# PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBON FROM OIL-PALM SHELL FOR CARBOXYLIC ACID ADSORPTION

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ABSTRACT: In this study the recovery of short-chain carboxylic acids is explored by adsorption onto activated carbon from palm-oil kernel shell using $H_3PO_4$ and KOH as activating agents. The surface of activated carbons was characterized physically and chemically. An adsorption-desorption study was performed finding that carbon CA60B exhibits greater adsorption capacity (1300mg of adsorbed acids/g carbon). Five adsorption isotherms models were fitted to experimental data where the Langmuir-Freundlich model described best the adsorption phenomena. The adsorbent CA60B presented a higher amount of acid desorbed by temperature change (44.1mg of carbon desorbed for initially containing 276mg of acid). Because of the difficulty in separating the adsorbed acids, the use of activated carbon does not seem an implementable alternative for the recovery of carboxylic acids produced in fermentation stages of the MixAlco® process.

KEYWORDS: carboxylic acids; activated carbon; oil-palm kernel shell; equilibrium isotherms.

## 1. INTRODUCTION.

Colombian economic growth generates an increasing demand of fuels. In order to supply it Colombia uses mainly fuels obtained from fossil resources, the use of these fuels generates pollution. Furthermore, these fuels are mixed with ethanol and first generation biodiesel, both of which are derived from monocultures, which promote deforestation (Chazdon, R., 2008).

The global panorama for the development of biofuels is similar. These discussions have generated great interest in production of second generation fuels amongst researchers. The MixAlco® process, shown in Figure 1, is a biorefining technology developed to obtain chemical products of high commercial value (e.g. acetic acid, ketones, esters and alcohols) from lignocellulosic waste. These substances are generated within a consecutive hydrogenation process. The alcohols produced in the end of the chain can be used as fuels or transformed into the so-called “biogasoline” (Terrabon, MixAlco®-Overview).

The initial stages of the process are: 1) Pre-treatment of the lignocellulosic material, 2) Fermentation, 3) Carboxylic acid production. These acids can be transformed into biogasoline using one of three parallel routes: 1) Esterification 2) Catalytic Conversion 3) Thermal Conversion.

Carboxylic acids are produced during the fermentation stage. These acids are recovered as carboxylic salts which are diluted in the fermentation medium. (Maximum concentration measured: 30g/L). The salts must be separated, which is normally achieved by evaporation, once separated, they must be reconverted into acids (Zhihong Fu & Holtzapple, 2009).

As an alternate way of retrieving them, the adsorption of acids produced during fermentation has been proposed using sheets of ion exchange resins. This alternative goes against some of the objectives of the MixAlco® process by using petroleum derived materials in the production of the resins. In this project this problematic is attacked by evaluating the alternative adsorption of carboxylic acids on activated carbon, synthetized from low costs and high available lignocellulosic waste (oil-palm shell) (Dias and others,2007)

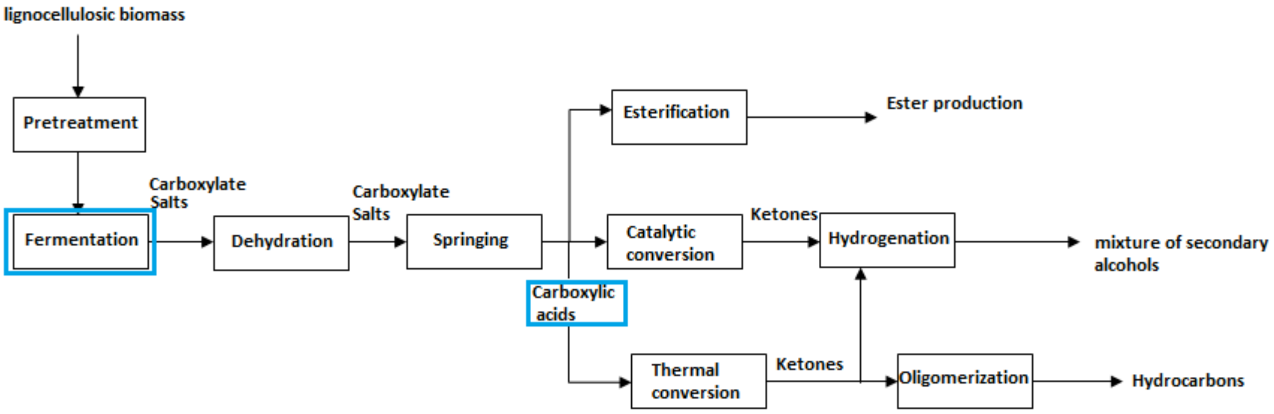

**Figure 1.** General scheme of the MixAlco® Process.

## 2. MATERIALS AND METHODS

### 2.1. Preparation of adsorbents

***2.1.1. Precursor selection:*** Oil palm-shell was provided and collected from an extractor plant in Puerto Rico, Meta - Colombia. The original sample picked contained palm shell as well as nut residue, so manual separation was necessary.

