# Loquate Stones, a novel feedstock for Activated carbon production through chemical activation

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## Abstract:

The objective of this study is to produce activated carbons with high adsorption capacities from Loquate stones. Chemical activation using phosphoric acid and potassium hydroxide was used to produce the activated carbons. Surface area of the produced carbon were determined through various methods namely adsorption from solution by using iodine, p-nitro phenol and methylene blue as solutes, adsorption from vapor phase by using hexane and ethanol vapors, and retention method by using ethylene glycol mono ethyl ether (EGME) as an adsorbate .Surface area of the produced carbons were high using iodine as adsorbate implying that the produced carbons have micro porous structure. Furthermore, adsorption isotherms of the adsorption of methylene blue and PNP were determined and found conform with Langmuir type of adsorption which indicates the micro porous structure of the produced carbons.

**Keywords:** Laquate stones; Activated carbons ; chemical activation; Adsorptive capacity Surface area.

## 1.Introduction

Activated carbon is a highly porous material which has various applications in the adsorptions of both gases and solutes from aqueous solution**[1]** Activated carbons are usually used worldwide for water treatment , wastewater reclamation, gas purification and also as a catalyst support**[2]**. Almost any carbonaceous material with low organic volatile content, high in elementary carbon, and of sufficient strength can be converted into an activated carbon**[3]**.

In the recent years , many other agricultural by-products have been used as sources for activated carbons production such as cherry stones, olive stones ,oil plam stones, apricot stones, almond shells, sugar cane bagasse, walnut shells, pecan shells,cotton stalks and date stones**[4]**. With the increasing demand on activated carbon due to its environmental applications, a great interest has been developed to seek steadier and cheaper feed stocks for the manufacture of active carbons**[5,6]**. In the these agricultural by- products have proved to be promising raw materials for the production of activated carbons because of their availability at a low price. They have been used for the production of activated carbons with a high adsorption capacity**[7]**. adsorption characteristics of activated carbon are determined by its pore structure (magnitude and distribution of pore volume) and surface chemistry (kind and quality of surface-bound heteroatomic functional groups). The existence of functional groups such as carboxyl's, phenols, lactones, aldehdes, ketenes', quinones, hydroquinone's and anhydrides has been postulated. These functional groups determine the acid base character of activated carbons. The electrical change of the surface groups may also enhance or decrease the adsorption of the target molecules on the carbon surface. If the adsorbate has the same electrostatic charge as that of the carbon surface, repulsion occurs, this leads to decrease in adsorption. However, if adsorbate and carbon surface carry opposite charges adsorption increases**[8]**.

The following study investigates the production of activated carbons with high adsorption capacities from fruit waste viz. Loquate stones (Eriobotrya Japonica Lindl). Activated carbons preparation is achieved by a two-step carbonization and chemical activation by using phosphoric acid ($H_3PO_4$) and potassium hydroxide (KOH) as the activating agents. Iodine, methylene blue (MB), p-nitrophenol (PNP), ethylene glycol mono ethyl ether , hexane, and ethanol were chosen as solutes for their well-established value in the determination of the adsorption capacities and surface areas of the active carbons samples ($AC_S$). The surface areas of the produced bio chars were determined through various methods. Adsorption isotherms of the produced carbons were also determined.

## 2. Experimental

### 2.1 Feedstock preparation

Laquate stones (LS) as a carboneous precursor for activated carbon (AC) production was dried in an oven at 60c° for 2h. The dried stones were then ground and sieved by a 20-40 mesh sieve. Particles of 30-40 mesh were used to produce the activated carbons.

### 2.2 Production of activated carbons

Activated carbons from LS were produced through two- step, carbonization and activation. Particles of 30-40 mesh were carbonized at 500°C for 2h to obtain a semi carbonized material (SCM). The latter was converted into activated carbons through chemical activation using phosphoric acid ( $H_3PO_4$) or sodium hydroxide (NaOH) as activating agents.

