

PRODUCTION OF ACTIVATED CARBON FROM THE ENDOCARP OF COCONUT NUCIFERA. CASE OF THE EAST COAST OF MADAGASCAR

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ABSTRACT

This research work is a contribution to the search for ways of recovering the waste endocarp of coconut nucifera. Dry distillation is the appropriate technology for material recovery. A prototype laboratory distiller has been built in the framework of this work with a view to obtaining real results from the various laboratory tests.

The results of the experimental work confirm that the transformation of coconut endocarp waste into activated carbon is technically feasible using a reactor operating on the principle of dry distillation and the physical activation process. The results of the tests carried out have shown that the activated carbon produced has a high adsorption capacity that is competitive with imported products. This will not only reduce our imports of activated carbons, especially those for water treatment, but will also generate a new source of income.

Keyword: waste, activation, coconut endocarp, activated carbon, dry distillation.

1. INTRODUCTION

Waste, whether from domestic, agricultural or industrial sources, is one of the unavoidable problems of the 21st century. Indeed, the increase in the world's population and its concentration in cities, as well as the development of industrial equipment and consumer goods generate large quantities of waste. Waste therefore follows man as the shadow of his presence. Garbage is the traces of his life and technical waste is the traces of his activities. In view of the potential nuisances and dangers conveyed by waste, its rational management and reduction have become essential to preserve the environment and the future of future generations. Faced with this situation, we are currently witnessing the emergence of various research activities into innovative techniques for recovering the energy contained in waste, transforming and/or recycling it.

In Madagascar, particularly in the large cities, the problem of waste management is one of the major concerns of most municipalities, both socially and financially. In this context of waste management, waste of plant origin such as coconut residues is added.

Being an island with a surface area of about 587,000 km², Madagascar has a vast coastal area. It is one of the driving countries in the field of coconut exploitation. The coconut tree of Madagascar produces fruits rich in pulp

oil, walnut oil, palm cake paste and coconut shells which are residues. Precisely, after the extraction of the coconut, the coconut shells are sometimes directly thrown away and are destined to be domestic waste. Their use is rather limited, mainly as building decorations (ashtrays, jewellery boxes,...) as an industrial fuel substitute (boilers and cement kilns) but the majority is put in wild dumps. However, this residue may have a high potential for use in the production of activated carbon, an interesting value-added product, which is in great demand on the world market for its industrial applications.

Despite the abundance of coconut waste for the production of activated carbon in Madagascar, its manufacture is not yet considered. As a result, the country continues to import activated carbon for various applications, particularly in the field of drinking water. This is one of the major problems facing the country.

It is within this framework that this research work entitled "Production of activated carbon from coconut endocarp" was initiated. This study is therefore a contribution to the recovery of agricultural waste, in particular the coconut *nucifera*.

2. METHODOLOGIES

2.1. Study area: The city of Tamatave, Atsinanana region

2.1.1. Location

The urban commune of Tamatave also called capital of Betsimisaraka, the first ethnic groups occupying the city, is located at 18°08'50" South latitude and 49°23'43" East longitude.

The urban commune of Tamatave is located in the Atsinanana region to the East of the big island, at a distance of 370Km from Tananarive, capital of Madagascar bordering the Indian Ocean on a distance of about 20Km from North to South.