***2.1.2. Washing and drying of the precursor:*** Once the sample is nut free, the oil-palm shell is washed multiple times with distilled water to eliminate dirt or fibers in the sample. After the washing, the residue is distributed over shallow aluminum trays and placed in an oven at 74°C for four days to eliminate the free moisture.

***2.1.3. Milling and sieving:*** Dry sample is grinded in a mill with national fabricated blades and sieved using Tyler nets, 4 (4.75 mm), 8 (2.38 mm) and 12(1.68 mm). The collected fraction used was -4/+12 in order to standardize the size of the palm shell particle between 2-5 and 4.75 mm of diameter, corresponding to more than 90% of the material.

***2.1.4. Chemical Impregnation:*** The chemical impregnation is carried out using two phosphoric acid solutions (10 and 60% w/w) and two potassium hydroxide solutions (10 and 60% w/w). Oil-palm shell was impregnated in a solution of twice its volume (impregnation ratio 1:2). Mixture was shaken for 1h, left to impregnate for 24 hours and then placed in an oven at 74°C for three days in order to dry the sample completely.

***2.1.5. Carbonization:*** Carbonization of impregnated palm shell was carried out in a tube furnace under a high purity nitrogen flow of 80mL/min by raising the temperature at a rate of 5ºC/min to 800ºC. The carbon obtained was thoroughly washed with distilled water in a Soxhlet extractor in order to eliminate any presence of acid or base in the carbon. The carbon was dried in a furnace at 74°C. The obtained material after drying is denominated activated carbon. Adsorbents (CA) were named according to concentration (10 and 60%) and impregnation agent (A: phosphoric acid; B: potassium hydroxide base). e.g. CA60B was carbon from impregnation with KOH 60% w/w.

### 2.2. Characterization of the activated carbons and precursor

For the physical and chemical characterization of each of the activated carbons produced (CA10A, CA60A, CA10B and CA60B), several tests were performed in order to obtain a detailed description of the properties of the material.

***2.2.1. Nitrogen adsorption isotherms:*** Isotherms were measured in an AutosorbIQ2 porous solids analysis equipment. Prior to these measurements, the samples were degasified at 250°C for two hours. Surface area was estimated through the Brunauer- Emmett-Teller (BET) model, pore volume through the Dubinin-Radushkevich (DR) model and pore distribution through Density Functional Theory (DFT) model.

***2.2.2. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA):*** In this technique a mass of a carbon sample is measured continuously while it is subjected to a controlled heating program (Ania, 2003). The four different adsorbents samples corresponding to the four different carbons are heated using a temperature ramp of 0°C to 900 °C, with a heating rate of 10°C/min.

***2.2.3. Fourier transform infrared spectroscopy (FT-IR):*** FT-IR is performed for all four carbons and for the raw material to study the surface functional groups.

***2.2.4. Boehm titration:*** Boehm method is used to quantify surface functional groups of the carbon. This method consists in titration with different solutions, (basic and acid) with a known content of activated carbon. Samples of 0.25g of adsorbent were placed in falcon tubes. 25 mL of the following 0.1M solutions were added respectively: sodium hydroxide (NaOH), sodium carbonate ($Na2CO3$), sodium bicarbonate ($NaHCO_3$) and hydrochloric acid (HCl). The tubes were sealed and shaken for 5 days at room temperature. Samples are then filtered and 5mL of each are analyzed. The excess of acid or base was titrated with HCl (0.1 M) or NaOH, (0.1M) with 0.05 mL increments in an automatic CG840B Schott titrator(ref).

***2.2.5. Point of zero charge (PZC):*** The value of the pH to provide a net superficial charge equal to zero of a determined carbon sample is the PZC. To determine the PZC, ten different carbon masses were taken for the four carbons. Each one of the samples was placed in a falcon tube and 25 mL of 0.1 M sodium chloride solution (NaCl) was added. Samples were shaken for 2 days at a constant temperature. The pH of each solution was measured.