### 2.2.1 Production of activated carbon using $H_3PO_4$

A specified amount of the SCM was mixed with a solution of 50% $H_3PO_4$ and left for a 24h. Then the mixture was filtered and dried. The product was then activated at 700-750 °C for 1h by means of a tubular furnace. Finally, the produced AC was washed by a solution of 1N of NaOH to remove the excess acid, and then thoroughly washed by warm distillated water until a $_PH = 7$ was obtained. The AC was finally dried in an oven for 5h at 110°C and kept in a sealed container to be assessed later. The sample was labeled as $AC_A$.

### 2.2.2 Production of activated carbon using NaOH

A known amount of the SCM was mixed with a solution of 50% NaOH and left for a 24h. Then the mixture was filtered and dried. The product was then activated at 700-750 °C for 1h by means of a tubular furnace. Finally, the produced AC was washed by a solution of 1N HCl to remove the excess base, and then thoroughly washed by warm distillated water until a PH = 7 was obtained. The AC was finally dried in an oven for 2h at 110°C and kept in a sealed container to be assessed later. The sample was labeled as $AC_B$**.**

### 2.2.3 Production of activated carbon through thermal activation

For comparison purpose, the SCM was thermally activated at 700-750°C for 1h. The sample was labeled as $AC_T$.

### 2.3 Characterization tests

### 2.3.1 Adsorption from solution phase of methylen blue and p-nitro phenol

Adsorptive capacity of the prepared carbons were determined through their adsorption to iodine, methylene blue (MB) and p-nitro phenol (PNP).

Adsorption of the iodine was used as a function of the surface area of the produced carbons. The iodine adsorption number is defined as the milligrams of iodine adsorbed by 1 g of carbon. Titration against sodium thiosulphate method was used to determine the quantity of iodine adsorbed per gram of activated carbon according to (ASTM D 4607-94].

Adsorption of methylene blue (MB) and p-nitro phenol (PNP) used to detect the ability of the produced carbons to remove colored molecules from their aqueous solutions. Batch adsorption experiments were carried out in 100 mL stoppard conical flasks at room temperature using solutions of known concentrations. A specified amount of the AC sample was agitated with a 50 mL of 250 ppm solution of MB and 200 ppm PNP individually until equilibrium was attained (after 24h). Afterward, the samples were filtered and the dye concentration in the supernatant solution was determined spectrophotometricaly using a Shimadzu UV-Vis 1260 PC. The wavelength was selected so as to obtain maximum absorbance for each dye stuff and the $\lambda_{max}$ values are given as follows: for MB (665nm) and for PNP (318nm ). The amount of dye adsorbed on the carbons, *Qe* (mg/g) was calculated by mass balance relationship by the following equation :

$$Q_e = [C_o - C_e]\, V / W \quad \textbf{...........(1)}$$

where $C_o$ and $C_e$ are the initial and equilibrium liquid phase concentrations, respectively (mg/L), $V$ the volume of the solution and $W$ is the weight of the carbon used (g).

### 2.3.2 Determination of the surface area by adsorption from vapor phase

The adsorption of some organic vapors ( hexane and ethanol) on the surface of the produced carbons were also tested in this study. A gravimetric method was used for this purpose. It is based on passing a saturated dry air with an adsorbate vapor through a bed of the adsorbent under atmospheric pressure. The adsorption process continued until a constant weight was obtained which was detected by a four digital balance (0.0001 mg).

### 2.3.3 Determination of the surface area by retention method (EGME method):

The procedure includes wetting a sample with *EGME*, equilibrating, and then removing the excess liquid by evacuation. The sample was removed periodically and weighed until a constant weight was obtained. The specific surface area was calculated from the weight of the retained liquid assuming that a monomolecular layer of *EGME* was adsorbed on the surface. The procedure applied in this work was implemented according to Lutengger method [7-8].

## 3. Results and discussions

### 3.1 Ultimate and proximate analysis of Laquate stones

Ultimate and proximate analysis of Laquate stones (LS) are given in Table-1. It is obvious from Table-1 that LS is suitable precursor for AC preparation for its low ash content.

