



Optimization of Conditions for the Preparation of Activated Carbon from Lapsi (*Choerospondias axillaris*) Seed Stone Using $ZnCl_2$

Rinita Rajbhandari Joshi

Department of Science and Humanities, Pulchowk Campus
Institute of Engineering, Tribhuvan University Nepal

Abstract: Activated carbon was prepared from Lapsi (*Choerospondias axillaris*) seed stone by chemical activation method using $ZnCl_2$. The effect of experimental variables; $ZnCl_2$ ratio, temperature and carbonization time on the quality of the activated carbon were systematically investigated by determining the carbon yield, iodine number, methylene blue number, surface area and pore volume. Lapsi seed stone powder (LSP) of particle size $< 300 \mu m$ was used to prepare activated carbon under N_2 atmosphere. An increase in $ZnCl_2$ ratio in general increased the iodine number and methylene blue number, but on increasing zinc chloride above 50 percentages, iodine and methylene blue number increased only marginally. An increase in carbonization temperature increases the iodine number, methylene blue number, and surface area and pore volume. Increase in carbonization time from 3 hour to 4 hour increases iodine number and methylene blue number and thereafter the increase in iodine number and methylene blue number is gradual. Regarding the carbon yield, it decreases with the $ZnCl_2$ ratio above 50 percent, and the yield also decreases with increase in temperature and carbonization time. Therefore the optimum conditions for the preparation of activated carbon from Lapsi seed stone using $ZnCl_2$ as follows: carbonization temperature of $400^\circ C$, zinc chloride ratio as LSP: $ZnCl_2$ equals 1:1, and carbonization time of 4 hour. This resulted an activated carbon with 791 iodine number, 364 methylene blue number, 1167 surface area and 0.65 pore volume.

Key words: activated carbon, Lapsi seed, iodine number, methylene blue number, surface area

1. Introduction

Lapsi (*Choerospondias axillaris*) is an indigenous fruit tree of Nepal. It is a wild large deciduous and dioecious plant belonging to the family Anacardiaceae. The edible part of the fruit (skin and pulp) comprises 71 % and seed stone of 29% [1]. The seed is not a consumable part of Lapsi and is usually discarded as waste. To make better use of cheap and abundant agricultural waste, it is proposed to convert Lapsi seed into activated carbon. This conversion will address problems of unwanted agricultural wastes been converted into useful, value-added adsorbent and also the use of agriculture by-products to represent potential source of adsorbent which will largely address problems of waste management and will have positive impact in the industry based on Lapsi fruit.

Activated carbon has become one of the most technically important and most widely used adsorbents because of its high adsorptive capacity. The high adsorption capacities of activated carbons are related to the properties like surface area, pore volume and pore size distribution. These

unique characteristics depend on the type of precursors used for the preparation of activated carbon and the preparation conditions [2]. Present technology demands a large production of activated carbons with appropriate characteristics for application in drinking water purification, waste-water treatment and chemical processing.

2. Literature

In general, an activated carbon which is used in any of the most common applications must have adequate adsorptive capacity as well the cost of activated carbon must be low for wide spread application. Bevla et al [3], prepared activated carbon from almond shells by chemical activation with H_3PO_4 , K_2CO_3 , Na_2CO_3 and $ZnCl_2$. They found that activated carbon prepared by using $ZnCl_2$ as activating agent was best with highest adsorption capacity. Activated carbon can be prepared from fruit seeds, agricultural byproducts and any other lignocellulosic materials. Coconut shell, almond and pecan shell, pistachio nut shell, apricot stone, olive, sugar beet pulp, tamarind wood [4,5,6,7,8,9,10] etc. have been extensively used for the preparation of activated carbon. As far as known, no study has been carried out using carbon yield, iodine number and methylene blue number approach in analyzing the production process of activated carbon from Lapsi seed stone using $ZnCl_2$ as activating agent.

A good quality activated carbon should have high iodine number and methylene blue number. As the Iodine number and methylene blue number increase, the surface area also increases. The iodine number correlates with surface area [11]. Bacaoui et al, [12] reported that for economic viability, activated carbon should have a surface area of 1000- 1300 m² /g. Activated carbon had been prepared from Lapsi seed stone powder by chemical activation with Zinc Chloride and its characterization by SEM, TEM, FTIR, XRD, Raman, BET isotherm and its application for the adsorption of arsenic from water were done [13, 14,]. In the present study, the optimal experimental conditions; carbonization temperature, activation time, activating agent, $ZnCl_2$ ratio required to prepare activated carbons from Lapsi seed stone by correlating with the yield of activated carbons, iodine number and methylene blue number is presented.