## 2.3. Adsorption studies

For the adsorption experiments a stock solution with 13.85g/L acetic acid, 0.67 g/L propionic acid and 4.95 g/L butyric acid was prepared. This solution was used for each of the described procedures.

The quantity of absorbed acids expressed as the adsorbent phase concentration was calculated according to the following equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (01)$$

Where $q_e$ is the adsorbent phase concentration in milligrams of acid adsorbed per gram of adsorbent (mg/g), $C_0$ and $C_e$ are the initial concentration and equilibrium concentrations (mg/L), $V$ is the volume of solution, and $m$ is the mass of adsorbent.

***2.3.1. Effects of adsorbent mass:*** To determine the effect of the activated carbon mass used in the adsorption of carboxylic acids, different masses of activated carbon (0 - 0.55g) were introduced in Schott containers. 25mL of stock solution were placed on each one and were then shaken for 24 hours at 30°C.

***2.3.2. Equilibrium isotherms:*** The adsorption phenomena of the short chain carboxylic acids on the surface of the synthesized carbons were studied by varying initial concentration. Ten solutions were prepared with different acid concentrations by diluting stock solution (5-100%). Solutions were placed in Schott containers and 0.1 g of activated carbon was added. The solutions were placed in a shaker at 30°C for 24 hours. The procedure was repeated at 40°C.

***2.3.3. Adsorption-desorption:*** To determine the adsorption and desorption capacity of each one of the carbons, 5 g were weighted and placed in Schott containers. 25mL of stock solution were added. The Schott containers were shaken for 24 hours at 30°C. Samples for analysis were taken after adsorption. The activated carbons were filtered and placed in a tray dryer for two hours without heating. The dry carbons were placed in Schott containers with 25 mL of water. The containers were placed in a shaker at 40°C for 24 hours, after which another sample for analysis was taken. After desorption the carbons were placed in a tray dryer for two hours without heating.

***2.3.4. Gas chromatography (GC) analysis:*** All samples for GC analysis were mixed with internal standard (valeric acid, 3.53g/L) (Zhihong Fu & Holtzapple, 2009). 1 mL of sample was placed in a vial and acidified with phosphoric acid 85% (w/w). Samples were analyzed by gas chromatography using a FID detector in order to measure the final concentration of acetic, propionic and butyric acid in each sample.

## 3. RESULTS AND DISCUSSION

### 3.1. Physical characteristics

The nitrogen isotherms for activated carbon CA10A, CA60A, CA10B and CA60B are shown in Figure 2.

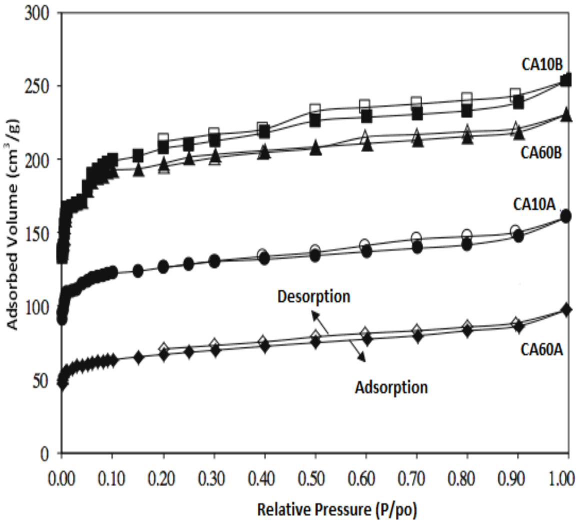

**Figure 2**. Nitrogen adsorption isotherms for CA10A, CA60A, CA10B and CA60B.

The nitrogen isotherms for all the samples are type 1 in respect to the IUPAC classification. Type 1 isotherms are given by microporous solids having relatively small external surfaces, the uptake limit being governed by the accessible micropore volume rather than by the internal surface area (IUPAC). The activating agent ($H_3PO_4$ and KOH) used in the synthesis of the activated carbons does not change the type of nitrogen adsorption isotherm presented.

Pores with a maximum width of 2 nm are called micropores, while mesopores are pores with a width between 2 to 50 nm. The pore distribution for each activated carbon is shown in Figure 3. The porous structure is composed of micropores and mesopores. For carbons CA10A and CA60A a similar pore distribution is present, 1-4 nm for the CA10A and 1-4.2 nm for the CA60A. For the activated carbons with a basic agent, the pore size range is 0.96-5 nm.