Figure 1: Location of the city of Tamatave by Google Earth

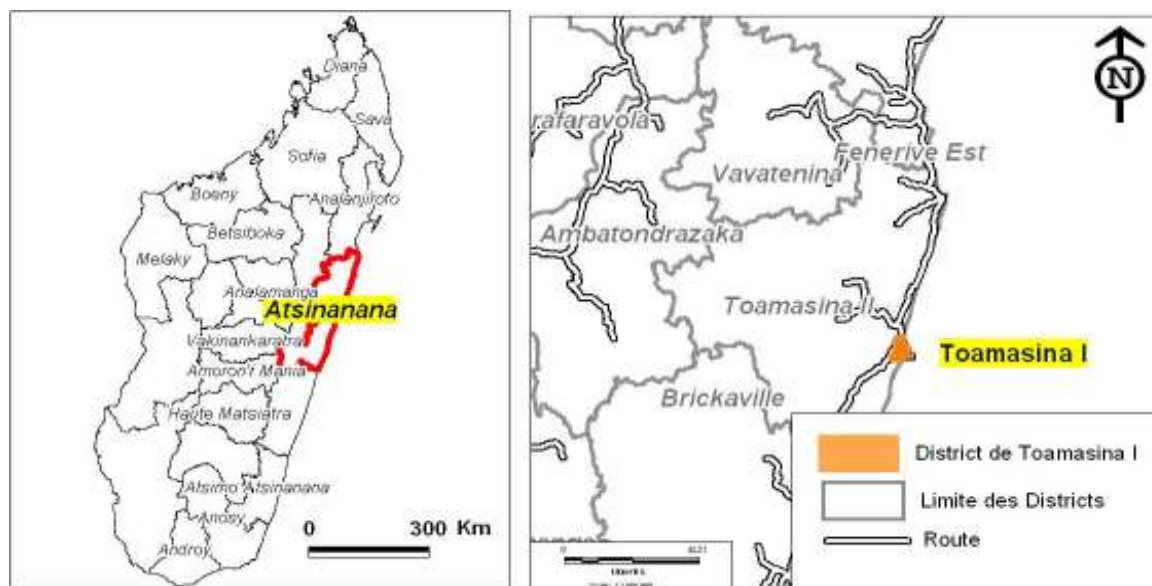


Figure 2: Location of the city of Tamatave

2.1.2. Geographic and climatic location

Geographically, it extends over an area of 28 km². The urban municipality of Tamatave is limited:

- In the North by the sub-prefecture of Toamasina II;
- To the West by the sub-prefecture of Toamasina II;
- To the South by the sub-prefecture of Toamasina II;
- To the East by the Indian Ocean.

The city of Tamatave is made up of five districts with 134 Fokontany.

Table 1: The boroughs of the city of Tamatave

Arrondissements	Nombre de Fokontany
Ambodimanga	19
Tanambao V	20
Anjoma	37
Ankirihiry	33
Morarano	25

2.1.3. Climate and temperature

The climate is tropical, hot and humid, characterized by abundant rainfall brought by eastern air currents and a short dry season. The annual average temperature varies by 24°C, and the rainfall of about 3000mm, one of the favorable conditions for coconuts. The hot season is often disrupted by cyclones which can sometimes be extremely violent. At the level of the " Alizé " wind, the wind from the intertropical regions blows almost all year round and the rainy season extends from December to April.

2.2. Situation of the coconut palm in Madagascar

Madagascar has several industrial regions producing coconuts, among which the SOAVOANIO company in Sambava is part of these production units.

According to agricultural statistics obtained from the Ministry of Agriculture, Livestock and Fisheries, Madagascar has an enormous quantity of coconuts practically in the coastal regions. In 2002, the number of coconuts produced at the national level is estimated at more than 32 million, i.e. around 25,600 tons; this quantity would generate 11776 tons of residues, of which 3072 tons are coconut husks and 8704 tons are husks (data corresponding to minimum values).

Coconut remains make up a large part of the residues and garbage in the large coastal cities and tourist sites of Madagascar's coasts.

Table 2: Madagascar's recorded coconut exports from 2003 to 2006

2003		2004		2005		2006	
Value (Ar)	Net weight (Kg)	Value (Ar)	Net weight (Kg)	Value (Ar)	Net weight (Kg)	Value (Ar)	Net weight (Kg)
635512	6000	1592816	3150	29151334	84571	682206340	960802

2.3. Physic-chemical characteristics of the coconut endocarp (ENC)

Coconut endocarp, which are residues, account for 10 to 50% of the weight of the fruit. It is one of the materials that can be recovered by an energy technique in which certain properties can interfere with the transformation processes. Thus, it is necessary to begin the study on their physicochemical characteristics.

The following table summarizes the respective mass percentages of the organic compounds constituting ENC.

