Production and Characterization of Activated Carbon from Dashen Brewery Gondar Spent Label as Precursor

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Abstract: The purpose of this work is to identify a precursor from brewery industry waste to produce activated carbon and the same could be used for the treatment of brewery inlet water. Among the wastes generated in the industry, it was found that spent label paper has good potential as precursor since it has good cellulose content. One more attractive feature of this spent label is that it is in-house generated waste and is available at free of cost. The activated carbon was prepared by following chemical activation process. The various activation agents like potassium chloride, phosphoric acid, potassium hydroxide and Zinc chloride were used as the chemical activation agent and their effect on Iodine value and the yield and was studied. A methodical study of the effect of concentration of activation agent, impregnation time, activation temperature and activation time on the iodine value and the yield % during the production of activated carbon from spent label was studied. The prepared activated carbon was characterized by measuring the iodine number and yield percentage. The apparent density of the chemically activated carbons was examined and found to be 0.43 g/ml. Also, the adsorption power of the prepared activated carbon was checked by using methylene blue. During the test it was visually observed that the color intensity reduced enormously, which is an indication that the product was successfully activated. The optimum conditions for the production of activated carbon are a 2 N concentration of zinc chloride activating agent with 20 h of impregnation time and at a activation temperature of 600oC for an activation time of 1 h gave rise to an iodine number of 734.7 mg/g, which is relatively a good number.

Keywords: Activated carbon, spent label, activation temperature, adsorption

1. Introduction

The adsorption capacity of an activated carbon (AC) is attributed to its large surface area which is the characteristic of meso pores and micro porous present in it. This development of pores is obtained from the heat treatment of carbon precursor. It is therefore used as an adsorbent. In spite of its successive use in the water and waste water treatment sectors, activated carbon stays a costly material. Taking into account the significant expense and the tedious time-consuming methods for the planning and recovery of activated carbons, there is a proceeding with look for affordable potential adsorbents. The precursors used for the preparation of AC are cellulosic materials [17] such as charred coconut shell, palm kernel shell, bamboo, agricultural wastes, bone, rice husks, waste newspaper, industrial sludge etc. [1,3,6,10,13 &18]. But, here in this work the selected raw material is spent label paper collected from Dashen brewery factory, Gondar. This spent label from brewery is selected for 4 reasons 1. It has high cellulose content, hence potential precursor with less lignin and hemicellulose content 2. It is a waste generated inhouse mainly during bottle cleaning process 3. It is available free of cost and finally, 4. To avoid environment hassles.

AC is prepared by any of the two processes. First is physical activation, where the precursor is converted to activated carbon by utilizing gases. This is done by carbonization and activation process or by using one selective process. A. Carbonization, here the material with apparent carbon content is pyrolyzed at temperature going between 500–950 °C [9] without oxygen, ordinarily in an dormant environment with gases like nitrogen or argon. In the above process strength of the material is increased and new pores are created that will be again supported by activation process. Here the change in the process parameters will affect the characteristics of the prepared AC. B. Activation/Oxidation, where the carbonized material is introduced into an oxidizing atmosphere such as steam, oxygen or carbon monoxide at temperatures over 250 °C, normally in the temperature range of 600–1200 °C [14]. The second process is Chemical activation process. Here both the carbonization and activation processes are believed to occur at the same time [4,11] Firstly, the sample is impregnated with chemicals that are classified as an acid, salt or a strong base. For example, sodium hydroxide, potassium hydroxide, phosphoric acid, and zinc chloride are few chemicals to name. Chemical activation is preferred over physical activation because of the smaller operating temperature and shorter time is provided by this technique [5,19].

In brewery industry, to avoid recontamination of stored water chlorine is added before using it as the process water for beer production and service water for utility purpose. To remove the residual chlorine currently imported activated carbon is used by the industry. Hence activated carbon from the spent label is a good option. In addition

to that the most attractive feature about the activated carbon prepared from the spent label is that the precursor is available at free of cost and it is economically feasible solution for the disposal of spent label waste. The scope of this work covers the collection of various spent label papers from Dashen brewery, Gondar and other materials required for the preparation and analysis of AC from Debre Tabor University. This work embraces quality and cost effectiveness. Moreover, the use of spent label paper from brewery factory for the preparation of AC have not yet been reported. Thus, little information is available in this area. Therefore, this work is expected to fill this knowledge gap and open door for the coming researchers in the area by providing relevant base line information. The emphasis of this study is to find the effect of concentration of activation agent, impregnation time, activation time and activation temperature and to optimize these parameters and to characterize the activated carbon prepared from the spent label.