**Table 1**. Surface area

| Sample | $S_{ext}$ $(m^2.g^{-1})$ | $S_{micro}$ $(m^2.g^{-1})$ | $S_{meso}$ $(m^2.g^{-1})$ |
|---|---|---|---|
| CA10A | 490 | 474 | 16 |
| CA60A | 280 | 265 | 15 |
| CA10B | 810 | 784 | 26 |
| CA60B | 772 | 705 | 67 |

The nitrogen isotherms allow calculation of the surface area of each one of the adsorbent, the total volume of pores and the average diameter.

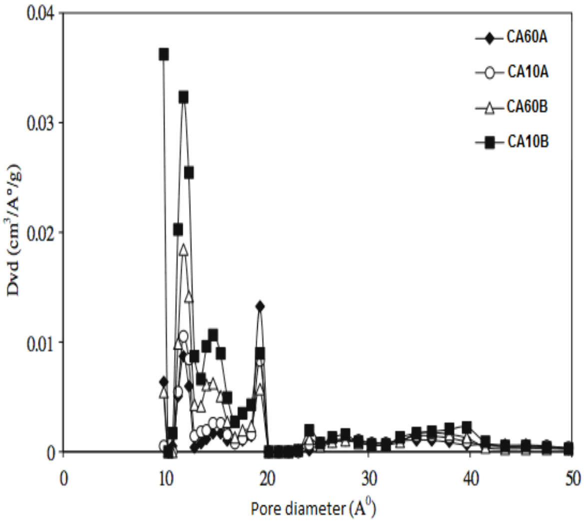

**Figure 3.** Pore distribution for CA10A, CA60A, CA10B and CA60B

Carbons CA10B and CA60B present the greatest superficial area, where the CA10B carbon has an area 5% larger than the CA60B and a total pore volume larger in a 5.1%. The CA60A carbon presents the lowest superficial area and pore volume.

**Table 2.** Pore volumes

| Sample | $V_{total}$ ($cm^3.g^{-1}$) | $V_{micro}$ ($cm3.g^{-1}$) | $V_{meso}$ ($cm3.g^{-1}$) |
|---|---|---|---|
| CA10A | 0.254 | 0.212 | 0.042 |
| CA60A | 0.173 | 0.132 | 0.041 |
| CA10B | 0.367 | 0.289 | 0.078 |
| CA60B | 0.345 | 0.275 | 0.070 |

## 3.2. Surface chemistry

Knowing the PZC, functional groups, and the acid and basic groups present on the surface of each one of the synthesized adsorbents is of great use to determine the affinities of these towards the adsorption of carboxylic acid. Additionally it provides information on the influence of electrostatic forces in the adsorption phenomena.

The PZC is the required pH to obtain a net superficial charge equal to zero. Carbon CA10A's surface is acidic, with a $pH_{PZC}$ of 5.9; carbon CA60A has an acidic surface with a $pH_{PZC}$ of 3.8. Both CA10B and CA60B carbons present a basic surface with $pH_{PZC}$ of 9.1 and 6.9 respectively.

Carbons activated with phosphoric acid presents surfaces with an acid behavior. For higher concentrations of the H3PO4 PZC is lower as evidenced for carbon CA60A.

On the other hand, for carbons activated using KOH the surface behaves in a basic way. When the concentration of KOH is increased, the PZC decreases. It would be expected that an increment in KOH concentration would increase the $pH_{PZC}$ as the presence of basic groups on the carbon increases (Ania, 2003); however carbon CA60B presents a lower $pH_{PZC}$. Carbon CA60B has a similar pore size as carbon CA10B but also has a greater mesopore volume which allows a more effective washing, i.e. the elimination of the activating agent is produced in an easier way compared to carbon CA10B, whence carbon CA10B presenting a higher value of $pH_{PZC}$ than CA60B.

Given the complexity of the superficial chemistry of carbonaceous materials, the characterization and quantification of the different functional groups that form it does not come easy. The Boehm titration is realized for the four studied carbons and the results are shown on Table 3.

**Table 3.** Functional groups

| | mmol/g | | | | |
|---|---|---|---|---|---|
| | $pH_{PZC}$ | CG | LG | PG | BG |
| CA10A | 5.98 | 1.69 | 0.060 | 0.080 | 2.95 |
| CA60A | 3.80 | 1.71 | 0.040 | 0.060 | 2.90 |
| CA10B | 9.07 | 1.67 | 0.005 | 0.028 | 3.10 |
| CA60B | 6.09 | 1.60 | 0.050 | 0.040 | 2.67 |

CG: carboxylic groups; LG: lactonic groups: PG: phenolic groups; BG: basic groups.