3. MATERIALS AND METHODS

3.1 Materials

Lapsi, (*choreospondiasAxillaris*), were collected from vegetable market at Kalimati, Kathmandu. The fleshy part of this fruit was removed and the seed stones were washed several times with distilled water and dried in electric oven at 110° C for 6 hours. Then the well dried seed stones were crushed and grinded in an electric grinder and sieved to obtain the particles of uniform size 300 μm as Lapsi seed Powder (LSP). Zinc chloride of purity higher than 98 % was used from Qualigen. The nitrogen is of ultra high pure (UHP) grade.

3.2 Methodology

3.2.1 Preparation of activated carbon

The Lapsi seed powder (LSP) of particle size of 300 μm was treated with $ZnCl_2$ in the ratio from LSP: $ZnCl_2$ = 1:0.25 (AC – 0.25), 1: 0.50 (AC – 0.50), 1: 1 (AC – 1), 1:2 (AC-2) and 1:4 (AC – 4) and left for 24 hours. Then the mixtures were heated in hot plate till dry mass was obtained. The dry mass was transferred to a quartz tube and placed in horizontal tubular furnace (Accumax, India) and carbonized at different temperature from 400°C to 800°C and carbonization time from 3hour to 6

hour (table 3.1) in continuous flow of nitrogen gas at flow rate of 100 mL /minute The product was cooled to room temperature and treated with 0.1 M HCl, and then washed with distilled water till free from zinc ion, and the pH value of the final rinsed water was between pH 6-7. The resulting carbons were then dried in an electric oven at 110°C for 3 hours. The well dried activated Carbon (AC) was sieved and material of particle size 106µm was used for further investigations. Care was taken to ensure the material was not forced through the sieve by hand pressure.

Table 3.1 Preparation of activated carbon activated with different ratio of LSP:ZnCl₂ carbonized for 4 hours at different temperature

S. N.	LSP:ZnCl ₂	Weight in gram		Carbonization temperature o C	Activated carbon
		LSP	ZnCl ₂		
1	1: 0.25	100	25	400	AC-0.25
2	1: 0.5	100	50	400	AC-0.5
3	1: 1	100	100	400	AC-1
4	1: 2	50	100	400	AC-2
5	1: 4	25	100	400	AC-4
6	1: 0.5	100	50	600	6 AC-0.05
7	1:1	100	100	600	6 AC-1
8	1:2	50	100	600	6 AC-2
9	1: 0.5	100	50	800	8 AC-0.05
10	1: 1	100	100	800	8 AC-1
11	1: 2	50	100	800	8 AC-2

To study the optimum carbonization time, LSP:ZnCl₂ were mixed in 1:1 ratio and carbonized at 400°C for different time as in table 3.2.

Table 3.2: Activated carbons prepared at the same ratio i.e. LSP : ZnCl₂ equal to 1:1 carbonized at 400 °C for different time.

S.N.	Carbonization time in hour	Activated carbon
1	3	AC-1 (3h)
2	4	AC-1 (4h)
3	5	AC-1 (5h)
4	6	AC-1 (6h)

To study the optimum carbonization temperature, LSP:ZnCl₂ were mixed in 1:1 ratio and carbonized for 4 hour at different temperatures as in table 3.3.

Table 3.3. Activated carbons prepared with the same ratio i.e. LSP : ZnCl₂ equal to 1:1 carbonized for 4 hour at different temperature.

