Production of Activated Carbon from Cellulose Wastes

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Abstract

Cellulose wastes of a wood and paper factory were used to produce activated carbon. Several chemical agents under various conditions were used for production of activated carbon and hence their adsorption properties have been evaluated. In addition the effect of process parameters such as raw material, chemical agent concentration, impregnation ratio, carbonization temperature, carbonization time, activation temperature, activation time, particle size and soaking time on adsorption properties and product yield have been studied. Based on experimental results, the optimum values of process parameters were determined. As an achievement, samples of activated carbon with specific surface area up to 1100 m^2/g and iodine adsorption number up to 1080 mg/g were prepared.

Keywords: Activated carbon, Cellulose waste, Chemical activation, Adsorption

Introduction

Activated carbon (AC) is amorphous solid with high specific surface area and high porosity that is considered as one of the most important allotropes of carbon. The main component of AC is carbon (87-97%). The remaining of which contains a little amount of hydrogen, oxygen, sulfur, nitrogen, mineral substances that are used as ash content (residual substances after combustion), alkaline and soil alkaline metals silicate [1].

AC is used as an adsorbent material for the removal of hazardous components in gases, water and waste water. The demand for AC is increased due to its various applications and special properties [1, 2].

Many researches have been done on AC production from waste materials such as used scrap wood, organic waste sludge, bean-curd refuse, bagasse, almond shell, waste exchange resin, waste phenol resin, etc.

Production of AC involves two steps: the carbonization of raw carbonaceous materials in an inert atmosphere and the activation of carbonized carbon. The purpose of activation is to enlarge diameters of fine pores and derive new pores after the carbonization step. Activation can be carried out by physical (hydro-thermal), chemical or physic-chemical method. In physical activation process, generally the raw materials are activated at high steam temperature or CO_2 that is within a range of 800-1100˚C. In chemical activation process, certain chemical agents such as acid (H_3PO_4, HCl, H_2SO_4, etc.) strong base (KOH, NaOH, etc.) or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, and zinc chloride 25%) are mixed with raw materials in the lower temperature ranging from 300 to 800 ˚C. In this method carbonization/activation step carried out simultaneously with chemical agents. Chemical activation is better comparing to physical activation because of the lower temperatures and shorter activation time. However, due to the increasing need to activated carbon in various industries; all three methods are used depending on practical conditions and available facilities [3-7].

In the present study, production of AC using recycled cellulose wastes in paper making industries especially that of

Mazandaran wood and paper factory was investigated. The cellulose waste generation at Mazandaran's factory exceeds 140 tons/day.

Various parameters such as chemical activator agents and its concentration, impregnation ratio, carbonization time and temperature, activation time and temperature, the size of raw material as well as the soaking time were investigated and the optimized conditions were determined. The most important adsorption properties of produced activated carbons were assessed and results were compared with commercial samples.

2. Experimental
2.1. Raw materials

Meandering woods of two different units in Mazandaran's paper factory namely the wood chips from wood unit (sample 1) and the wastes from pulp unit (sample 2). Basing on other references [8, 9], different chemical activator agents such as: ammonium chloride, calcium chloride, hydrochloric acid, nitric acid, magnesium chloride, phosphoric acid, potassium carbonate, potassium hydroxide, sodium carbonate, sodium hydroxide, sulphuric acid and zinc chloride-all from Merck chemical Co were used.

2.2. Production of activated carbon

First, the samples were rinsed and initially dried in the air and then were put in an oven for further dehydration at 110˚C for 24 hours. Dried samples were grounded using a laboratory mill. The grains were graded with sieves of the standard size of ASTM E11, into five sizes of 0.5, 1, 2, 4, and > 4 mm. Thereafter, a specified weight of each sample (w_1) as well as the activator agent (w_2) was put in a crucible and mixed thoroughly. That is to achieve a homogeneous mixture.

The weight ratio of chemical activator to raw material is called impregnation ratio (R) .The mixture was kept for a specified time (t_s) and then was put in the furnace and carbonized in a neutral nitrogen atmosphere. Optimized carbonization temperature and time (T_c, t_c) were determined by various experiments. After carbonization procedure, the sample was kept in nitrogen atmosphere at activation temperature (T_a) until the final activated carbon was prepared. Then the crucible was put in desiccators until it reached to the ambient temperature, and then was weighted (w_3). Final product was mixed with 500 ml hydrochloric acid solution (0.1 Normal) and was gently stirred for two hours. The mixture was then filtered and rinsed until pH reached to neutral.