Carboxylic groups are found in greater measure in the carbons CA10A and CA60A, with greater presence in the latter, which is related to the low pH value of the PZC and is accounted to the activating agent used (phosphoric acid). Carbon CA10A has a mayor presence of lactonic groups (LG). Carbon CA10B presents the highest quantity of basic groups on is surface, matching with the pH of the PZC.

***3.2.1. Fourier transform infrared spectroscopy (FT-IR):*** A notable difference exists in the spectra obtained for the precursor before and after activation. Oil-palm shell and the four adsorbents produced present (C=C) double-bonds. However, after activation (C-O) bonds become present. Formation of oxygen-carbon bonds is the result of the hydration of alkenes. Adsorbents produced present a change in surface functional groups after activation. These functional groups determine the affinity of the material to certain compounds.

## 3.3. Thermogravimetric Analysis (ATG) and Thermic Differential Analysis (ATD)

The four samples present a similar behavior (Figure 4), nevertheless on the figure there two tendencies, one for the activated carbons with an acid agent (CA10A and CA60A) and one for the activated carbons with a basic agent (CA10B and CA60B).

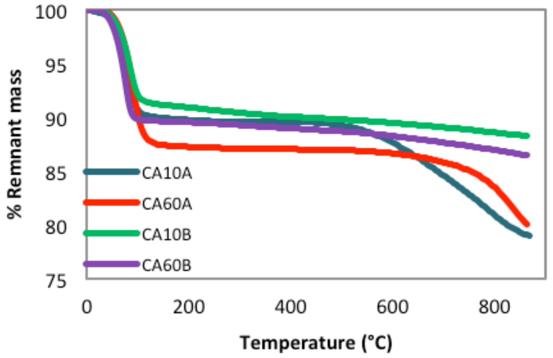

**Figure 4.** Thermogavimetric analysis for the carbons CA10A, CA60A, CA10B and CA60B.

The mass loss between 30 to 100°C is attributed to the elimination of water absorbed in the pores of the carbon (Mettler Toledo, 2001). The carbon with the highest mass loss rate in this temperature range is the CA60A, with 14% followed by the carbon CA60B with 10%, the carbon CA10A with 9% and last CA10B with 7.5%.

In the range of 145 to 575°C no considerable mass loss occurs for none of the four carbons, but the decomposition of the material continues.

Between 580 and 850°C the four carbons present mass loss, being more important for samples CA10A and CA60A, with a loss percentage of 10% and 5 % respectively. For carbons CA10B and CA60B the loss is less significant, with an approximated loss of 1%. These losses can be related to chemical reactions that take place within the carbon due to the high temperatures (Mettler Toledo, 2001), such as the pyrolysis of the material (L.Giraldo, 2007).

TGA and DTA analysis shows that during carbonization regeneration, carbons CA10B and CA60B would be preferable as they present lower total mass loss at high temperatures.

## 3.4. Effect of adsorbent mass

Figure 5 shows the effect of adsorbent mass on the adsorption process. Results evidence an increase in acid removal as activated carbon mass is increased. On the contrary, adsorption capacity, expressed as equilibrium adsorbent phase concentration, decreases as carbon mass used is increased. This occurs in the case of all four adsorbents studied. Two factors may contribute to this effect: as adsorbent dose increases, adsorption sited remain unsaturated during the adsorption reaction, leading to a decrease in adsorption capacity; or the aggregation and agglomeration of carbon on the test jars, leading to less superficial area becoming available and increasing the distance for acid diffusion (Li and others , 2009).

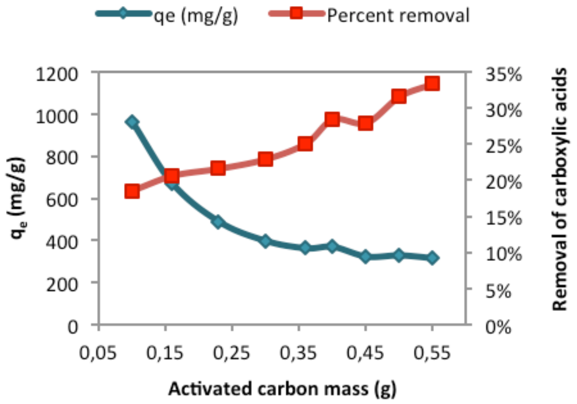

**Figure 5.** Effect of adsorbent mass on adsorption of carboxylic acids. CA60B, T=30ºC.

This effect is observed for the four carbons studied. Experimentally, carbons which were impregnated with KOH presented higher carboxylic acid removal percentage. According to these results, CA60B adsorbent had a higher adsorption capacity and presented a larger removal of acids of interest. Using the tendency of experimental data, it was estimated that 2.64 grams of CA60B would be required to achieve almost complete removal of carboxylic acids from the solution at 30°C.