S.N.	Carbonization Temperature °C	Activated carbon
1	300	3 AC-1
2	400	4 AC-1
3	500	5 AC-1
4	600	6 AC-1
5	700	7 AC-1
6	800	7 AC- 1

3.2.2 Yield of Activated carbon

The yield of activated carbon is regarded as an indicator of the process, efficiency for the chemical activation process. The yield of activated carbon (AC) was calculated on a chemical free basis. The yield of AC was calculated as the percentage weight of the resultant activated carbon divided by weight of dried Lapsi seed powder.

$$\text{Yield (\%)} = \frac{\text{Weight of activated carbon after carbonization}}{\text{Weight of lapsi seed powder}} \times 100 \quad (1)$$

3.2.3 Determination of Iodine Number

Iodine number [mg²/g] indicates the extent of micro pore distribution in the carbon. It is defined as the milligram of iodine adsorbed by 1.0 g of carbon. The iodine number correlates with surface area [11]. The iodine number is determined according to the ASTM D4607, 2006 method [15]. In this method, 100 mg of activated carbon was added to 5 mL of 5 % HCl and then boiled and cooled. To the cooled solution 10 mL of 0.1 N iodine solution was added, shaken for 30 second and filtered. The filtrate was titrated with 0.1 N sodium thiosulphate solutions with starch as an indicator. The iodine number is determined by the following formula.

$$\text{Iodine Number} = \frac{\text{Amount of iodine adsorbed by carbon}}{\text{Weight of carbon taken in gram}} \quad (2)$$

3.2.4 Determination of Methylene blue number

Methylene blue number [mg²/g] indicates the extent of meso pore distribution in the carbon. The methylene blue (MB) is the maximum amount of dye adsorbed on 1.0 gm of adsorbent. For the determination of Methylene blue number (MBN) of activated carbon, 0.05 g of activated carbon was added to 100 ml of MB of concentration 100 ppm and then equilibrated for 3 hours at 200 rpm. Then the solution was filtered through filter paper Whatman 41, and the remaining concentration of methylene blue was determined by measuring the absorbance at 664 nm using a UV/Vis spectrophotometer (CECIL-CE-100).

The Methylene blue number was calculated by the following equation (Raposo et al, 2009).

$$\text{MBN} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_e)}{M} \times V \text{MBN} \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_e)}{M} \times V \quad (3)$$

where,

M = mass of activated carbon in gram

V = volume of test solution in litre

C₀ = initial concentration of MB

C_e = concentration of MB at equilibrium

3.2.5 Nitrogen Adsorption-Desorption

Surface areas, pore volumes and pore size distributions were evaluated from nitrogen adsorption-desorption isotherms by Brunauer, Emmett and Teller (BET), method by recording N₂ adsorption-desorption isotherms. The measurements were carried out in an automatic adsorption instrument (Quantachrome Instrument, Autosorb-1 USA). For each measurement about 20 mg of activated carbon was taken and degassed for 24 h at 100 °C prior to the measurement. The adsorption-desorption isotherms were recorded at liquid nitrogen temperature 77.35K.

Preparation of the reagents

1. 0.1N Iodine solution: It was prepared by dissolving 3.175 gm of iodine in 10 % KI and diluted the solution in distilled water to 250 mL.
2. 5 % HCl: It was prepared by dissolving 5 ml of conc HCl in distilled water and diluted to 100 mL.
3. 0.1M Sodium thiosulphate: It was prepared by dissolving 6.2 gm sodium thiosulphate in distilled water to 250 mL.
4. 1% Starch solution: It was prepared by dissolving 1.0 gm starch in distilled water to 100 mL and heated to boil.
5. 100 ppm. Methylene blue: It was prepared by dissolving 100 mg methylene blue in distilled water to 1000 mL.

4. Results and Discussions

4.1 The Yield of Activated carbon

The Yield of Activated carbon (AC-1) at different carbonization temperature

The figure 4.1 shows the percentage yield of activated carbons as a function of carbonization temperature. The yield decreased continuously with the increase of carbonization temperature.

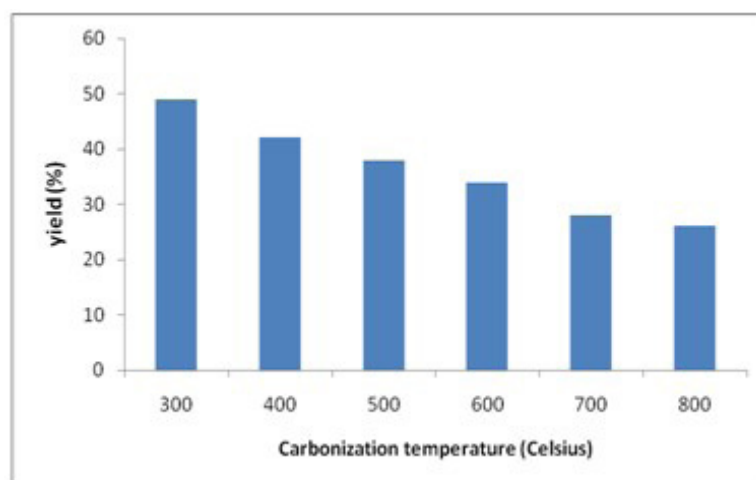


Figure 4.1. The yield of activated carbons at different carbonization temperature

The decrease in yield at high temperature may be due to the release of oxygen and hydrogen as CO, CO₂ and CH₄ from lignocellulosic materials rather than H₂O [16].