2.Methodology :

2.1.Sample preparation and proximate analysis

For preparation of activated carbon (AC), the sample of spent label papers were collected, cleaned and made ready to start the experiment. The label papers were washed completely to remove any dirt and soil adhering to it and dried under sun for 24 h. After that the sample was pulverized using pestle and mortar. The pulverized sample was screened to get particle size in the range of 600 μm-0.2mm. This size reduction increases surface area which facilitates further activation process. Then proximate analysis of the sample was carried out following the ASTM [2] procedure to find the moisture content, volatile matter, fixed carbon and ash content of the sample. Sample preparation is shown in Figure No. 1.

Figure No. 1 Preparation of sample precursor and activated carbon

2.2. Carbonization and activation

AC was prepared by following the procedure stated in the literature [9,16]

- The spent label was dried in a hot air oven at 110^{o}C for nearly one day, then pulverized and screened to obtain particles of required size range approximately 600 μm.
- Next, various activating agents like zinc chloride, potassium hydroxide, potassium chloride and phosphoric acid [7,12] were used on the sample to activate it chemically. Magnetic stirrer was used to ensure through contact between the sample and activating agent for upto 7 h and at 85^{o}C.
- Once the activation is over, it was followed by drying at 110^{o}C to provide appropriate impregnation time over a time range of 9-37h and optimum time for impregnation was determined.

- However, the sample was left in the atmospheric condition for about 22 h and allowed to face the light and humidity before proceeding to the next step. This helped in even carbonization of the sample when it was pyrolyzed.
- Then, after following the above steps the sample was pyrolyzed in a furnace under nitrogen atmosphere at 400-900 ^{o}C based on the set temperature. This pyrolysis treatment was carried over for 60 min -120 min depending on the set time. A temperature ramp of 10^{o}C was used to achieve the appropriate temperature. Moreover, after completing the cycle the sample was removed from the furnace, cooled and crushed to breakdown the lumps.
- Finally, the sample was rinsed with 500 ml of 1.2 N hydrochloric acid followed by 500 ml of distilled water to remove excess activating agent and remaining inorganic materials.
- Then the AC made from the spent label precursor was stockpiled in an airtight container for further characterization purpose.

2.3. Characterization of the activated carbon

Iodine Number: Iodine number is nothing but the amount of iodine adsorbed in mg by 1 of AC when the residual concentration of iodine is 0.02 N. It is the standard measure for liquid phase applications. It is calculated by following the procedure in ASTM [2].

Iodine value = D x conversion factor

conversion factor = [127 $(Mol.wt)_{Iodine}$ x $(Normality)_{Iodine}$x 40]/$(Weight)_{AC}$ x blank

D = Blank reading – Burette reading

Apparent Density: Apparent density was calculated using a clean and dry 10 ml measuring cylinder. A measured quantity of 5 g of AC sample was emptied into the graduated cylinder and the volume was observed and noted. When filling the cylinder care was taken to tap it gently so as not to create any void space. Then by knowing the mass and volume the density was calculated. Higher density refers to more volume activity

Adsorption power: How much adsorbate is adsorbed in one gram of prepared AC is referred as adsorption power. The adsorption power of the prepared AC sample was evaluated using methylene blue (MB) as adsorbate using the equation

Qp = [(Ci-Co) X volume of solution in L] /mass of the AC in g

Where, Qp is adsorption power (mg/g), Ci is initial concentration of the dye, Co is the equilibrium concentration of dye in the sample solution.

Ash and moisture content: To measure the ash content of the AC a measured quantity of 1 g of the sample was taken in a crucible and the crucible was loaded into muffle furnace and burnt at 973 K for 4 h. After 4 h, the sample was withdrawn from the furnace, cooled and weighed. The final weight was subtracted from the initial weight and the value was recorded as ash content per 1 gram of the sample. Similarly, to find the moisture content 10 g of the AC was weighed and dried in an oven for 3 h at 105^{o}C. The AC was cooled to atmospheric temperature in desiccator to avoid humidity build up in the sample and weighed. The final weight of the sample was subtracted from the initial weight and then reported the loss as weight loss for 1 g.