At a later stage, activated carbon was dried in the atmosphere and was then kept in an oven for 24 hours at a temperature of 110˚C temperature until it was dried and weighed again (w_4), packed in an appropriate dish for determination of adsorption properties. Following the weight measurement, three important factors of produced activated carbon were calculated:

1. Weight reduction percentage with respect to the dry weight

$$LW = \left[\left(W_1 - W_4 \right) / W_1 \right] \times 100$$

2. Activating reagent recovery percentage

$$R.R = \left[\left(W_3 - W_4 \right) / W_2 \right] \times 100$$

3. Yield percentage

$$Y = \left(W_4 / W_1 \right) \times 100$$

2. Results and Discussion

In chemical activation process, various parameters have different important effects on final activated carbon adsorption properties. In order to have a comprehensive survey on the effects of these parameters, many experiments were carried out following which the parameters were optimized. Two samples from different sections of paper factories were chosen.

2.1. Selection of an appropriate activating agent

In this research, various activating agents were used for sample 1 and 2

(H_3PO_4, H_2SO_4, HNO_3, HCl, $ZnCl_2$, NH4Cl, K_2CO_3, $CaCl_2$, $MgCl_2$, NaOH, KOH). Sample 1 and 2 had different Ta and ta. Table1 shows each samples conditions.

The effect of activating agent on AC adsorption and yield for the two samples, are shown in Fig.1 and Fig.2, respectively. The results indicate that phosphoric acid and zinc chloride are the best activating agents. However, because of lower cost, good accessibility and desirable adsorption properties of achieved activated carbon, industrial phosphoric acid (d=1.76 gr/cm^3) was chosen for other experiments.

Table 1: Experimental conditions for determination of an appropriate activating agent

Parameters	Sample 1	Sample2
R	2	2
t_s(h)	24	24
T_c(˚C)	200	200
t_c(h)	2	2
T_a(˚C)	450	500
t_a(hr)	1.5	2
D(mm)	2	2
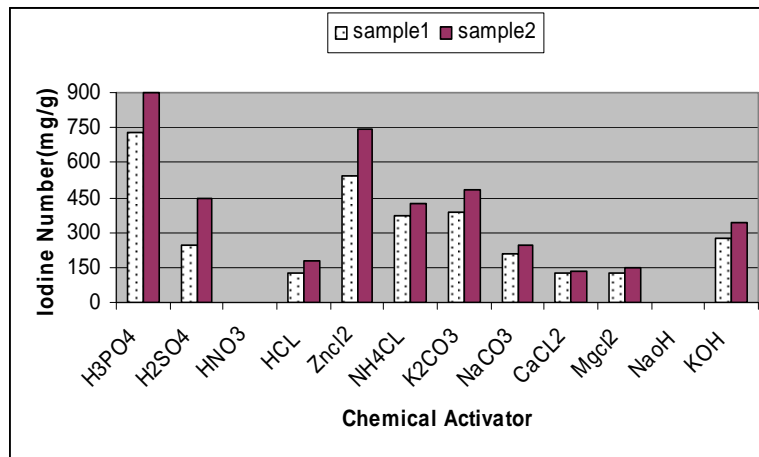
Figure 1: Effect of activating agent type on AC adsorption for samples 1 and 2
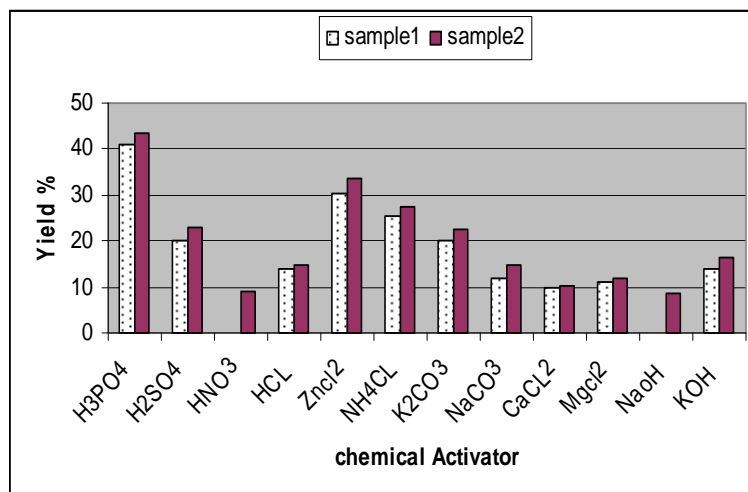
Figure 2: Effect of activating agent type on AC yields for samples 1 and 2
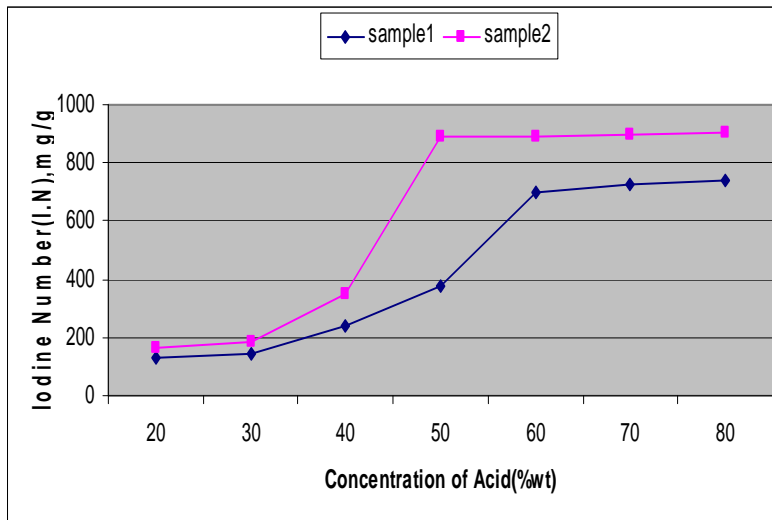
Figure 3: Effect of activating agent concentration on AC adsorption for samples 1 and 2
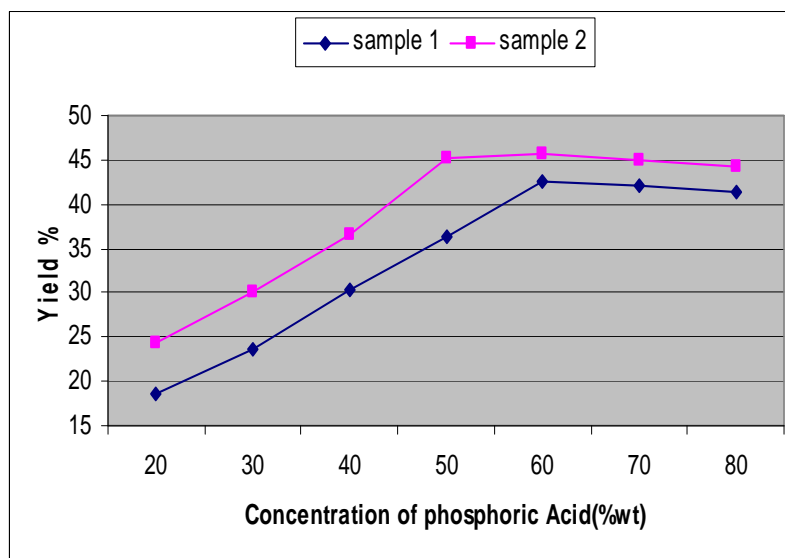