The yield of activated carbons (AC-1) at different carbonization time

The figure 4.2 shows percentage yield as a function of carbonization time. The percentage yield of activated carbon decreased with the increase of carbonization time. The yield decreased at longer carbonization times because of the higher carbon burn-off [17] and attributed to the release of carbon and hydrogen in the form of CO, CO₂, CH₄ and hydrocarbon from lignocelluloses materials rather than as H₂O.

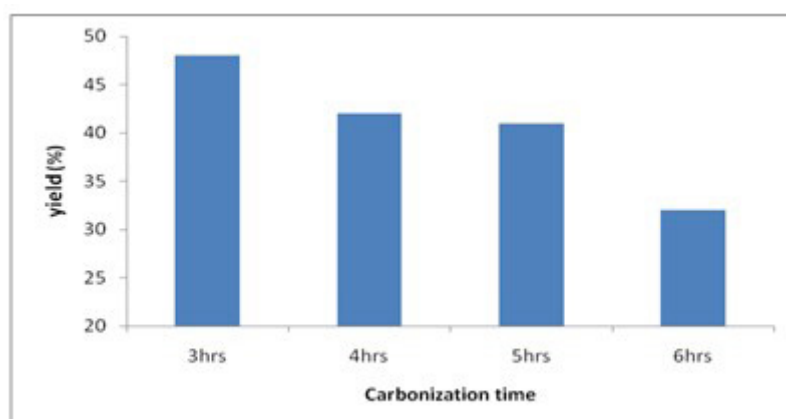


Figure 4.2. The yield of activated carbons at different carbonization time

The yield of activated carbons with different ratio of ZnCl₂

In the figure 4.3, it is observed that on increasing the ratio of activating agent, ZnCl₂ the percentage yield decreases due to the increase release of volatile matter from the sample. The lower yield with the higher activating agent might be caused by the enhancement of carbon burn-off by extra activating agent [17].

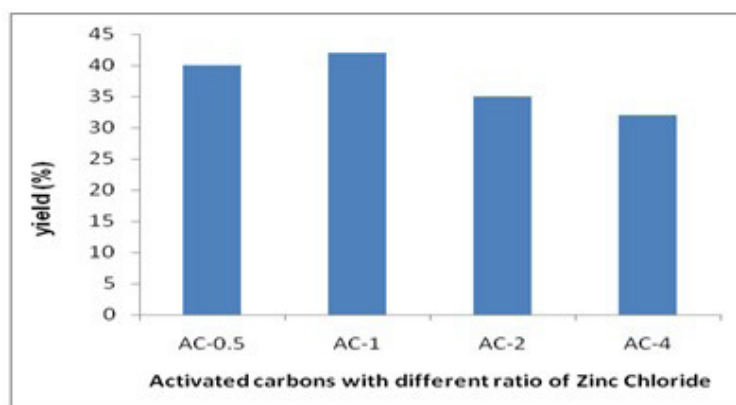


Figure 4.3. The yield of activated carbons with different ratio of ZnCl₂

3.2. Iodine number and Methylene blue number

The Iodine number of the activated carbons from Lapsi seed stone chemically activated with zinc chloride in different ratio at different carbonization temperature is given in figure 4.4.

