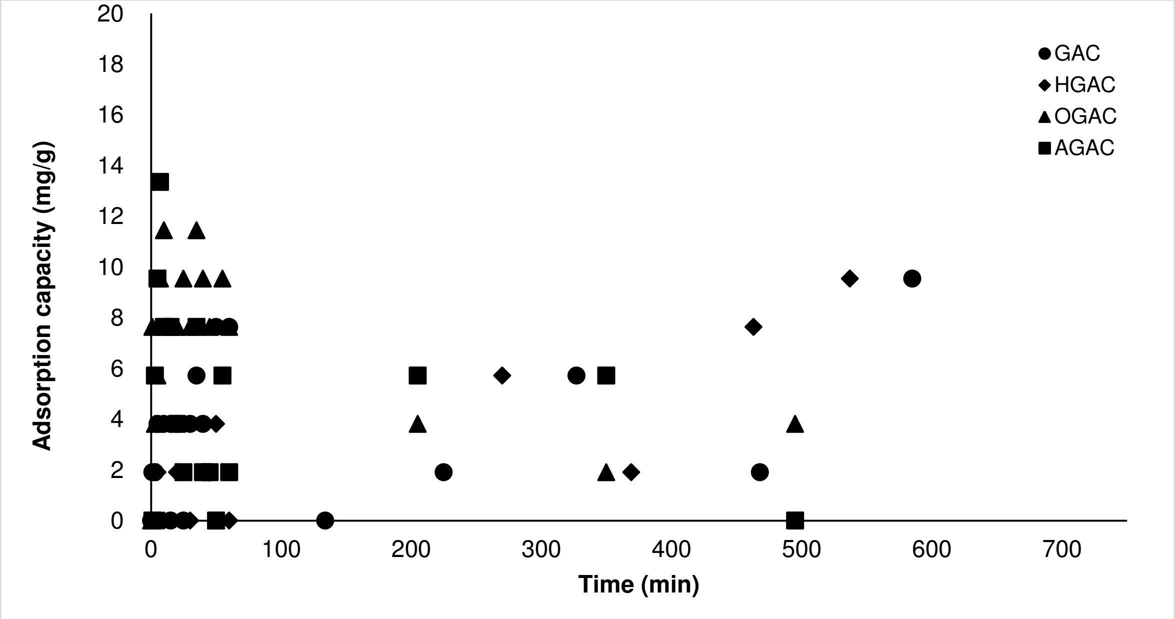

Figure 18. Adsorption kinetics for congo red with GAC, HGAC, OGAC and AGAC.

6. CONCLUSIONS

For the bituminous activated carbon used in this work, a heat treatment in an inert atmosphere increased its surface area, while an acid treatment with nitric acid and a combined treatment with nitric acid and ammonium hydroxide caused the surface area to decrease.

After all of the treatments, surface basic sites decreased for HGAC, OGAC and AGAC, and acid surface sites, particularly carboxylic and lactonic, increased for OGAC and AGAC.

Activated carbon possess an amorphous structure and contains aluminum, calcium and silicon due to its mineral origin.

Adsorption capacity at equilibrium was higher for phenol, then methylene blue and then congo red for all of the carbons used in this work.

Adsorption capacity for phenol was higher for HGAC, then GAC, AGAC and OGAC, and was well described by Langmuir model, being the predominant adsorption mechanism pi-pi interactions between the aromatic ring of phenol and the activated carbon surface.

For methylene blue, adsorption capacity was higher for GAC, then HGAC, AGAC and OGAC, and the process was well described by Freundlich model, being electrostatic attraction the predominant adsorption mechanism.

The values for the parameter b of Temkin model indicate that phenol and methylene blue adsorption in GAC, HGAC, OGAC and AGAC is mainly by physical mechanisms.

For phenol and methylene blue, a higher and more available surface area allowed more molecules to approach the carbon surface and to enhance the adsorption capacity.

Congo red adsorption could not be fitted by any model used in this work, and adsorption capacity for all of the carbons was very low compared to the results obtained for phenol and methylene blue, due to the molecular size of congo red that makes difficult the approach and diffusion on the activated carbon and, therefore, the adsorption process.

Phenol kinetics in a differential packed bed reached equilibrium after about 700 min, and adsorption capacity was higher for HGAC, then GAC, then AGAC and OGAC.

Methylene blue kinetics in a differential packed bed reached equilibrium after about 6000 min, and adsorption capacity was higher for HGAC, then GAC, then AGAC and OGAC.

Adsorption kinetics for congo red did not show a clear tendency and could not be described by any model used in this work.

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