## 3.5. Effect of initial concentration

Figure 6 shows the effect of initial concentration of carboxylic acids on the adsorption process, in this case butyric acid. Results evidenced a decrease in acid removal with higher initial concentrations. On the contrary, adsorption capacity increased with initial concentration of acids in the solution.

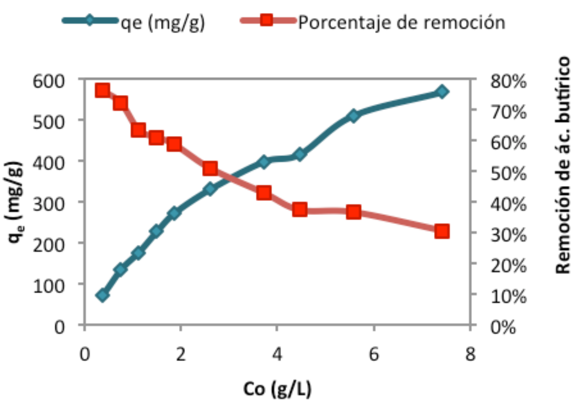

**Figure 6.** Effect of initial concentration on adsorption of butyric acid. CA60B, T=40ºC.

The effect of initial concentration is similar for the four adsorbents studied. This would indicate that in general the adsorption process is benefited by a larger concentration, possibly due to a higher availability of acid molecules and a larger flow thanks to a bigger concentration gradient. On the other hand, the reduction of removal percentage could be caused by a descent in adsorption rates due to the saturation of open pores and surface available. According to these results CA60B adsorbent presents a higher acid removal.

## 3.6. Equilibrium isotherms

Adsorption isotherms qualitatively describe information on the nature of surface-solute interactions and specific relations between the adsorbate concentration and its accumulation on the surface of the adsorbent at a constant temperature (Li, y otros, 2009).

In order to study the nature of the adsorption of acetic, propionic and butyric acid on four adsorbents (CA10A, CA60A, CA10B y CA60B) five models were used to fit experimental data, Langmuir, Freundlich, Tempkin, Redlich-Peterson and Langmuir-Freundlich. Equations for each model are presented in Table 4. Model parameters were determined by non-linear regression using Minitab16® statistical software and are presented in Table 5. Figure 7 illustrates the different adsorption isotherm models for CA60B adsorbent at 40°C. .

**Table 1.** Adsorption isotherm models used and their parameters (Li and others , 2009).

| Isotherm | Model | Parameters |
|---|---|---|
| Langmuir | $q_e = bq^0/(1+bC_e)$ | $C_e$: liquid phase equilibrium concentration (mg/L);<br>$q_e$: equilibrium adsorption capacity mg/g);<br>$b$: Langmuir constant (L/mg);<br>$q^0$: maximum adsorption capacity; |
| Freundlich | $q_e = K_F C_e^{1/n}$ | $K_F$ : Freundlich constant (L/mg); $1/n$: heterogeneity factor; |
| Tempkin | $q_e = (RT/b_T)\ln(AC_e)$ | $A$: Tempkin constant (L/g); $b_T$ :  Tempkin constant; |
| Redlich-Peterson | $q_e = (K_R C_e)/(1+aC_e^{\beta})$ | $K_R$: Redlich-Peterson constant (L/g);<br>$a$: constante de Redlich-Peterson (L/mg);<br>$\beta$: constante Redlich-Peterson (L/g); |
| Langmuir-Freundlich | $q_e = \frac{q^0 (K_{LF} C_e)^{a_{LF}}}{1+(K_{LF} C_e)^{a_{LF}}}$ | $K_{LF}$: Langmuir-Freundlich constant (L/mg);<br>$a_{LF}$: heterogeneity parameter. |