Burn off and solid yield: There are two steps involved in the formation of AC, initial one is carbonization, that is conversion of the spent label to char and the final one activation which means conversion of the char to AC. During the above two steps there is a loss of total mass, which is called as burn off. For a given mass of the spent label precursor, the weight of the char produced and the AC produce were recorded. Moreover, based on the recorded observation the solid yield and the burn off was calculated.

3.Result and Discussion

3.1. Result of proximate analysis of the precursor

From the proximate analysis the fixed carbon content is more in spent label. In fact, as shown in Table No. 1 spent label has a carbon content of 39.4% which is similar to that of rice husk. In the elemental analysis of rice husk performed by the author Subhashree the carbon content is 38.7% as reported in the literature [16]. From this we can understand that spent label forms an excellent precursor for the preparation of AC.

Table No. 1 : Proximate analysis of spent label

Sl.No	Component	Spent label (wt %)	Rice husk (wt %) (Subhashree Pradan, 2011)

1.	Moisture content	1.9%	0.4%
2.	Ash content	6%	19.2 %
3.	Volatile matter	52.8%	64.7%
4.	Fixed carbon	39.4%	15.7%

3.2. Effect of chemical activating agent

The effect of different activating agents such as zinc chloride, potassium hydroxide, potassium chloride and phosphoric acid were evaluated and shown in the Table No. 2 and Fig. No. 2. Furthermore, the conc. of the chemicals used for the activation purpose are taken as 1N and the activation was carried out for a fixed time of 20 h. Activating agent ZnCl2 produced highest yield of 18.9 % and 648.2 mg/g highest iodine number. Hence ZnCl2 was selected for further processing.

3.3. Concentration effect of zinc chloride on the resultant AC

To study the concentration effect, various concentration of activating chemical, ZnCl2 was taken and the corresponding yield and iodine number was studied. It can be seen from the Table No. 3 and graph, Figure No. 3 that at 2N concentration the value of yield and iodine number is maximum, hence this concentration is selected for further processing.

Table No. 2: Effect on the yield and Iodine value of AC by various activating agents

Sl. No	Activating Chemicals	Conc. Of activating Chemicals (N)	Yield (wt. %)	Iodine No. (mg/g)
1.	ZnCl2	1	18.9	648.2
2.	KOH	1	10.4	610.8
3.	KCl	1	14.1	530.7
4.	H_3PO_4	1	17.6	630.2

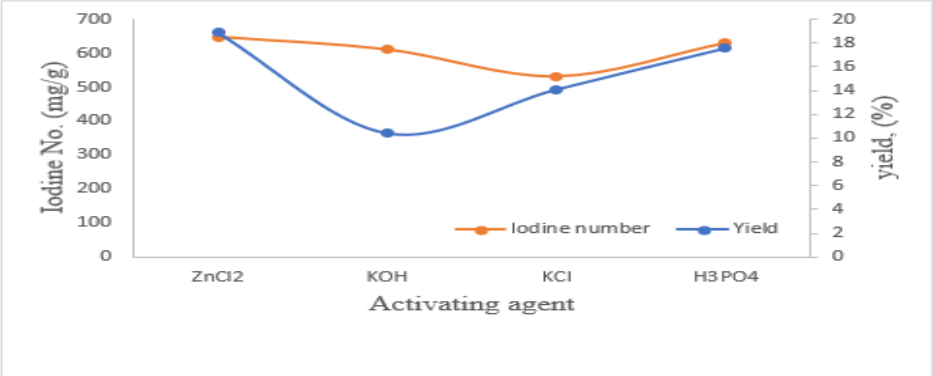

Figure No. 2 : Effect of various activating agents on yield and Iodine Number

Table No. 3: Effect of concentration of activating agent

Sl.No	Conc. Of activating Chemical (N)	Yield (wt %)	Iodine No. (mg/g)
1.	1	18.9	648.2
2.	2	10.4	730.42
3.	3	14.1	610.7
4.	4	17.6	550.3