**Table-1. Ultimate and proximate analysis of Loquate stones**

| Ultimate analysis (%) | wt. (%) | Proximate analysis (%) | wt. (%) |
|---|---|---|---|
| **Carbon** | 40.72 | **Moisture** | 10 |
| **Hydrogen** | 5.96 | **Volatile matter** | 62.50 |
| **Nitrogen** | 0.76 | **Fixed carbon** | 2.50 |
| **Oxygen** | 52.56 | **Ash** | 6.749 |

### 3.2. Activated Biochars properties

Activated carbon is a highly carbonaceous material with high surface area and porosity. Many tests can be used for determining its activity.Table-2 shows adsorption capacity of the produced ACs toward various adsorbates. It can be seen from Table2 that the yield of $AC_A$ was lower compared with other samples ($AC_B$ and $AC_T$). The reason belongs to the extensive removal of volatiles and oxygenic structures from the cellulosic material of LS. The acid can penetrate deeply in the structure of the starting material resulting in further removal of water molecules, and hence forming of different macromolecular networks which resulted in promotion of cross linking of structure and reduction of tar formation during the carbonization[9].

Iodine number determination can be used as a test for the capacity of adsorbents to remove color compounds from their aqueous solution. This test can determine relative activation level and the surface area available for micro pores. Besides, this test is complementary to the $N_2$/77 K adsorption isotherm and is used to measure surface area of micropores ≥ 10 $A^2$ [9]. Usually adsorbents with a high iodine number have a high surface area and are suitable for adsorbing small molecules[10]. It can be seen from Table-2 that among the prepared carbons, $AC_A$ exhibited higher surface area represented by its high IN (606 mg/g). This may be attributed to the possibility that acid treatment enhanced removal of volatiles and oxygenic groups from the cellulosic structure of LS, resulting in the formation of a micro porous structures. The lower yield and higher IN is in support of our conclusions.

Surface area determination through adsorption from solution was conducted using MB and PNP as solutes. The linear form of Langmuir equation which is valid for monolayer sorption onto a surface was used for determining the amount which represents the monolayer adsorption $Q_m$ as expressed in Eq. (2):

$$C_e / Q_e = 1/ K_L Q_m + C_e / Q_m \quad \ldots\ldots (2)$$

Where $Q_m$ is the amount adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage on the surface bound at high $C_e$ and $K_L$ is the constant related to the affinity of binding sites. Langmuir linear plots of PNP and MB for the produced carbons are shown in Figures 1 and 2 respectively.

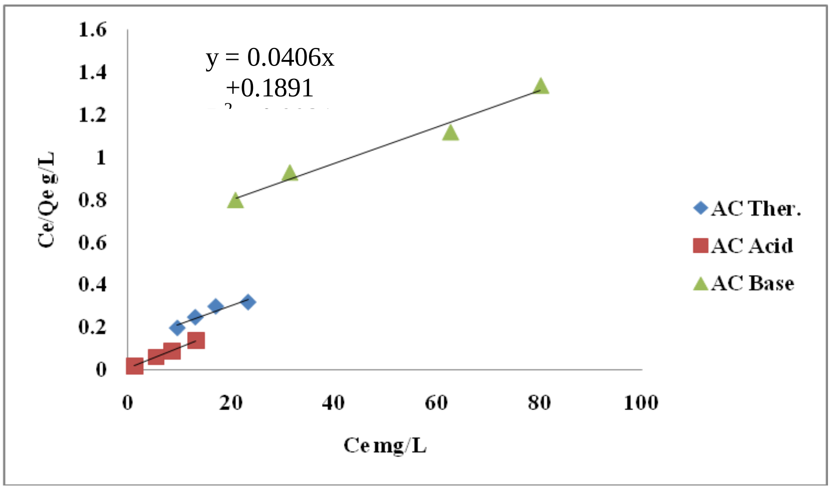

Figure-1. Langmuir linear plots of PNP on the produced carbons.