Figure 4: Effect of activating agent concentration on AC yields for samples 1 and 2

2.2. Optimization of phosphoric acid concentration

Basing on the previous results achieved; the phosphoric acid concentration act as a key parameter in adsorption properties and also for the production cost of active carbon [10]. Therefore, some experiments were here carried out to optimize acid concentration for each sample. Fig.3 and Fig.4 show the iodine number and yield versus phosphoric acid concentration respectively. As can be seen in these figures, the iodine number and process yield increases with increasing of phosphoric acid concentrations until an optimum value (60%w and 50%w for sample 1 and 2

respectively). This trend is due to the fact that the increasing viscosity of acid solution with acid concentration can cause the mixing of raw materials with activator agents to be difficult.

2.3. Optimization of impregnation proportion (R)

Impregnation proportion (R) has very important effects on process's economic. According to Fig.5 and Fig.6, iodine number and yield increase with R until a maximum and then reach to a nearly constant value. In either figure, the optimized impregnation ratios for samples 1, 2 are 2 and 1.5 respectively.
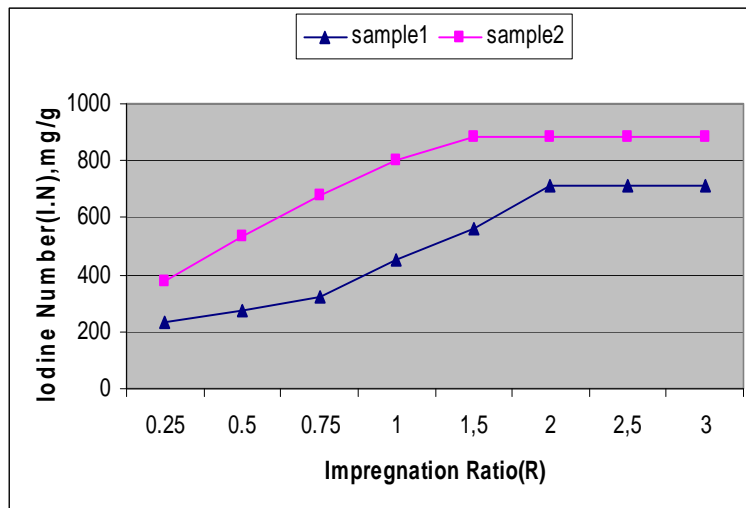
Figure 5: Effect of impregnation ratio(R) on AC adsorption for samples 1 and 2
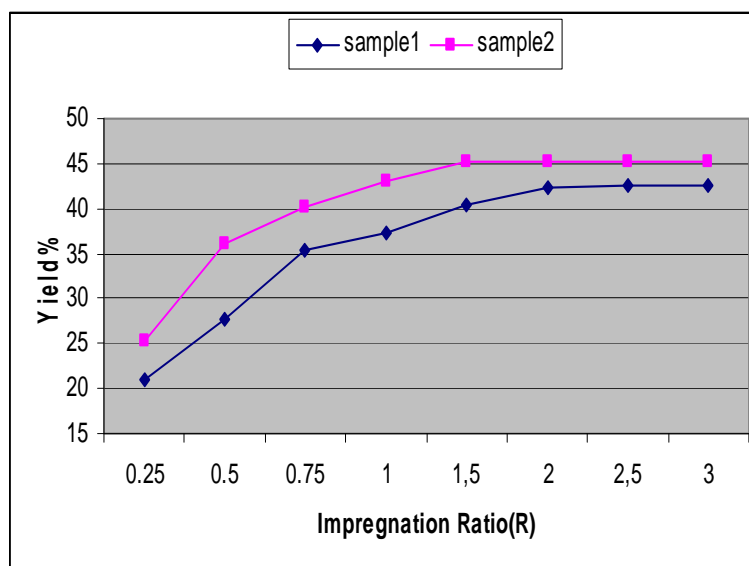

