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Preparation of Activated Carbon: Forest residues activated with Phosphoric Acid and Zinc Sulfate

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Abstract.

This paper describes the preparation of activated carbon by chemical activation. The selected biomass used as precursor is sawdust from both Cuban and Swedish Pine tree. Phosphoric acid and Zinc Sulphate are the chemical reagents. The objective is to study the influence of acid concentration, impregnation ratio and activation temperature on adsorption performance of the obtained activated carbon.

The experiments with phosphoric acid activation show that treatment with 40% acid concentration at 400 ℃ produce an activated carbon with good properties for ammonia adsorption and good iodine number. If a 30% phosphoric acid is used for activation, an activation temperature of 500 ℃ is recommended. With an impregnation ratio of 1, good adsorption was obtained in the activated carbon produced from Swedish pine while using Cuban pine a higher adsorption was obtained with an impregnation ratio of 2.

The experiments with Zinc Sulphate activation show that activation conditions of 20% zinc sulphate concentration, 400 ℃ and impregnation ratio: 1 are enough to produce an activated carbon with good properties for ammonia adsorption. The adsorption of carbon tetrachloride was lower. Activated carbons produced with 10 % zinc sulphate concentration, 0.5 impregnation ratio and 400 ℃ activation temperature (the mildest studied conditions) show already good iodine number and BET surface area.

1. Introduction

Activated carbon is a highly adsorbing material and has various scopes of uses depending on needs. It´s used in many industries and applications e.g. to clean industrial wastewater, in medicine, discolour sugar and so on.

In the process of manufacturing AC there are two methods of activation, physical and chemical (Ioannidou, 2007)

There are two steps in the activation process when coming to physical activation. The first one is heat treatment in an inert environment, pyrolysis. This is done at a temperature of about 1100 ^{0}C. In this process the volatile matters leave the material and mostly carbon in form of char is left, with an initial carbonaceous structure. The second step is the activation, then a gas stream of carbon dioxide and steam treats the char and by oxidizing with the carbon creating pores in the material. (Bansal et al 1988).

In chemical activation, the raw material is first impregnated with the activating reagent, which degrades the cellulosic material. This enables the precursor to carbonize at lower temperatures. Chemical activation is preferred over physical activation because of the lower temperatures and shorter time needed in activating the material. After the impregnation, in absence of air, the impregnated material is then heated in a rotary kiln between 400 and 800 ^{0}C. After the activation the material is cooled, washed and dried. The most commonly used activating agents are phosphoric acid (Vernersson et al., 2020; Soleimani et al., 2007), zinc chloride and sulphuric acid.

2. Experimental

In this paper samples of Cuban Pine tree and Swedish Pine tree from Iggesund are activated using phosphoric acid. Activation using zinc sulphate is performed with sawdust from a Cuban sawmill as precursor.

2.1 Activation using phosphoric acid

The samples (Cuban pine and Swedish pine from Iggesund) are dried in an electrical oven at 100 ℃ for 24 hours. The samples are prepared by mixing an activating agent, in this case phosphoric acid (30, 40 and 50 wt %), with the pre dried wood particles. The required amount of phosphoric acid is based on the dry weight of the sampled wood particles and the dry weight of the phosphoric acid. The impregnation ratio (IR) that is used for chemical activation is 1 and 2. When the phosphoric acid has been stirred and worked into the granular the mixture of phosphoric acid and wood is left to soak overnight so that the reagents are fully absorbed by the precursor. The conditions for the experiments (acid concentration, impregnation rate and type of wood) are shown in tables 1 and 2.

2.1 Activation using zinc sulphate

In the experiments involving production of activated carbon using zinc sulphate for activation, the selected raw material was sawdust, residues from a Cuban sawmill. Three variables were used when producing the activated carbon: concentration of the zinc sulphate solution (S), relationship of impregnation mixture, zinc sulphate to wood (IR) and temperature of carbonization (T). The conditions for the experiments are shown in table 3 and 4.