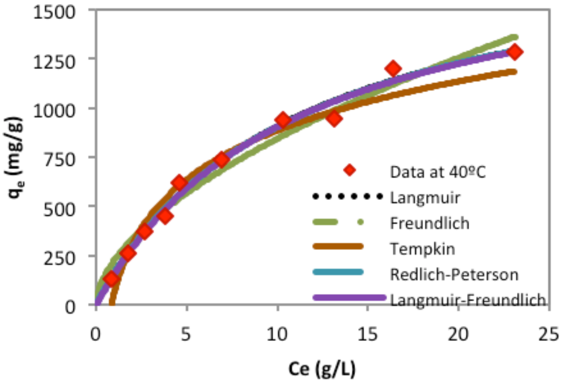

**Figure 7.** Comparison of different isotherm models for adsorption of carboxylic acids on CA60B at T=40ºC.

The Langmuir model is usually implemented on the assumption of ideal monolayer adsorption. (Langmuir, 1918). The Langmuir-Freundlich model is usually used for heterogeneous adsorption surfaces. The Redlich-Peterson model, for its versatility, is applicable to homogeneous and heterogeneous systems over a wide range of concentrations (K.Y. Foo, 2010). The Freundlich model describes appropriately multilayer adsorption process with interaction between adsorbed molecules (K.Y. Foo, 2010). The Tempkin model is employed to show the effect of some indirect adsorbate-adsorbate interactions (K.Y. Foo, 2010).

Using the determination coefficient ($R^2$) as only indicator it was found that the Redlich-Peterson model presented the best fit for the experimental data. This evidences the versatility of the Redlich-Peterson model. However, this model is highly affected by experimental variability. This makes it not the best alternative to predict the behavior of the adsorbents.

The Langmuir-Freundlich model was found to be the best representation of experimental equilibrium data for the four carbons used at both temperatures. This suggests that the surface of the four adsorbents might be heterogeneous with different energy distributions (Derylo-Marczewska, Jaroniec, Gelbin, & Seidel, 1984). Additionally, as Langmuir model presented a better fit than Freundlich model, it is inferred that in most cases adsorption occurred in monolayer and not multilayer (Langmuir, 1918), with the exception of CA10B. The value of the determination coefficient for the models using CA10B shows a change in goodness of fit with temperature, where at 30°C Langmuir model presents a better fit than the Freundlich model. The opposite occurs at 40°C.

**Table 5.** Adsorption isotherm parameters for CA60B.

| Isotherms | Parameters | 30ºC | 40ºC |
|---|---|---|---|
| Langmuir | $q_0$ (mg/g) | 1565.88 | 1906.96 |
| | b(L/mg) | 0.061 | 0.090 |
| | $R^2$ | 0.946 | 0.987 |
| Freundlich | $K_F$ (L/mg) | 119.49 | 228.05 |
| | n | 1.475 | 1.754 |
| | $R^2$ | 0.938 | 0.971 |
| Tempkin | A (L/g) | 1.264 | 1.168 |
| | $b_T$ | 10.80 | 7.00 |
| | $R^2$ | 0.883 | 0.963 |
| Redlich-Peterson | $K_R$ (L/g) | 68.40 | 173.50 |
| | a (L/mg) | 8.35E05 | 0.094 |
| | β | 3.064 | 0.990 |
| | $R^2$ | 0.952 | 0.987 |
| Langmuir-Freundlich | $q_0$ (mg/g) | 1549.18 | 1882.90 |
| | $K_{LF}$ (L/mg) | 0.062 | 0.093 |
| | $a_{LF}$ | 1.006 | 1.011 |
| | $R^2$ | 0.946 | 0.987 |

## 3.7. Adsorbent comparison

Figure 8 compares the adsorption capacities of the four adsorbents studied at 40°C. A similarity is observed between carbons activated in acid medium, both of which showed the lowest adsorption capacities. The adsorption capacity of

CA10A is slightly higher than that of CA60A. This might happen due to a less favorable superficial chemistry for adsorption of carboxylic acids when activation occurs in an acid medium. Increasing concentration of the acid impregnation medium for the activation would therefore decrease adsorption capacity of short chain carboxylic acids. Carbons activated in a basic impregnation medium have higher adsorption capacities. CA60B is presents the highest adsorption capacity, well above the other carbons.