Table 3: Percentage of organic compounds constituting the coconut husk

Organic compounds	Rate in percent by mass (%)
Carbon	46,39
Oxygen	31,82
Hydrogen	3,63
Nitrogen	1,81
Ashes	5,45

2.4. Other properties

ENC also behaves similarly to wood material, so it is generally made up of celluloses, hemicellulose, pentosan, hexosan and lignins and other constituents, whose corresponding mass proportions are shown in the following table

Table 3: Mass proportions of the other constituents of ENC

Constituents	Mass proportions
Hexosane	3
Pentosane	4
Cellulose	1
Lignins	8
Ashes	6
Others	2

2.5. Method for calculating the Specific Surface Area of an adsorbent

Based on the basic assumptions of the BET theory, an adsorption isotherm expresses, for an adsorbate-adsorbent pair at a given temperature, the adsorption capacity at thermodynamic equilibrium as a function of partial pressure or gas phase concentration. The higher the partial pressure of the gas in the medium, the higher the partial pressure, the method for calculating the Specific Surface Area of an adsorbent.

the greater the amount of compound adsorbed per unit mass of adsorbent. The adsorption isotherm provides access to the specific surface area. The specific surface areas are calculated according to the BET method or the BET equation is as follows

$$\frac{P/P_0}{Q(1 - P/P_0)} = \frac{1}{Q_m c} + \frac{c-1}{Q_m c} \cdot P/P_0$$

Q= quantity adsorbed under pressure

Q_m= quantity of gas required to cover 1 g of adsorbent with a single layer of gas

c = BET constant defined as follows:

$$c = \exp [(\varepsilon_l - \varepsilon_L)/RT]$$

ε_l = Differential heat of adsorption of molecules on the surface of the solid.

ε_L = latent heat of liquefaction of steam at the temperature considered.

R= Perfect Gas Constant

T= absolute temperature (K)

$\frac{P/P_0}{Q(1-P/P_0)} = f(P/P_0) \rightarrow y = ax + b$, this affine line has as slope: $a = \frac{c-1}{Q_m c}$ and intercept $b = \frac{1}{Q_m c}$. From a and b we deduce Q_m and c.

Hence $b = \frac{1}{Q_m c}$ and $c = a/b + 1$.

The obtained straight lines of slope and ordinate at the origin allow the determination of the constants Q_m etc. Thus, the knowledge of Q_m makes it possible to determine the specific surface by applying the following relation:

$$S_{BET} = Q_m N c$$

Or: surface occupied by an adsorbate molecule
 Wastewater treatment steps

2.6. Wastewater treatment steps

Wastewater can undergo three treatments

2.6.1. Preliminary treatment

It consists of removing debris and coarse waste (wood, clothing, plastic, glass, metal, sand or gravel...) from the water as soon as it enters the plant. This stage only eliminates 10 to 15% of the initial pollution in the three following stages:

-Screening

Simple physical separation using grids that retain solid waste from the wastewater flowing through them.

-Desanding

Large basin, at the bottom of which sand and gravel are deposited that can damage downstream installations (silting of pipes, basins, wear and tear on pumps and other metal components, etc.).

-De-oiling and degreasing

It is done by injecting fine air bubbles that allow oils and greases to rise to the surface where they are removed [8].



Figure 3: Preliminary processing steps

2.6.2. Primary treatment (physicochemical)

Wastewater enters a settling tank, usually in the form of a cyclone, and remains there for several hours so that the solids can settle to the bottom; the accumulation of these solids leads to the formation of a layer of sludge known as primary sludge.

Lighter solids, such as fats, oils and greases, remain on the surface to form a sludge cap.

Settling performance can be improved by the addition of chemicals or coagulants (alumina sulphate, ferric chloride) that cause the particles still present to clump or agglomerate into flakes. The flakes agglomerate and settle to the bottom of the basin by settling, as summarized in the following figure:

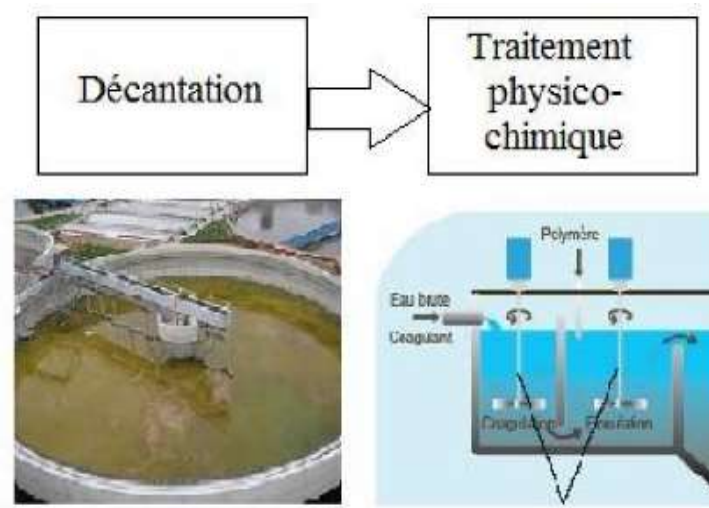


Figure 4: The stages of decantation and coagulation-flocculation.