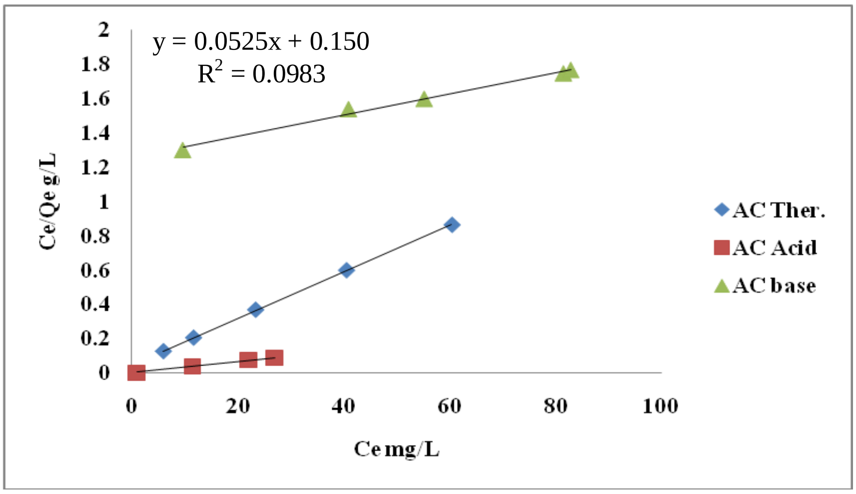

Figure-2. Langmuir linear plots of MB on the produced carbons.

Surface area was calculated using the following equation [11-13]:

$$SA_{Dye} = Q_m \cdot N \cdot \acute{O} / n \text{ …………… (3)}$$

Where $SA_{Dye}$ is the surface area related to dyestuff in ($m^2/g$), $Q_m$ is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of the adsorptive sites and determined from Langmuir linear plots, $N$ is Avogadro's number, $\acute{O}$ is the cross sectional area of the solute in ($nm^2$) which equals to $1.2 nm^2$ for *MB* and $0.52\ nm^2$ for *PNP* and *n* is the aggregation factor. Table-2 shows adsorptive capacities for MB and PNP adsorbed over the produced carbons. Values of surface areas calculated using the former equations are listed in Table-3.

**Table-2. Adsorption properties of the produced ACs.**

| Sample | Yield % | PH | Moisture % | Organic vapor adsorption mg/g | | Solution Adsorption mg/g | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Hexane | Ethanol | $I_2$ | PNP | MB |
| $AC_T$ | 20.6 | 9 | 1.96 | 48 | 56 | 285 | 116 | 74.0 |
| $AC_A$ | 30.7 | 3 | 2.89 | 201 | 397 | 606 | 101 | 301 |
| $AC_B$ | 35 | 8 | 2.24 | 113 | 123 | 364 | 118 | 161 |
| $AC_{com}$ | ND | ND | 0.53 | – | – | 297 | 88 | 64 |

Adsorption of PNP can be used as indication for removal of low molecular weight dyes from their aqueous solution. Surface area determination through adsorption of PNP was used by many investigators [11-13]. On the other hand, adsorption of PNP can also be used as indication of micro porosity in activated carbons, because this molecule has a cross sectional area of $0.52\ nm^2$. The activated carbons $AC_B$ and $AC_T$ showed higher surface area determined through adsorption of PNP. This could be ascribed to many reasons. First, those samples have micro pores wider than those exist in $AC_A$ . Second, surface chemistry of the carbon surface plays an important role in the adsorption process. The PH value of $AC_A$ is the lowest among other samples. According to the acidic nature of the surface of $AC_A$ , a repulsion could arise between the PNP molecules and the surface of $AC_A$ resulting in lower adsorption of PNP on $AC_A$.

Methylene blue( MB) adsorption studies are widely used for the evaluation of adsorbents because this dye can be viewed as a model for visible pollution and is an indicator of mesoporosity[10]. Surface area determination through the adsorption of MB from its aqueous solution was higher in $AC_A$ compared to the other carbons. This means that $AC_A$ could be used to remove both low and high molecular weight pollutants from their aqueous solutions . Adsorption of humidity is another indication for the micro porosity in activated carbon. $AC_A$ showed the highest adsorption for humidity among the produced carbons. This belongs to the micro porous structure in this sample.