2.3 Analysis of Activated Carbon

The AC was analyzed with three different methods; adsorption of gases (Ammonia and Tetrachloride), Iodine number and BET- analysis.

2.3.1 Gas Adsorption

The AC are weighed and put into a sealed container with the ammonia or the tetrachloride in liquid form for evaporation. After 24 hours it is assumed that the samples have adsorbed all the ammonia they can, why they are taken out of the container and weighed once more. The weight difference between before and after adsorption determines the samples adsorption capacity.

2.3.2 Iodine number

In order to determine the Iodine number approximately 0.1 g of activated carbon is taken and put in to a flask with 25 ml of iodine solution. The sample is then being mixed with the iodine solution by circulating the bottle for one minute. Thereafter the activated carbon-iodine solution is filtered where upon 10 ml of the filtered solution is put into another bottle using a volumetric pipette.

Finally the filtered solution is titrated with sodium thio sulphate solution until it becomes clear. To find the Iodine number the following equation is used.

Iodine number = (I*(A- V) * N* M)/ (A*B)

Where
I = Amount of iodine mixed with the AC, ml
A = Volume $Na_2S_2O_4$ (0.04 N) solution used for titration of 10 ml iodine solution, ml
V = Volume $Na_2S_2O_4$ (0.04 N) solution used for titration of 10 ml filtrate solution, ml
B = Weight of the samples in grams
M = Molar weight of Iodine
N = Iodine concentration (0.046 N)

2.3.3 BET-analysis

Firstly the sample is heated and degassed by vacuum force, removing foreign adsorbed molecules. Then controlled amounts of an inert gas, in this case nitrogen, are introduced and adsorbed. At the temperature of liquid nitrogen and in vacuum the sample is exposed to varying pressures to generate adsorption isotherms. Adsorbed molecules are determined by the pressure variations due to the adsorption by the sample. (Beckman Coulter 2010). For the BET analysis a *Micrometritics ASAP 2010, computerised Accelerated Surface Area, Porosimetry and Chemisorption System* was used and the experiments were conducted at KTH.

3. Results and Discussion

3.1 Activation using phosphoric acid.

3.1.1 Gas adsorption (ammonia)

Table 1. The adsorbed amount ammonia by the studied activated carbons.

sample	H_3PO_4 [wt%]	IR	Precursor: Type of pine	AC activated at 500ºC Adsorption	AC activated at 400ºC Adsorption
1	50	1	Iggesund	39 %	57 %
2	50	2	Iggesund	55 %	45 %
3	50	2	Cuban	27 %	5 4%
4	50	1	Cuban	28 %	54 %
5	40	1	Iggesund	23 %	51 %
6	40	2	Iggesund	21 %	47 %
7	40	2	Cuban	25 %	49 %
8	40	1	Cuban	22 %	30 %
9	30	1	Iggesund	48 %	36 %
10	30	2	Iggesund	62 %	32 %
11	30	2	Cuban	48 %	34 %
12	30	1	Cuban	42 %	33 %

Figure 1 and table 1show the overall ammonia adsorption performance.