2.6.3. Secondary (biological) treatment

After settling, the effluent is introduced into basins equipped with aeration devices (turbines, air insufflation...) where microorganisms naturally present in the effluent decompose the organic contaminants. These microorganisms also exert a physical effect of pollution retention by their propensity to gather in films or flakes.

The most commonly used biological treatment techniques are :

- Activated sludge,
- Bacterial beds (fixed bacteria),
- Biofilters,
- Membrane processes have been used for a few years.



Figure 5: Biological treatment.

2.7. Laboratory work

We have chosen coconut endocarp nucifera as the basic raw material for the manufacture of activated carbon. Thus, different steps were followed to achieve this end:

First, the collection, drying, sorting and weighing of the raw material;

Then comes the grinding followed by carbonization and activation;

And finally the adsorption test and experimental characterization of the activated carbon produced.

2.7.1. Determination of the physic-chemical characteristics of the endocarp of coconut nucifera

a) Determination of moisture content

The ENC wet and unsuitable to be used during its transformation. It is therefore necessary to dry them. Storage and climatic conditions determine the evolution of humidity over time; however, it should be noted that humidity tends during drying to balance with temperature and relative humidity.

Determining the moisture content of a BMS is only possible after knowing the value of the dry matter M_s . Thus, the value of M_s must first be determined in order to know the moisture content.

Determining the M_s

For a solid biomass to be valuable, its dry matter content must be higher than 2%.

The value of the dry matter is obtained by steaming at 105°C, appropriate samples for 24 to 30 hours and weighing them several times until it is established that the matter in question is completely dry, while avoiding any change in its composition or basic structure. Standard ISO 589 prescribes that the sample shall be dried in a ventilated oven at a temperature of 105 °C to a constant mass.

This value is used to determine the initial and final moisture content of the products.

According to the European standard EN13774, the moisture content is obtained by the following formula:

$$T_H = \frac{M_{humide} - M_{sèche}}{M_{humide}} \times 100$$

T_H is expressed in (%)

Moisture: initial mass of the sample

M_{dry} : mass obtained after heating to 105°C.

b) Volatile Matter (VMO)

Biomass volatiles are the portion of organic matter that escapes as a gas during combustion. The level of volatile matter supports the flammability of biomass.

Measuring principle:

The same sample used to find the moisture content is heated in a muffle furnace at a temperature of up to 550°.

Its determination follows the French standard NF1985, the MOV rate is determined by the loss of mass during heating. The following formula is used to calculate the MOV rate

$$MOV = \frac{M_{105} - M_{550}}{M_{sèche}} \times 100$$

MOV: volatile matter content (%)

M_{105} : mass obtained after heating to 105°C

M_{550} : mass obtained after heating to 550°C

$M_{dry} = M_{105}$

c) The ash content T_c

The ash content represents the amount of MM contained in a biomass. It is important for the appreciability of the biomass because if it is very high, the ash becomes an obstacle to the progress of the transformation process.

Principle of measurement

The ash content is obtained by heating the sample to 850°C in a muffle furnace.

The ash content is determined by the mass of residue after incineration. The result is obtained with the following formula:

$$Tc = \frac{M_{850}}{M_{sèche}} \times 100$$

With Tc: ash content (in %)

M850: mass obtained after heating to 850°C

Msèche = M105

d) Fixed carbon content (TCF)

Generally if the carbonization is well conducted, the by-product obtained contains \cong 80% fixed carbon, an indispensable element in the composition of the biomass or fuel.

The fixed carbon has a great energy potential since it corresponds to the amount of carbon remaining after the removal of VOCs, ash and moisture, hence the following expression:

$$CF = 100 - (H + C + MOV)$$

With CF: fixed carbon content expressed in (%)

H: moisture content (%)

C: ash content (%)

VOM: volatile organic matter content (%)

e) Calorific Value (CV)

Calorific value is the amount of heat released by the complete combustion of a body. A distinction is made between Lower Heating Value (LHV) and Higher Heating Value (HHV). In the first case, the water vapor provided by combustion is not taken into account. In the second case, the calories released by the condensation of water vapor are taken into account.