Figure 6: Effect of impregnation ratio (R) on AC yields for samples 1 and 2

2.4. Optimization of carbonization temperature (T_c)

Carbonization temperature showed a great effect on adsorption properties of produced active carbon because through the carbonization process, a series of destructive reactions occurs during which and volatile materials were removed from raw materials and the porous carbon was performed. At low temperature, the destructive reactions and removing of volatile materials could not happen but at high temperature, tar is formed and consequently the pores were clogged. So an optimum temperature id expected. For this Fig .7 and Fig.8 show the effect of

carbonization temperature on iodine number and yield of activated carbon. Basing on these figures, the optimum value of T_c for both samples 1 and 2 is 200˚c.

2.5. Optimization of carbonization time (t_c)

The carbonization time is another important parameter of the process that affects the iodine number. If carbonization time is short, according to kinetic reactions, some of destructive reactions are not completed, and so the produced activated carbon has weak adsorption properties. On the other hand, if carbonization time is long, not only the destructive reactions do happen

completely, but also it would be possible that side reactions occur and affect the porous structure of the activated carbon. So there is an optimum value for carbonization time. Fig.9 and Fig.10 show iodine number and yield of activated carbon, from which an optimum carbonization time for samples 1, 2 is obtained to be 2, 1.5 hours respectively.

2.6. Optimization of activation temperature (T_c)

The activation temperature is one of the most important parameter in active carbon production, because at such temperature, the primary porous structure that was produced

in carbonization process would be developed and a material with a desirable adsorption property is made [12].

According to Fig.11, increasing the activation temperature causes the enhancement of adsorption properties of activated carbon, until a maximum value. This behavior is due to the removal of more removing volatile components by increasing the temperature and formation of pores and increasing porosity. At higher temperature, increasing the temperature leads to demolish the porous structure and losing weight of activated carbon that consequently decreases the adsorption properties of activated carbon.
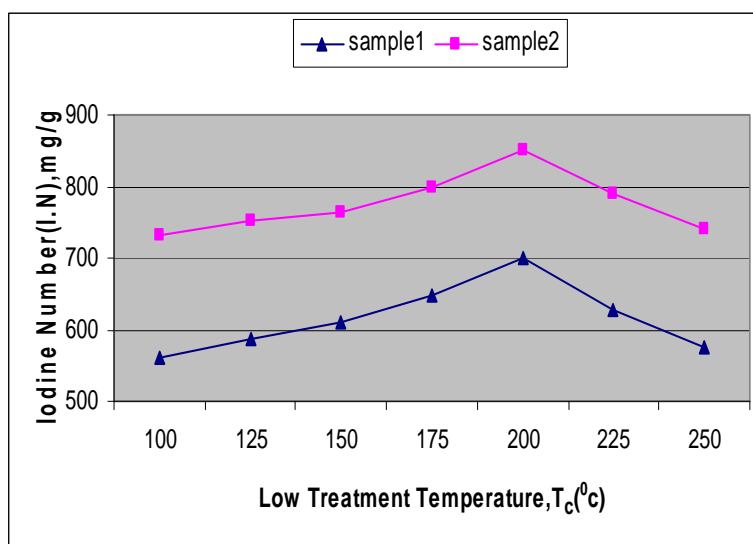