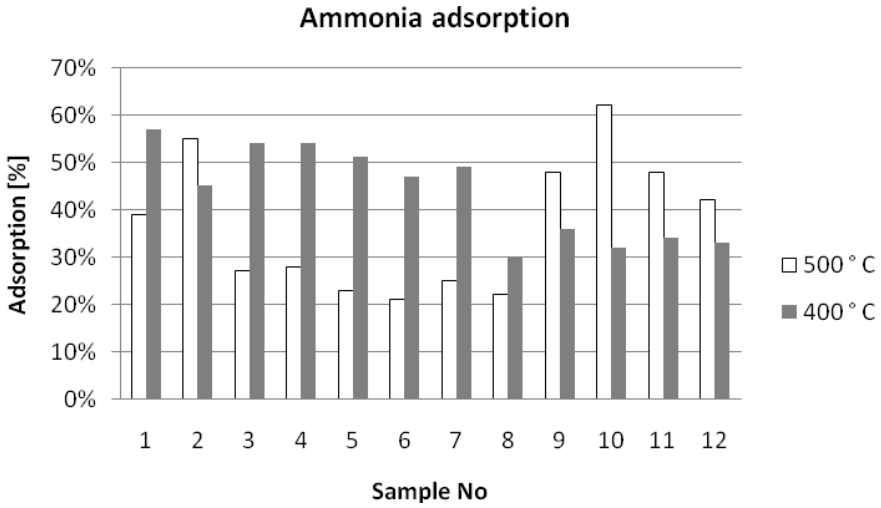


Figure 1: Ammonia adsorption on carbons activated using H_3PO_4

Samples 9 to 12 were prepared with 30% wt phosphoric acid as can be seen in Table 1.These samples have a good ammonia adsorption performance when activated at a temperature of 500 ℃ and a significantly worse ammonia adsorption performance when activated at 400 ℃ which is seen in Figure 3. This indicates that with an acid concentration of 30 wt % it is necessary to use an activation temperature of 500 ℃; otherwise the activated carbon won't have a sufficient pore volume available.

Samples 5 to 8 were prepared with an acid concentration of 40 wt %. Sample number 5 to 7 showed a good ammonia adsorption performance when activated at 400 ℃ in comparison to samples 9-12. This indicates that when using an activation temperature of 400 ℃ together with a slightly higher acid concentration of 40 wt % the activated carbon get a sufficient pore volume.

The activated carbons produced using acid of higher concentration than 30%, showed a good ammonia adsorption already when temperature in the activation process was 400 ℃. A higher temperature is not necessary in order to reach a good adsorption of ammonia. This is probably due to that a combined high acid concentration and a high activation temperature results in a too large pore volume and therefore in a lesser performance.

Sample 1 to 4 show a continued increased performance for higher acid concentrations (50 wt %) when activated at 400 ℃. Though, since the increase of ammonia adsorption is not high enough, it can be concluded that an acid concentration of 40 wt % is sufficient for activation at 400℃.

With an impregnation ratio of 1, good adsorption was obtained in the activated carbon produced from Swedish pine while using Cuban pine a higher adsorption was obtained with an impregnation ratio of 2.

3.1.2 Iodine number

Table 2 . The iodine number of carbons activated using H_3PO_4

sample	H_3PO_4 [wt%]	IR	Precursor: Type of pine	AC activated at 500ºC Iodine number	AC activated at 400ºC Iodine number
1	50	1	Iggesund	310	349
2	50	2	Iggesund	232	349
3	50	2	Cuban	220	349
4	50	1	Cuban	245	413
5	40	1	Iggesund	181	336
6	40	2	Iggesund	168	336
7	40	2	Cuban	155	439
8	40	1	Cuban	232	413
9	30	1	Iggesund	220	297
10	30	2	Iggesund	245	297
11	30	2	Cuban	271	297
12	30	1	Cuban	297	297

Figure 2 shows the iodine number of the produced activated carbons

It can be stated that the activated carbons activated at 400 ℃ had overall higher iodine number than those activated at 500 ℃.