Surface area determination using retention method (*EGME*) has been used by large number of investigators[7-8], the following equation is used for calculating the SA:

$$S_{SA} = W_a / 0.000286\ W_s \text{ ………… (5)}$$

Where, **SSA** is the specific surface area in $m^2/g$, $W_a$ is the weight of *EGME* retained by the sample in grams (sample Ws), 0.000286 is the weight of *EGME* required to form a mono layer on a square meter of surface ($g/m^2$) and $W_s$ is the weight of sample added (g). Surface area determined through the retention of EGME was higher in $AC_T$ as can be seen from Table3. This is because this sample has lower micro porous structure compared with the other sample. Another probable reason is the surface chemistry of this sample.

Surface area of the produced carbons was also calculated through adsorption from vapor phase. Hexane and ethanol vapors were used as adsorbates. The following equation was used to calculate the surface area of silicate $SA = V_m \cdot N \cdot \acute{O}$ ………………….. *(4)*

Where, $V_m$ is the volume required to form a monolayer on adsorbent surface ml/g, $N$ is Avogadro's number and $\acute{O}$ is the cross sectional area of the adsorbate molecule. Hexane and ethanol were used due to theis high vapor pressure at room temperature, Surface area of $AC_A$ showed higher surface area determined through the adsorption of ethanol and hexane vapors as can be seen from Table3. The vapors of both molecules can be used as a function of micro porosity in activated carbons. High adsorption of hexane vapor on $AC_A$ could be attributed to its surface area, while the high adsorption value of ethanol vapor belongs to the former reason and to the nature of the oxygen surface groups of the surface of this sample.

**Table-3. Surface Areas of the ACs Prepared from Loquate Stones**

| *NO* | *Sample* | $SA_{I2}$ $m^2/g$ | $SA_{PNP}$ $m^2/g$ | $SA_{MB}$ $m^2/g$ | $SA_{EGME}$ $m^2/g$ |
|---|---|---|---|---|---|
| 1- | $AC_T$ | 1150 | 261 | 84 | 306 |
| 2- | $AC_A$ | 545 | 228 | 341 | 287 |
| 3- | $AC_B$ | 480 | 266 | 182 | 253 |
| 4- | $AC_{com}$ | 564 | 198 | 72 | – |

### Adsorption isotherm

The adsorption isotherms, which represent the relationship between the equilibrium concentration and the adsorbed quantity, of the ACs have been determined using MB and PNP as solutes, as shown in Figures 3 and4. These figures show mixed types of Langmuir isotherms, according to Giles classification [14]. These types of isotherms were fitted to $L_2$ and $L_3$ types.

The adsorption isotherms of PNP and MB of our samples showed the presence of both mesoporosity and micro porosity in the structure of the prepared ACs.