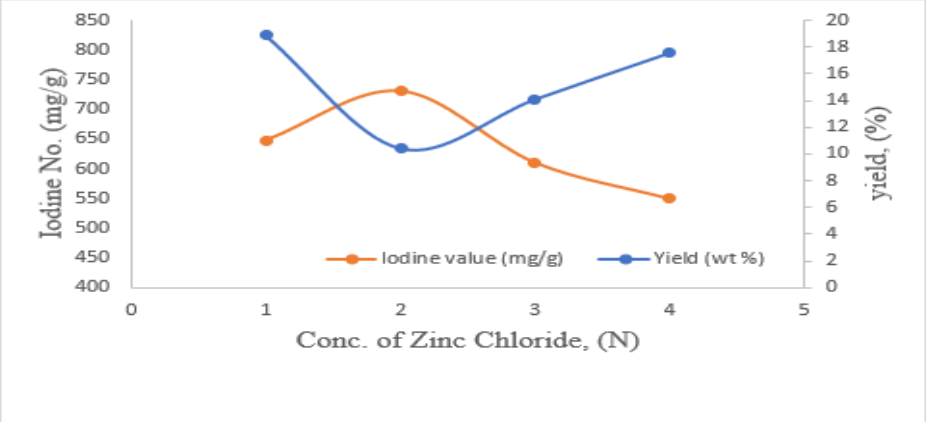

Figure No. 3: Effect of concentration of activating agent

3.4. Impregnation Time effect on the resultant AC

The iodine number of the AC was studied for various impregnation times, shown in Table No. 4 and Figure No. 4. The concentration of the impregnation agent ZnCl2 is taken as 2 N. It can be seen that 20 hours of the impregnation time is optimum because till that time the Iodine number is increasing and moreover after that there is no much visible increase in the value.

Table No. 4: Effect of impregnation time

Sl.No	Impreg. time (h)	Iodine No. (mg/g)
1.	10	595.3
2.	20	730.42
3.	30	732.8
4.	35	733.1
5.	40	734.7

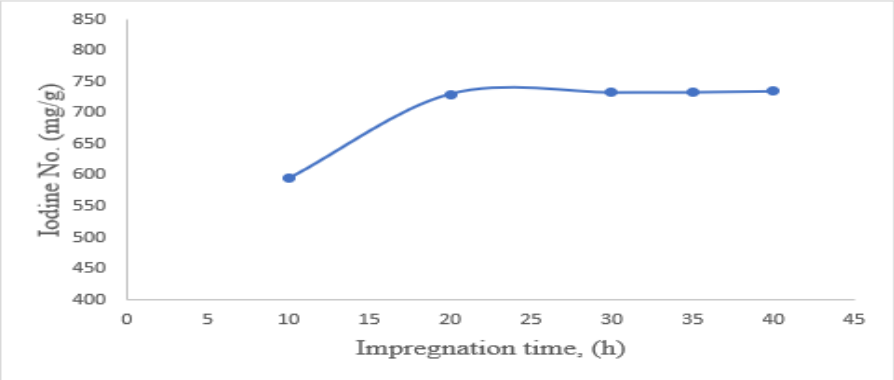

Figure No. 4: Effect of impregnation time

3.5. Activation temperature effect on the resultant AC

The pores formation in AC is mainly affected by the activation temperature. In turn this porous structure determines the adsorption effect of the prepared AC. The results are shown in the Table No. 5 and Figure No. 5. We can see that an activation temperature of 600 ^{o}C yields a maximum iodine number of 732.8 mg/g, after which the iodine number tends to fall down. It may be due to the destruction or burn out of the nearby pore walls.

Table No. 5 : Effect of activation temperature

Sl. No.	Activation temp. (°C)	Iod. No. (mg/g)
1	500	542.3
2	550	652.8
3	600	732.8
4	700	562.4
5	800	543.1

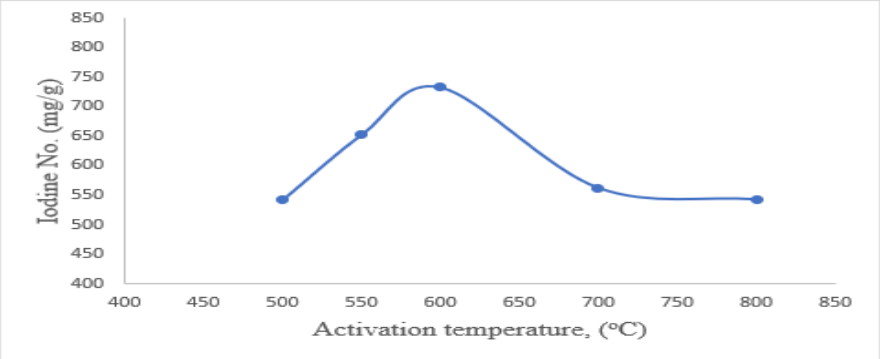

Figure No. 5: Effect of activation temperature

3.6. Activation time effect on the resultant AC

Activation time of the sample literally affects the pore formation and subsequently the adsorption capacity of the AC. This is shown in the Table No. 6 and Figure No. 6. The iodine number initially tend to raise up to 1 hour, maximum is 730.4 mg/g and then falls to a minimum of 518.7 mg/g. So an optimum time for activation can be considered as 1 hour.