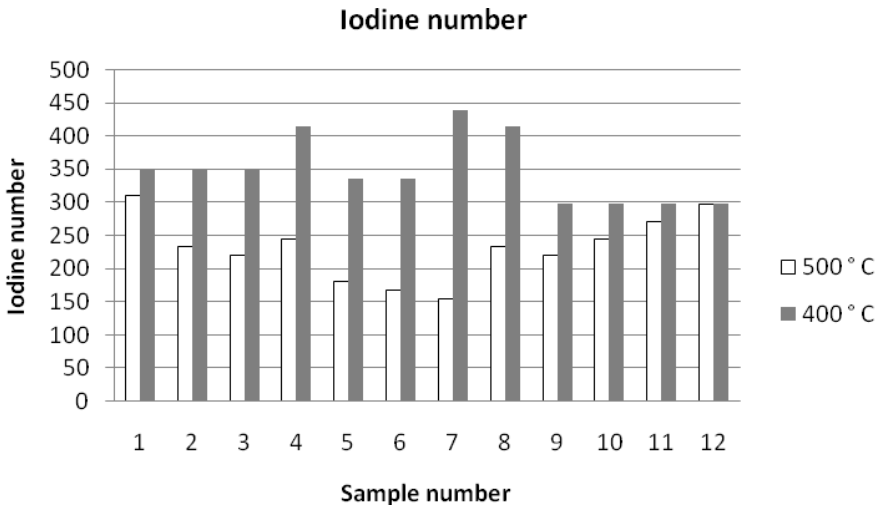


Figure 2: Iodine number of carbons activated using H_3PO_4

Samples 9 to 12, activated at 500 ℃, prepared with 30 wt % phosphoric acid achieve a good iodine number in comparison with those prepared with higher acid concentration. It means that it is recommended to use a low concentrated acid when the sample will be activated at 500 ℃.

When activated at 400 ºC, the results suggest that an acid concentration of 30 wt % is a too low concentration to achieve a good iodine number and that the pore volume is likely to be smaller in these samples. Samples 5 to 8, prepared with an acid concentration of 40 wt % achieve the highest iodine adsorption capacity. This indicates that an acid concentration of 40 wt % combined with an activation temperature of 400 ºC is optimal in order to obtain a good iodine number. Samples 1 to 4, that have been treated with a chemical reagent of 50 wt%, also show a high iodine number when activated at 400 ºC. But the use of a more concentrated acid (50 wt% instead of 40 wt %) does not increase the capacity to adsorb ammonia in comparison to sample 5 to 8.

3.2 Activation using zinc sulphate

3.2.1 Gas adsorption (ammonia and carbon tetrachloride)

In table 3 the adsorption of ammonia and carbon tetrachloride on the produced activated carbon is shown

Table 3. Adsorption of ammonia and carbon tetrachloride on carbons activated using $ZnSO_4$

$ZnSO_4$ [wt %]	IR	Adsorption ammonia 400 ºC	Adsorption ammonia 500 ºC	Adsorption CCl_4 400 ºC	Adsorption CCl_4 500 ºC
10 %	0.5	12	39	1.5	20
10 %	1	25	49	4.9	14
10 %	2	67	61	53	4.8
20 %	0.5	65	57 71 (at 450ºC)	11	7.8 8.3 (at 450ºC)
20 %	1	72	88 100 (at 450ºC)	7.7	9.1 8.3 (at 450ºC)
20 %	2	87	58 71 (at 450ºC)	2.3	10 6.3 (at 450ºC)
40 %	0.5	98	64	26	7.3
40 %	1	82	99	18	11
40 %	2	74	78	12	3.0

The adsorption of ammonia increases when the acid concentration is increased from 10% to 20% (figure 3). The adsorption of ammonia also increases when the carbonization temperature is increased from 400 ºC to 500 ºC in activated carbons produced using low sulphate concentration (10%). The increase of temperature from 400 ºC to 500 ºC has also a positive effect on the adsorption of ammonia in the activated carbon produced with 20% sulphate concentration and low impregnation ratio (0.5 and 1). The adsorption of carbon tetrachloride on the produced activated carbon is lower than the adsorption of ammonia.