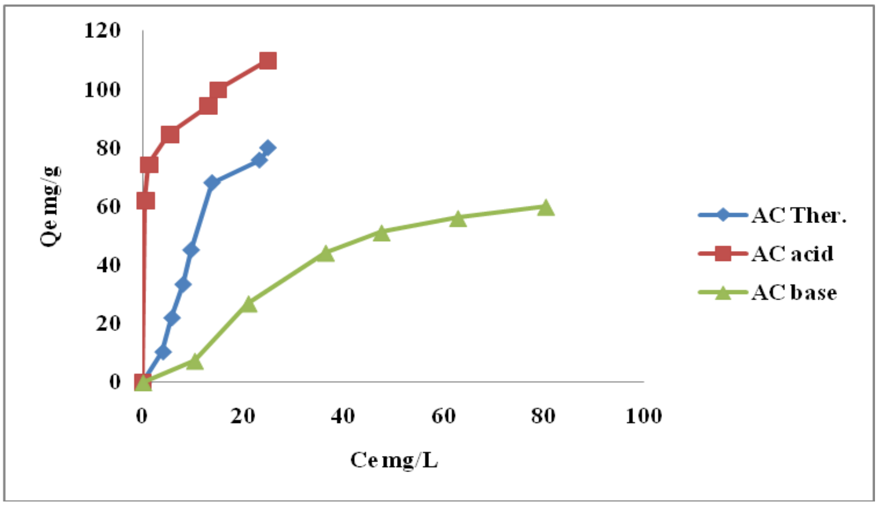

**Figure-3. Adsorption isotherms of PNP on the produced carbons.**

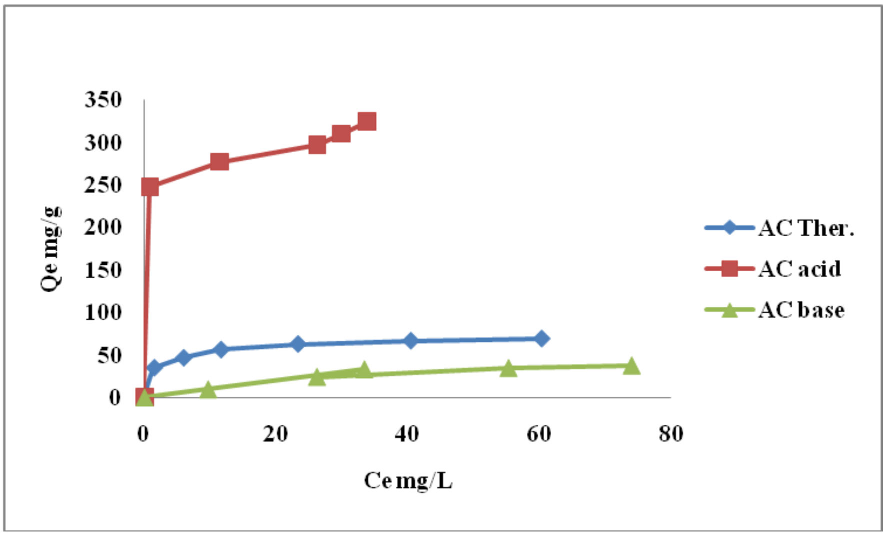

**Figure-4. Adsorption isotherms of MB on the produced carbons.**

## 4. Conclusion

1. Activated carbon prepared from the investigated biomass waste could be used as potential adsorbent for the removal of dyes from contaminated water and for air purification.
2. Selection of activated carbon as adsorbent for removing dyes from water and contaminated water requires knowledge of both the properties of the dyes which are to be adsorbed and AC characteristics.
3. Activated carbon obtained from Loquate stones showed better adsorptive properties and surface area as compared with the commercial sample studied in this paper.
4. The results showed that the adsorption process is usually complete when the surface is covered by a monolayer of dye.
5. Activated carbons of various molecular sieves were obtained from Loquate stones. This was detected from adsorption of various vapors of different molecular sizes.

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## الملخص

تهدف هذه الدراسة الى انتاج كاربون منشط ذو سعة امتزاز عالية من نوى العنكودنيا ، حيث تم في هذا البحث اعتماد اسلوب التنشيط الكيميائي باستخدام العوامل الكيميائية من حامض الفسفوريك وهيدروكسيد البوتاسيوم. المساحة السطحية النوعية للكاربون المنشط الناتج تم تعيينها بعدة طرق، طريقة الامتزاز باستخدام اليود، بارا نايترو فينول (PNP)، وصبغة المثلين الازرق (MB) للمذاب، طريقة امتزاز الابخرة باستخدام الهكسان والايثانول، وطريقة الاحتفاظ باستخدام اثلين كلايكول مونو ايثايل ايثر(EGME). كانت المساحة السطحية للكاربون المنشط الناتج عالية باستخدام اليود مما يعني ان الكاربون المنشط الناتج لديه بنية ذات مسامات صغيرة جدا، اضافة الى ذلك، تم تعيين ايزوثرمات الامتزاز للنماذج المحضرة من خلال الامتزاز من المحلول المائي لصبغة (MB) ومادة (PNP)، وكانت هذه الايزوثرمات متلائمة مع نوع لاكماير من ايزوثرمات الامتزاز مما يدل على ان الكاربون المنشط الناتج ذات تراكيب مسامية دقيقة .