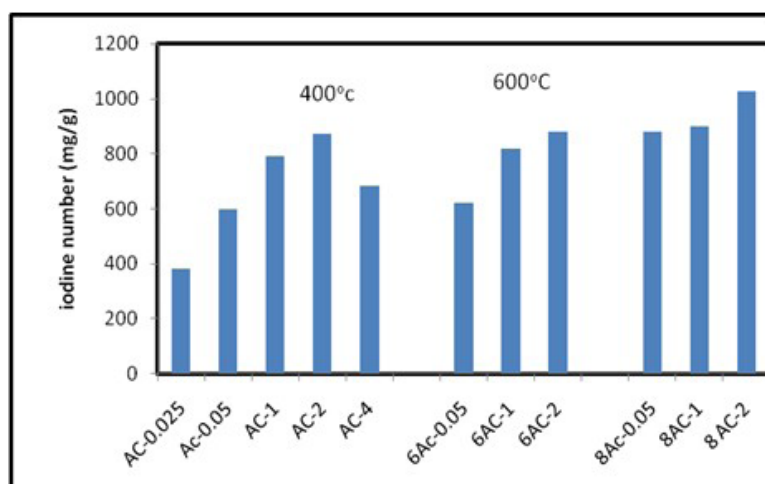


Figure 4.4: Iodine number of the activated carbons from Lapsi seed stone with different ratio of ZnCl₂ at different temperatures.

The figure 4.4 clearly shows that the increase in amount of zinc chloride, as an activating agent, increased the iodine number of the activated carbons. With the increase in ZnCl₂, this activating agent enters into the interior of the particles whereby it acts as a template for the creation of the microporosity, therefore high concentration of activating agent induces the formation of more micropores in the carbon resulting higher iodine number of the activated carbons up to LSP:ZnCl₂ equal to 1:2.

The figure 4.4 also shows that at higher temperature of carbonization increases the iodine number, this is because increase in temperature increases distillation of tar from the carbon thereby releasing more micro pores in the resultant product.

Thus higher amount of zinc chloride as an activating agent and higher carbonization temperature both are favorable for the preparation of activated carbons from the Lapsi seed stone. High temperature carbonization has some disadvantage as well, firstly the yield will be low owing to the removal of carbon with O and H (as CO_x and hydrocarbons) and the energy required for carbonization will be higher which results the increase of the cost of production of activated carbon.

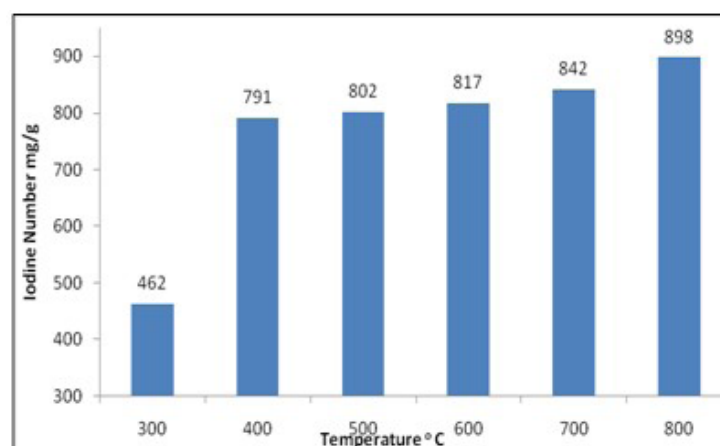


Figure 4.5 Effect of carbonization temperature on iodine number

The figure 4.5 shows the iodine number of activated carbon prepared by keeping the ratio of LSP: ZnCl_2 equal to 1:1 at different carbonization temperature. At carbonization temperature 300°C the iodine number is quite low. This may be due to incomplete charring of the lignocellulosic material. The product at this temperature is not a pure carbon but a mixture of the char and undecomposed precursor. When temperature is increased from 300°C to 400°C, the iodine number increased significantly from 462 to 791. At this temperature the decomposition of lignocellulosic material is almost complete as evident by the TGA curve [18]. Increase in iodine number with increase in carbonization temperature above 400°C is gradual. This gradual increase in iodine number may be due to increase in distillation of tar which release some pores for adsorption of iodine. This clearly indicated that 400°C is the optimum temperature for carbonization of Lapsi seed stone powder to get activated carbon with higher adsorption capacity.