Table No. 6 : Effect of activation time

Sl.No	Activation time (h)	Iodine No. (mg/g)
1.	0.30	673.2
2.	1	730.4
3.	1.30	612.9
4.	2	598.2
5.	3	518.7

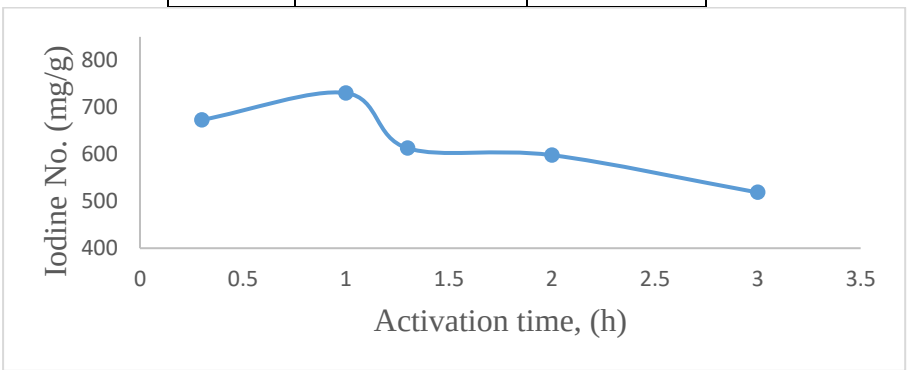

Figure No. 6 : Effect of activation time

3.7. Other physical properties of the AC

The ash content of the AC refers to the presence of non- carbon minerals like iron, silica, aluminium etc., present inside the AC network after the production process. The ash content of the obtained AC was 4.9%. This indicates the precursor was cleaned and free of dust and minerals. The apparent density of the AC prepared was 0.43 g/ml, whereas the moisture and pH were 7.3 % and 6.23 respectively. A low apparent density indicates that adsorption capacity of the AC is good. The pH value slightly inclines towards the acidic nature. This gives the information that the AC works well in the weak base, acid aqueous environment.

Table No. 7 : Physical properties of AC prepared from spent label

Sl.No	Component	AC from spent label
1.	Apparent density	0.43 g/ml
2.	Ash content	4.9%
3.	Moisture	7.3%
4.	pH	6.23

4.Conclusion and Recommendation

Chemical activation process was successfully used to prepare AC from the spent label from brewery industry. Zinc chloride had a better hand on creating pores in the sample compared to potassium hydroxide or potassium chloride or phosphoric acid. Furthermore, the maximum iodine number achieved during the above process was 648.2 mg/g. Also, in the process of finding the effect of concentration, the concentration of 2 N served better and the obtained iodine value was 730.4 mg/g. Moreover, during the study of impregnation time, at first there was an upsurge in the iodine number up to 20 h and then it stabilized. The maximum iodine value obtained was 734.7 mg/g. Similarly, during the study of effect of activation temperature, there was a steady increase in the iodine value up to a temperature of 600 ^{o}C, which is 732.8 mg/g and then started to fall down after that. Finally, during the study of activation time on the resultant AC up to 1 hour the Iodine number increased to a maximum value of 730.4 mg/g and then started falling down. Analysing the above and in terms of maximum iodine number, optimum condition of process parameters for the production of AC was obtained. When the precursor was treated with 2 N of zinc chloride solution with 20 h of impregnation time and activated at 600^{o}C for 1 hour produced relatively high iodine value of 734.7 mg/g hence considered as optimum process parameters. From the above results it can be understood that the spent label from the brewery industry can be successfully activated. Since the formation of meso pores and micro pores are good and hence the adsorption capacity is good, the resultant AC is recommended for the water treatment usage. In addition to that for brewery industry the cellulose rich precursor is available free of cost within the premises of the industry. Currently the imported activated carbon is used for the removal of residual chlorine from process and service water. To cut down the cost in long run it is recommended to use the activated carbon prepared from inhouse raw material.

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