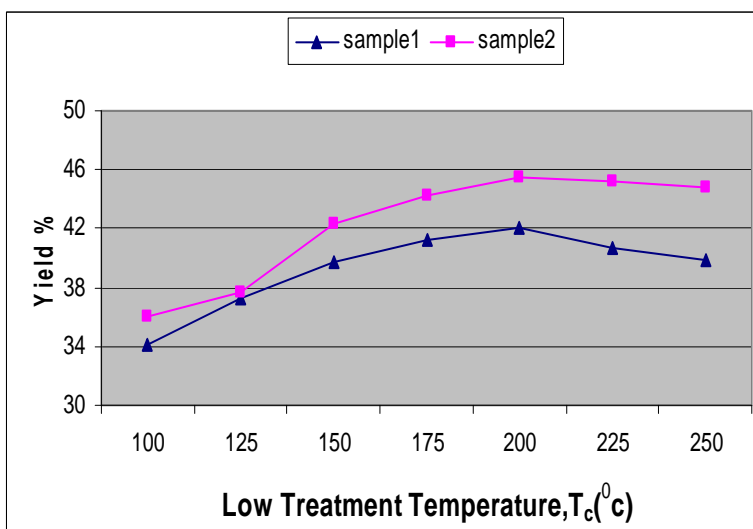Figure 7: Effect of carbonization temperature on AC adsorption for samples 1 and 2

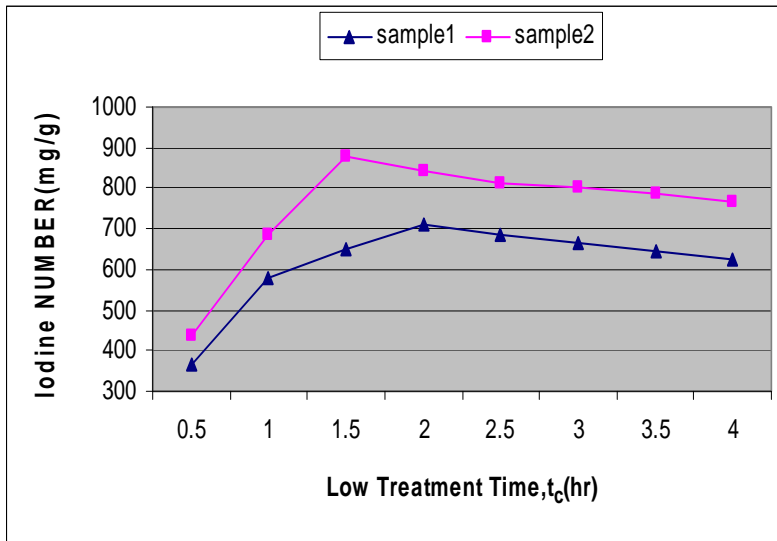Figure 8: Effect of carbonization temperature on AC yields for samples 1 and 2

Figure 9: Effect of carbonization time on AC adsorption for samples 1 and 2
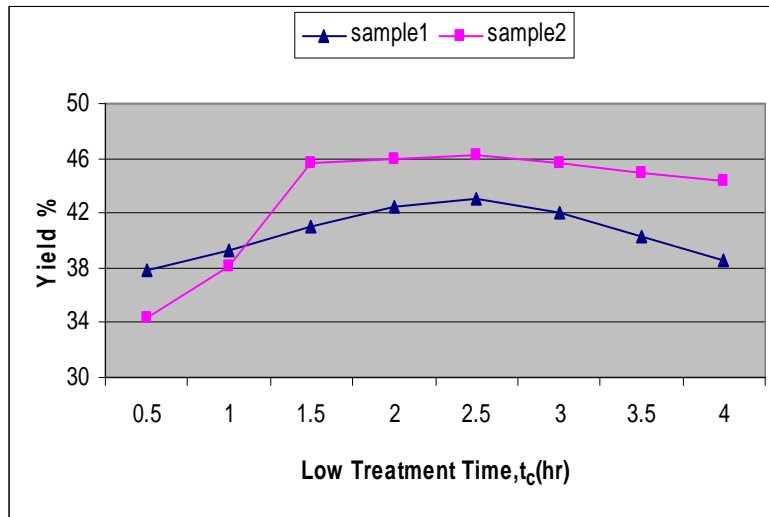

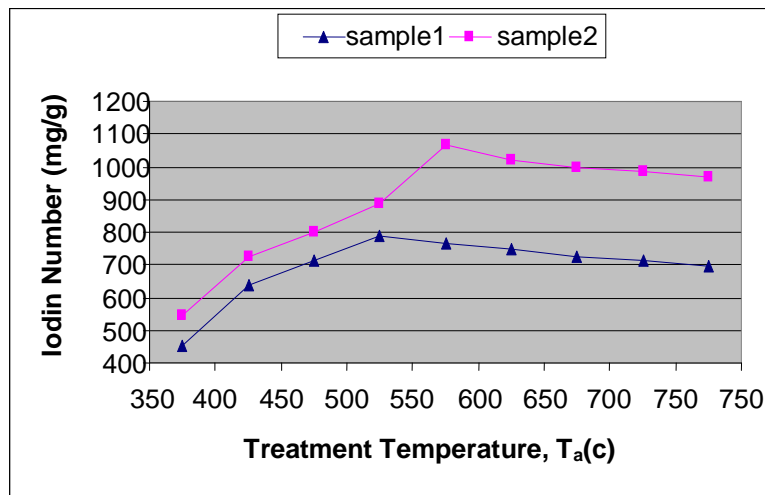**Figure 10: Effect of carbonization time on AC yields for samples 1 and 2**