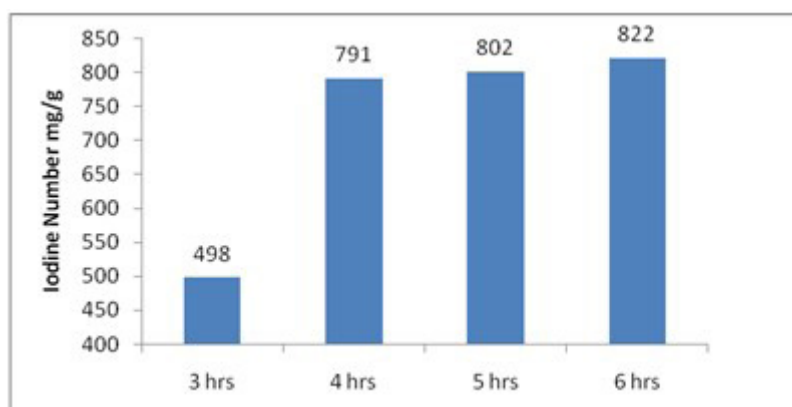


Figure 4.6. Effect of carbonization time on iodine number

The figure 4.6 shows the effect of carbonization time on the iodine number of carbon prepared at 400°C with the ratio of LSP:ZnCl₂ equal to 1:1. When the time of carbonization increased from 3h to 4h the iodine number increased significantly and thereafter the increase is gradual. This means that 4 hour is sufficient to prepare activated carbon from Lapsi seed stone.

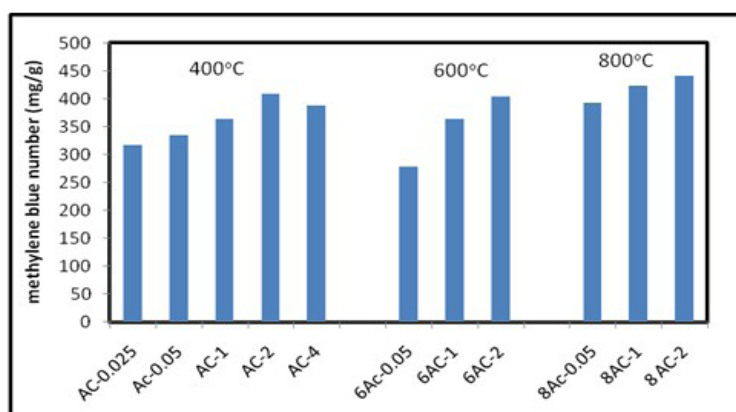


Figure 4.7: Methylene blue number of the activated carbons from Lapsi seed stone with different ratio of ZnCl₂ at different temperatures.

The figure 4.7 clearly shows that the increase in amount of zinc chloride, as an activating agent, increased the methylene blue number of the activated carbons. This observation could probably be due to the depolymerization of cellulose resulting in tar formation.

The figure 4.7 also shows that at higher temperature of carbonization, increases the methylene blue number, this is because increase in temperature increases distillation of tar from the carbon thereby releasing more meso pores in the resultant product.

Thus higher amount of zinc chloride as an activating agent and higher carbonization temperature both are favorable for the preparation of activated carbons from the Lapsi seed stone. High temperature carbonization has some disadvantage as well, firstly the yield will be low owing to the removal of carbon with O and H (as CO_x and hydrocarbons) and the energy required for carbonization will be higher which results the increase of the cost of production of activated carbon.

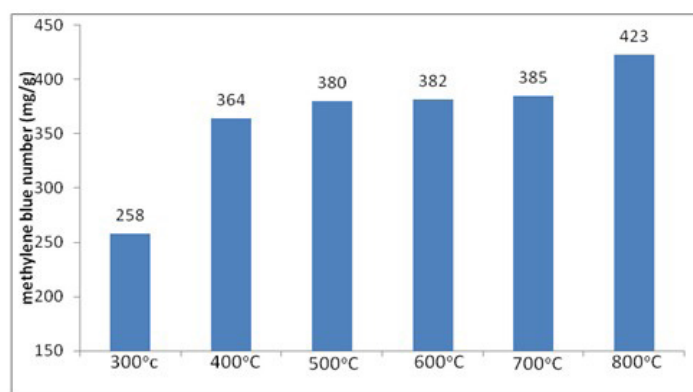


Figure 4.8. Effect of carbonization temperature on MBN

The above figure 4.8 shows that with increase of carbonization temperature from 300°C to 400°C the increase of methylene blue number is significant then with further increase in temperature the increase in methylene blue number is marginal.