In practice, when it comes to combustion; the calories provided by the condensation of water vapor are not taken into account and the ICP is mainly used.

Taking into account the physico-chemical characteristics of NSW, the CASSAN formula was used for the determination of ICP:

$$PCI = 80 \times (100 - Tc)$$

PCI expressed in Kcal/Kg

Tc: ash content (%)

2.8. Carbonization and activation

2.8.1. Physical pre-treatments

After collection, the ENC must go through preliminary pre-treatments before the carbonization and activation processes.

2.8.1.1. Sorting

It's a classic preliminary operation to eliminate foreign elements...

2.8.1.2. Drying

NSW undergoes natural drying in the open air for a few days to reduce humidity and facilitate grinding.

2.8.1.3. Grinding

Step to reduce the size of the ENC

2.8.1.4 Sieving

After grinding, the ENC is sieved to get rid of small residues and dust.

2.8.1.5 Weighing

Dosing of the quantity of ENC to be carbonized

2.8.2 Carbonization

It consists of a slow pyrolysis at a moderate temperature between 400 and 700°C. After crushing the ENC, the ENC is weighed and introduced into the activation reactor. Following the hermetic bolting of the reactor to the swan column, the fire of the ignited furnace, the pyrolysis begins. The fuel used is charcoal. However, other fuels such as dry wood can be used as well. The process was carried out in the open air.

2.8.3. Physical activation

After the carbonization step, the material is only slightly porous. As a result, it does not yet reach a more reactive surface. It has to undergo another heat treatment called "activation" in order to develop its porous structure and make its adsorption power higher.

2.8.3.1 Process Conditioning

Addition of oxidizing agent by CO₂ and H₂O vapor

Residence time equals 2 to 3 hours of time

Conditioning of carbonization

2.8.3.2 Processing sequence

The activation step is carried out at a temperature above a final carbonization temperature; at this temperature stage the addition of fuel will be necessary and a new energy input must be taken into account. To do this, the reactivation of the electric fan increases the heating speed of the combustion so that the temperature evolves to an optimal value of 1000°C;

3. RESULTS

3.1 Results obtained from the determination of the physic-chemical characteristics of the ink

The following table summarizes the results obtained in determining the physic-chemical characteristics of the coconut endocarp.

Table 4: Physico-chemical characteristics of the coconut endocarp

Humidity (%)	Volatile matter rate (%)	Ash content (%)	Fixed carbon content (%)
4,1	77,17	0,37	22,62

ENC with its fixed carbon content of 22.62 is therefore a recoverable biomass.

3.2 Carbonization results

We carried a series of tests of carbonization of CNE with an initial mass of 500g and 750g, respectively, for a duration of about three hours and in a temperature range of: 500, 600, 650, 700 °C. It should be noted that the maximum capacity of the crucible for ENC is 750g.

The following table shows the results of these tests:

Table 5: Result of the carbonization of the ENC

Tests	Initial mass of ENC (g)	Mass of carbonized ENC (g)	Temperature final (°C)	Duration (h)
1st	500	181,75	500	2H30
2nd	500	198,98	600	2H45
3rd	500	212,35	650	3H
4th	750	332,16	700	2H30
5th	750	332,16	700	2H45
6th	750	341,56	700	3H

These results show that low-temperature carbonization at 500°C, of short duration 2h30mn results in a low carbonization yield. In order to have a better

Carbonization efficiency, it is therefore interesting to exploit the full capacity of our 750g CNE reactor and to operate at a moderate temperature of 700°C and a longer duration of about 3 hours.