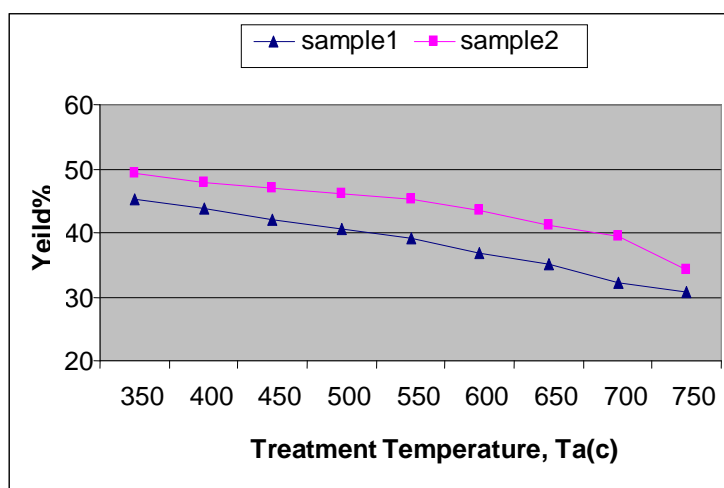**Figure 11: Effect of activation temperature on AC adsorption for samples 1 and 2**

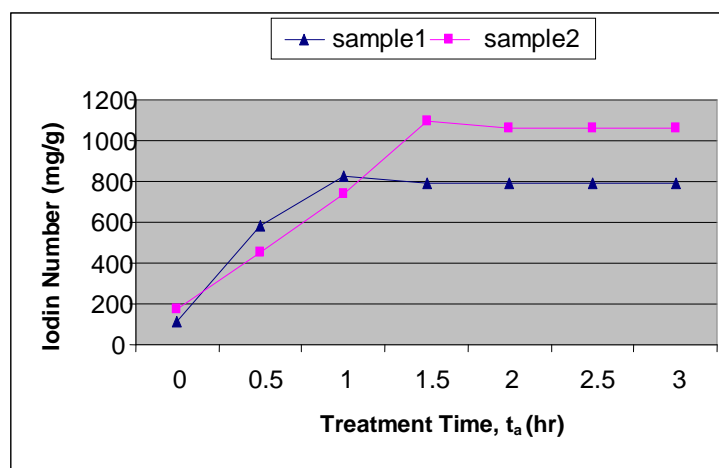**Figure 12: Effect of activation temperature on AC yields for samples 1 and 2**

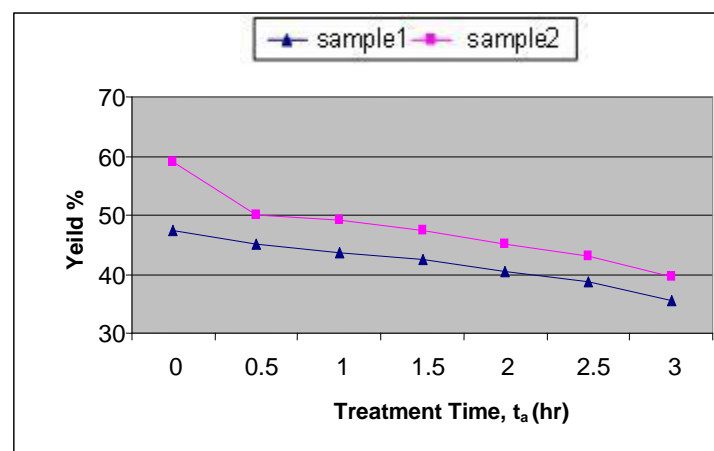**Figure13: Effect of activation time on AC adsorption for samples 1 and 2**

Figure 14: Effect of activation time on AC yields for samples 1 and2

The optimized activation temperature for samples 1 and 2 is 500 and 550°C respectively. Fig.12 shows the effect of activation temperature on yield for the two samples. The most noticeable point in this figure is the reverse relation between activation temperature and yield, i.e. the higher the temperature, the lower would the yield be. That is due to the fact that at higher temperature, the components are released from carbon.

2.7. Optimization of the activation time (t_a)

The activation time (t_a) is again another important parameter of active carbon production process. Fig. 13 shows the effect of this parameter on iodine number of two samples. It can be seen that by increasing the activation time, the adsorption properties of the produced samples are improved until it reaches to a maximum value, after which the iodine number marginally decreases and reaches to a constant value. The reason for this behavior is similar to the effect of carbonization time (t_c) [11]. The maximum value for samples 1 and 2 is 1 hr and 2 hr, respectively.