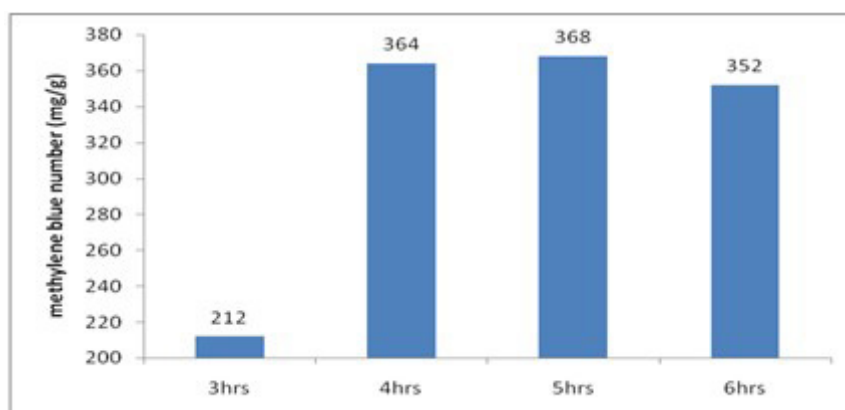


Figure 4.9. Effect of carbonization time on MBN

The figure 4.9 shows the effect of carbonization time on methylene blue number. The increase of methylene blue number is significant when the carbonization time increase from 3 hour to 4 hour. This is perhaps due to the increase in distillation of tar from the product and releasing the mesopores for adsorption of methylene blue molecule. The increase in methylene blue number with further increasing the carbonization time is very little and still increase of carbonization time to 6 hour has decrease the methylene blue number this may be due to the reduction of porosity in the carbon owing to destruction of mesopores producing macropores [19].

4.3 Nitrogen Adsorption

Nitrogen adsorption-desorption measurements were conducted to calculate the specific surface area, pore size distribution, and pore volume of the activated carbons is given in table 4.1.

Table 4. 1 Surface area, pore size and pore volume of activated carbons carbonized at different temperature with same ratio asLSP:ZnCl₂=1:1, carbonized for 4 hours.

S.N,	LSP:ZnCl ₂	Carbonization temperature °C	Surface area m ² /g	Pore size / nm	Pore volume cc/g
1.	1:1	400	1167	2.22	0.65
2.	1:1	600	1569	2.63	1.03
3.	1:1	800	1800	2.43	1.09

In above table 4.1 surface area, pore size as well as pore volume was observed to increase with increasing temperature. This observation could probably be due to drastic expansion of the carbon material leading to the creation of large surface area. Similar results were obtained by [20] using sorghums. Generally, as the temperature increase devolatilization also increases which further develop the rudimentary pore structure in the carbon and also enhance the existing pores thus creating higher surface area and higher porosities. Besides, the increase in temperature also caused the CO₂ and the surface metal complexes to further gasify the carbon leading to widening of pores and also increases pore volume [21] but control of the activation temperature is of economic interest

since lower temperature of complete carbonization are generally desired as this is equivalent to reduction in energy consumption.

5. Conclusion

The optimum conditions for the preparation of nanoporous activated carbons from Lapsi (*choerospondias axillaris*) seed stone were determined by studying systematically the effect of Lapsi seed powder/ $ZnCl_2$ ratio, carbonization temperature, carbonization time on yield of activated carbon, iodine number, methylene blue number and BET surface area. The increase in $ZnCl_2$ / Lapsi seed powder ratio in general increased the iodine and methylene blue number indicating the increase in adsorptive capacity and meso and micro porosities in the resulting activated carbon. On increasing LSP: $ZnCl_2$ equals 1:1, iodine number and methylene blue number increased only marginally indicating the attainment of equilibrium concentration of nanopores in the carbon. Similarly increasing carbonization time from 3hrs to 4hrs there was significant increase in iodine number and methylene blue number and there after the increase is gradual. Likewise increase in iodine number and methylene blue number with increase in carbonization temperature above 400°C is gradual. At 400°C the decomposition of LSP lignocellulosic material is almost complete as evident by the TGA curve [18]. The BET surface area of activated carbon prepared at 800°C is quit higher but the yield of activated carbon at this temperature is so low that it is economically not profitable to prepare activated carbon at this high energy consumption. So it is concluded that the Lapsi seed powder activated with $ZnCl_2$, ratio of 1:1, carbonized at 400°C for 4 hour is optimum condition for the preparation of activated carbon for further work.

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