3.3 Activation results

Carbonized ENC from the 500 g and 750 g raw materials were activated and have resulted in ENC activated carbon as shown in the following table:

Table 6: Result of the activation of the ENC

Tests	Mass of carbonized ENC (g)	Mass of activated ENC(g)	Optimum activation temperature (°C)	Duration (H)
1st	181,75	116	875	2H30
2nd	198,98	127	967	2H45
3rd	212,35	140	1024	3H
4th	332,16	212	829	2H30
5th	332,16	212	898	2H45
6th	341,56	218	769	3H

The curves corresponding to each test series are as follows:

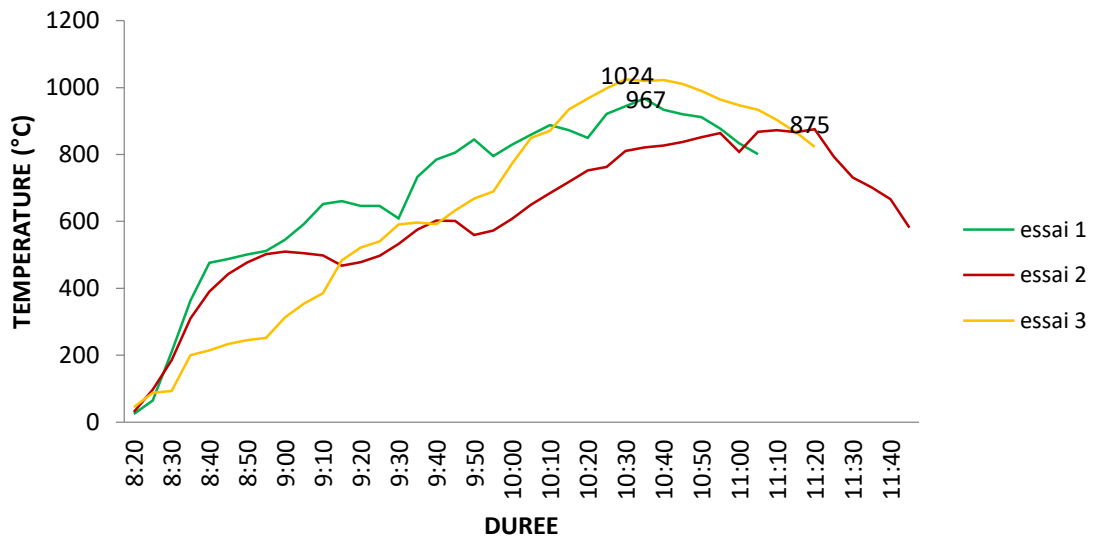


Figure 6: Activation temperature evolution curve for the 500 g ENC series

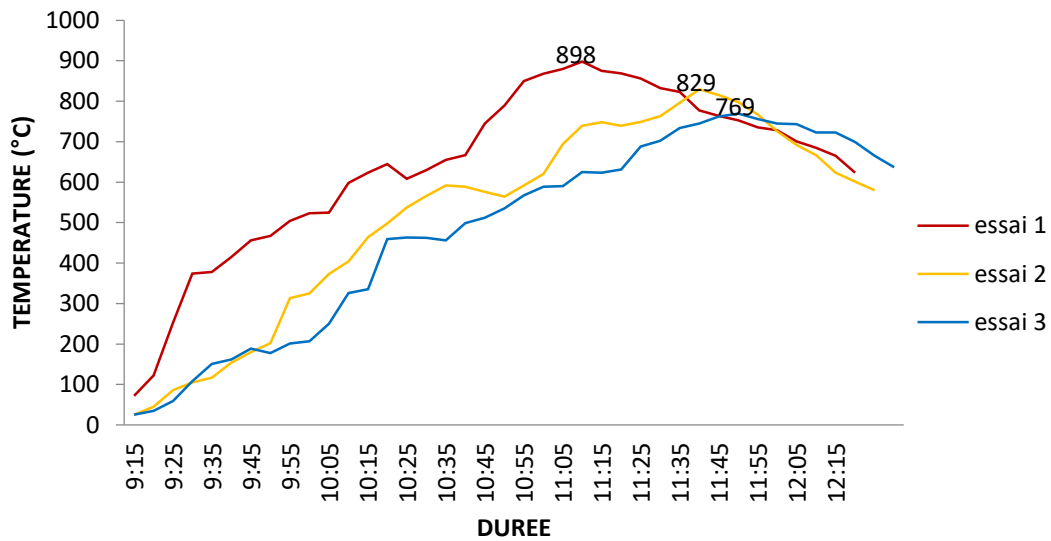


Figure 7: Activation temperature evolution curve for the 750g ENC series

The previous table and curves show the activation results of carbonized NSW. They show that the use of a small quantity of carbonized NSK allows a better activation temperature of 950 to 1000°C to be achieved. This will certainly lead to obtaining activated carbon with a high adsorption capacity.