Fig.14 shows the process yield versus t_a. As shown, the trend of this figure is different with that of carbonization time (t_c).

2.8. Optimization of raw materials size (D)

Other effective parameter on adsorption properties of the produced activated carbon is the size of raw materials (i.e. particles diameter). The smaller the particle size of raw materials, the better mixing with the activation agent, the easier release of the volatile materials are achieved during the activation process. Fig.15 and Fig.16 show the iodine number and the process yield for the two samples. According to the results, the best diameter of samples 1 and 2 is 1 mm and 2 mm respectively.

2.9. Optimization of soaking time

The contact time of raw materials with the chemical agent during mixing (soaking time) is another important parameter that is a function of mixing type, impregnation ratio and also the raw material size. Once mixing operation is begun, the best soaking time is the time that chemical agents completely penetrate into the material and a homogeneous mixture is formed. The soaking time for samples 1, 2 are determined to be 12 hr and 6 hr respectively. It is observed in Fig.17 and Fig.18 that by increasing the soaking time, the adsorption properties of the samples and the yield process are improved, and when it is reached to the maximum value, a steady state is reached and hence further time allowance, has no effect on the adsorption properties.
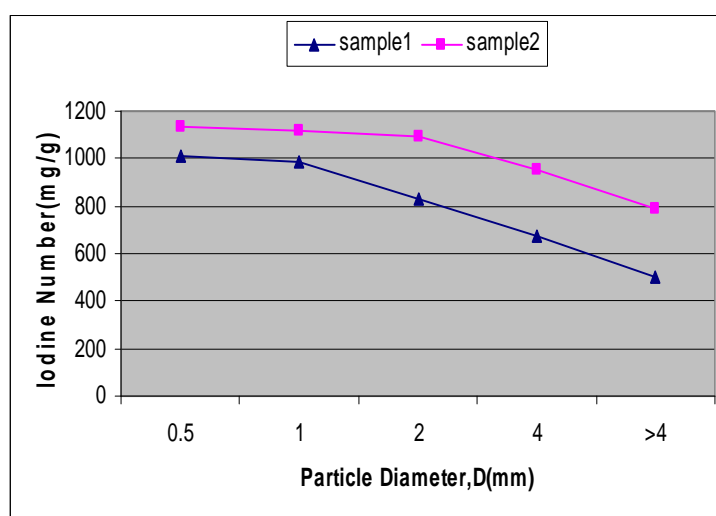

Figure 15: Effect of raw materials diameter on AC adsorption for samples 1 and 2
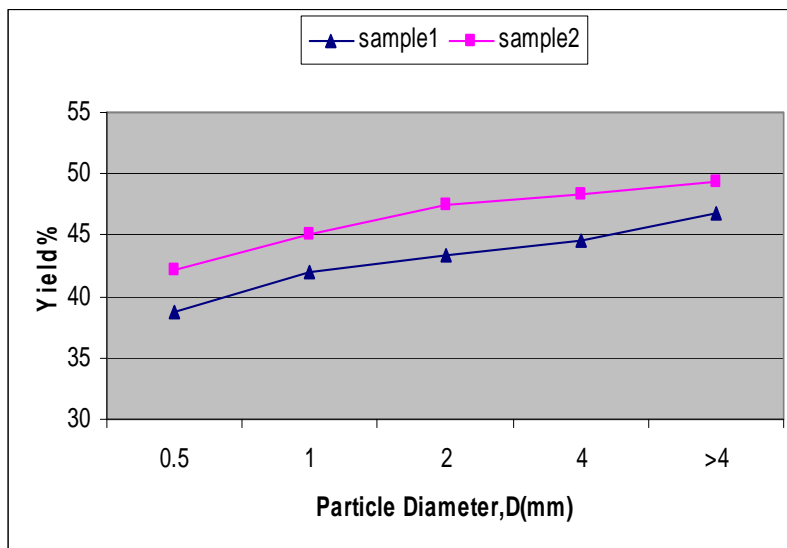
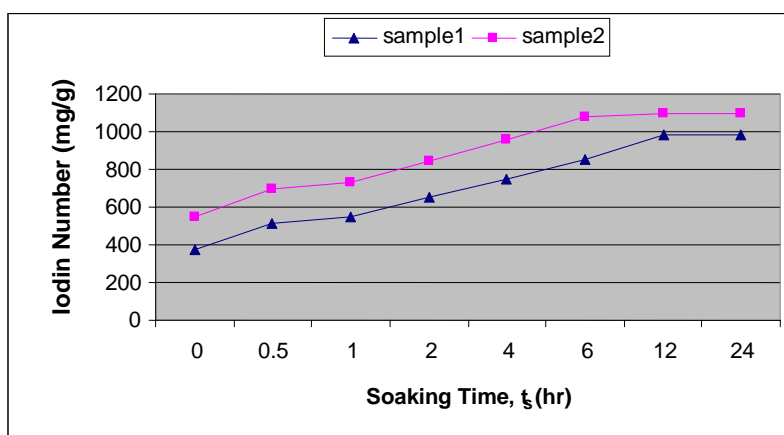**Figure 16: Effect of particles diameter on AC yields for samples 1 and 2**