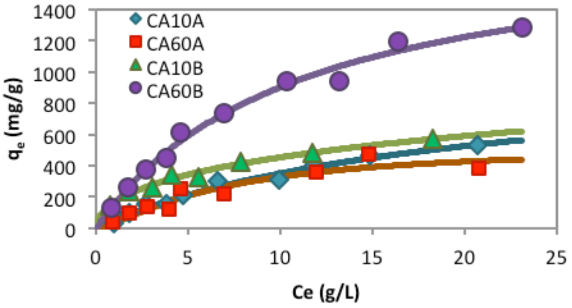

**Figure 8.** Comparison of activated carbons on the adsorption of carboxylic acids. T=40ºC. Fitted to Langmuir-Freundlich model.

Experimentally, it was found that changing temperature, initial acid concentration and adsorbent mass causes changes in adsorption capacities and carboxylic acid removal percentage. These experiments had in common CA60B as a dominating adsorbent for the recovery of carboxylic acids. Higher adsorption capacity for CA60B could be caused by a higher development in porosity and a more favorable superficial chemistry.

## 3.8. Desorption

A comparison is established between the four carbons in respect to: total acid adsorbent phase concentration after adsorption of acids and after desorption (Figure 9) and percentage of acids which are desorbed from the surface of the carbons.

For the first carbon synthesized (CA10A) a concentration of 62.5 mg/g of total acids adsorbed on the surface was found after adsorption. After desorption adsorbent phase concentration was reduced to 57.8 mg/g, which evidences that only 5 mg/g were desorbed. For carbon CA60A, adsorption of carboxylic acids is low with an adsorbent phase concentration after adsorption of 15 mg/g, which is reduced to 9 m<g/g after desorption. According to these results, for carbons activated using phosphoric acid the adsorption and desorption efficiency is limited possibly by the superficial chemistry this acids present, which could cause a low affinity in the adsorption of carboxylic acids.

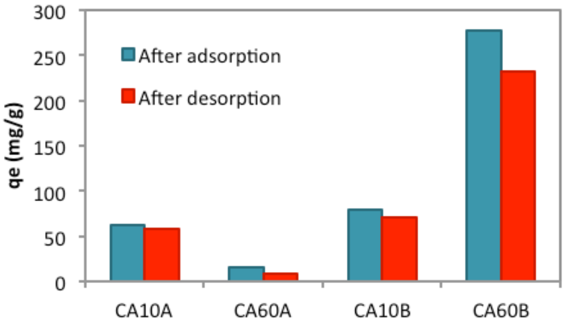

**Figure 9.** Adsorbent phase concentration comparison after adsorption and after desorption.

On the other hand for CA10B a surface concentration of 79.7 mg/g was found after adsorption which was reduced to 70.4 mg/g after desorption. For CA60B a higher adsorbent phase concentration of 232.6 mg/g was found, which decreased by 44.1 mg/g, presenting the highest amount of acids desorbed. However this value only accounts for 18.5% of acids originally on the surface of the carbon, a low percentage to consider activated carbon as an appropriate recovery mechanism for carboxylic acids in the MixAlco® process.

Adsorption of short chain carboxylic acids from aqueous solutions on activated carbon is ruled by two main interactions: physical and chemical (Yehya & Bandosz, 2008). Physical interactions are mainly dispersive interactions, including the effect of microporosity, and specific hydrogen bonds. Chemical interactions include the effects of surface chemistry such as acid-base interactions. Because of these interactions the surface of basic carbons, such as CA60B, allows acid-base reactions, generating a higher presence of acids on the surface of the carbon. Additionally CA60B's higher porosity favors both adsorption and desorption processes.

CA60B carbon presents a higher quantity of desorbed acids per gram of carbon with a total of 44.1mg from 276.71mg initially adsorbed, representing 18.5% of the acids present on the surface of the carbon. These prove activated carbons produced to be a difficult method for recovery of carboxylic acids. To improve desorption carbons produced should present higher mesopore volume.

## 4. CONCLUSIONS

CA10A and CA60A present an acidic surface with pore diameter between 1-4nm. CA10B y CA60B present a basic surface with pore diameter between 0.96-5nm.

CA60B carbon evidenced a greater adsorption capacity (1300mg of adsorbed acids/g of carbon, or 33.3% of acids present in the solution).

Langmuir-Freundlich model describes more appropriately the adsorption phenomena observed for all four adsorbents. The four carbons present a heterogeneous surface.

Desorption proved difficult during temperature shift studies using warm water. Difficulty in recovery of surface adsorbed acids make activated carbons produced less likely to be implementable in the fermentation stages of MixAlco® process. To improve desorption, activated carbons should be synthesized with higher mesopore volume.

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