Thus our reactor requires for the carbonization process the exploitation of its total capacity, but the success of the activation is based on the respect of the limit of the crucible filling: use of two thirds of the total volume.

3.4 Results on experimental characterization of activated carbon

3.4.1 Comparison of the CAP with the GAC

The interpretation of the difference in the adsorption capacity of CAP and GAC was based on a comparative test of the adsorption capacity of these two forms of CA. Wastewater from the residue of an alcohol distiller was used.

The following figure shows the result obtained



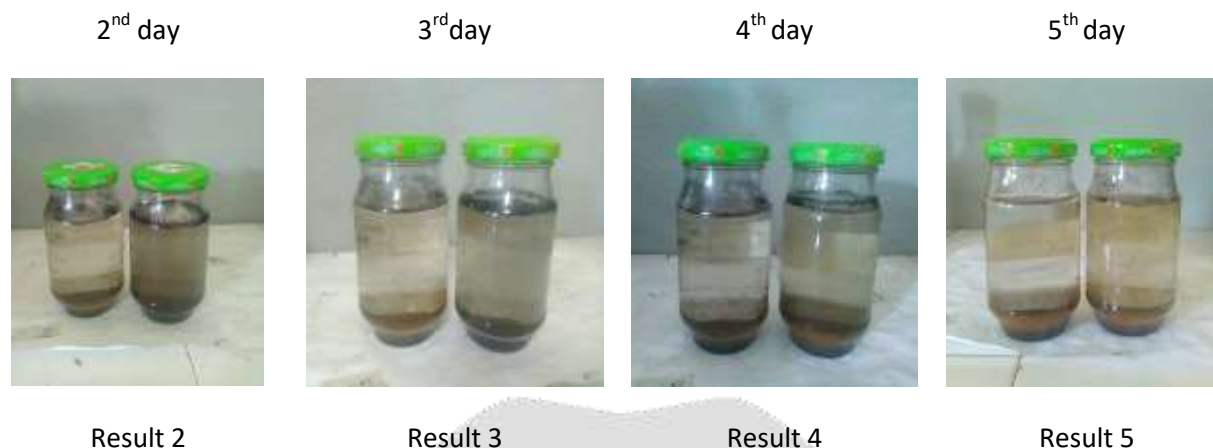
Picture 1: Result of the adsorption test of CAP and CAG

The figure shows that the solution treated with CAP (sample A) is clearer than the solution treated with CAG (sample B) by the CAG. The CAP is therefore more adsorptive than the CAG. This is obvious because the finer the size of the activated carbon, the greater its specific surface area and therefore its adsorbent power is higher.

3.4.2 Estimation of the specific surface area of the CA

The knowledge of the adsorbent power of carbon black with a specific surface area of 120 m²/g





Picture 2: Carbon black and CA adsorption test

The experiment was based on treating the same volume of wastewater with CA and carbon black. Thus, the process revealed that the adsorbent power of 2g of CA corresponds to that of 10g of carbon black.

Indeed, the series of figures above shows that obtaining the same limpidity of the two solutions of waste water treated respectively with CA and carbon black corresponds to the proportion: 10g of carbon black for 2g of CA.

4. DISCUSSION AND CONCLUSION

The waste management problem remains a heavy burden for most urban municipalities. This is the case of the urban municipality of Toamasina, faced with the proliferation of waste generated by coconut consumption.

This study therefore consists of making a contribution to remedy this scourge by transforming Coconut Endocarp waste into a recoverable product. To achieve this, we have used carbonization technology, followed by physical activation of this waste.

Thus a charcoal fuel reactor has been built. This reactor was used both as a carbonization and activation reactor. The results obtained are satisfactory both for the carbonization and for the activation, which is our objective. In fact, during the activation process, using a quantity of ENC not exceeding two thirds of the total volume of the reactor crucible, the experiments carried out affirm that activated carbon of good quality and not negligible commercial value is produced.

The realization of this study in a real environment will therefore be very beneficial for our country. It could not only reduce the harmful effects conveyed by the waste of ENC but could also become a new source of income generation.

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