Figure 17: Effect of soaking time on AC adsorption for samples 1 and 2
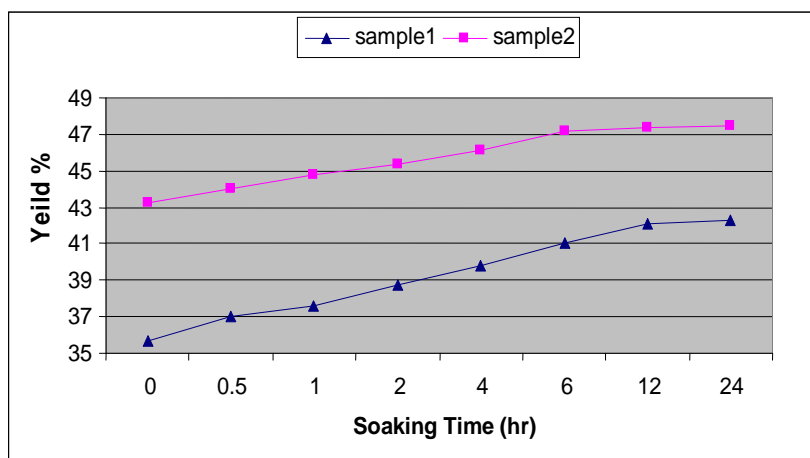

Figure 18: Effect of soaking time on AC yields for samples 1 and 2

Table 2: Optimized effective parameters on AC production by chemical activation method

Raw material	Sample1	Sample2
Activating agent	Phosphoric acid	Phosphoric acid
C (%w)	60	50
R	2	1.5
t_s (h)	12	6
T_c (˚C)	200	200
t_c (hr)	2	1.5
T_a (˚C)	500	550
t_a (h)	1	2
D (mm)	1	2

Table 3: Some of the properties produced of AC produced from samples 1 and 2 under the optimized operative condition

percentage	Sample1	Sample2
Weigh losing	57.9	52.8
Activating reagent recovery	68.7	66.4
Ash content	1.4	1.2
Moisture content	1.8	1.5
Iodine number	985	1090
Specific surface area	1139	1476
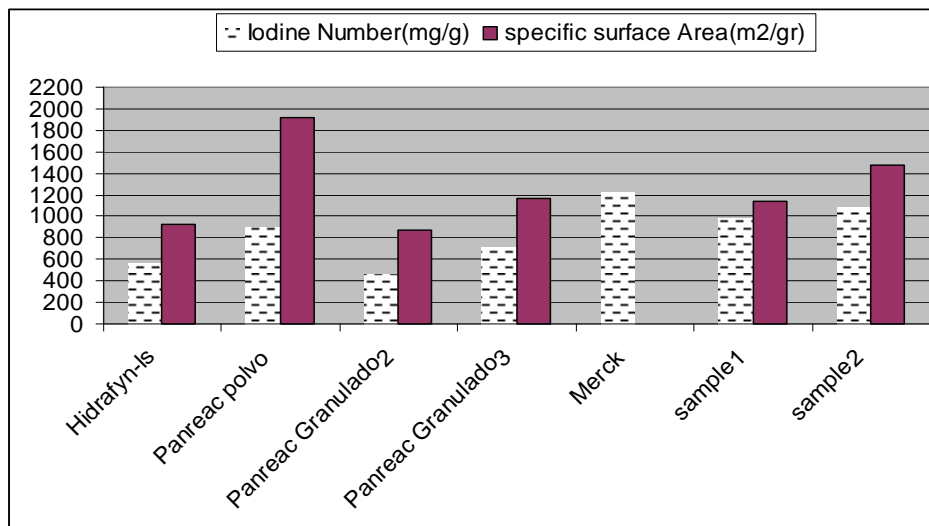
Figure 19: Comparison of produced AC for the optimized operative conditions with some commercial samples

Conclusion

The results indicate that cellulose wastes of wood and paper factories, particularly those maintained from pulp preparation unit (sample2) are physically more suitable to produce activated carbon. The most important parameters affecting the production of activated carbon by chemical activation method have been investigated, and the optimized values for the operative

conditions were determined and presented in Table 2.

Some of the properties of produced activated carbon, such as specific surface area, weight loss (based on dried weight content), activating reagent recovery, yield, moisture content, iodine number and ash content under the optimized operative condition, have been determined for samples 1 and 2, (Table 3).

Fig.19 shows a comparison between the produced active carbon and some commercial samples. It's obvious that produced active carbon has an acceptable comparable quality.

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