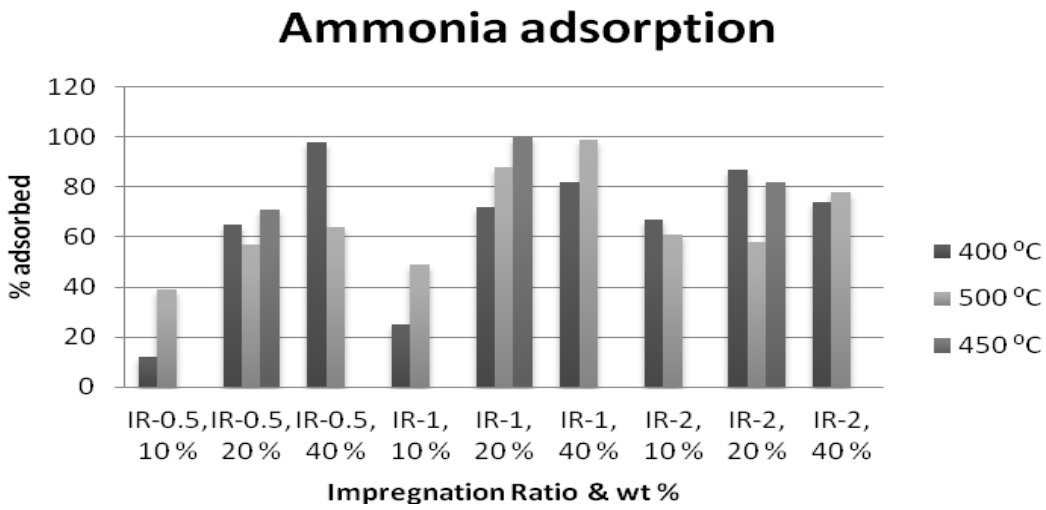


Figure 3: Iodine number of carbons activated using zinc sulphate

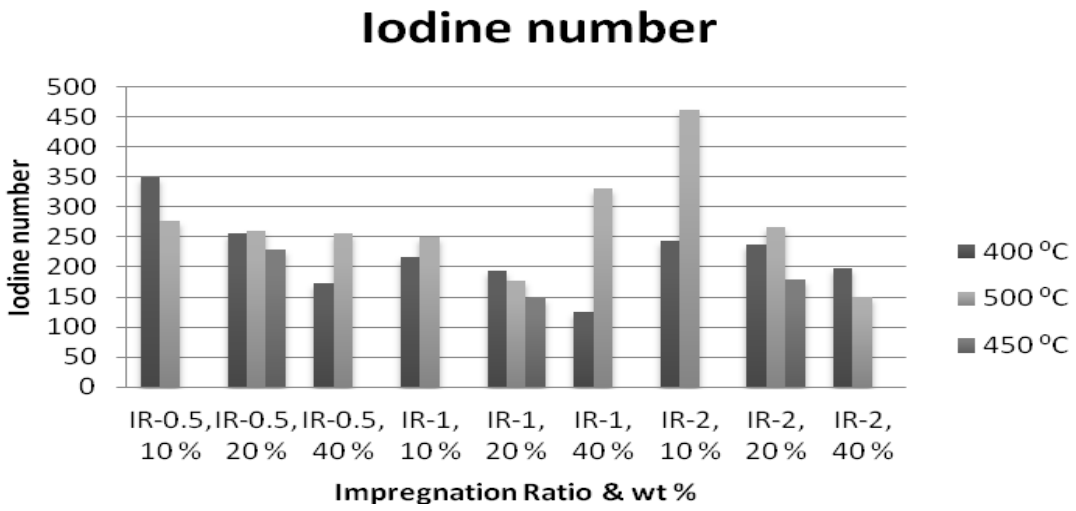
3.2.2 Iodine number

The iodine number of the carbons activated using $ZnSO_4$ is shown in table 3 and figure 4. BET-analysis has been performed in some of the samples and reported in table 3.The measured surface area was low.

Table 4. Iodine number and BET surface area of the carbons activated using

$ZnSO_4$ [wt %]	IR	Iodine number 400 °C	Iodine number 500 °C	BET surface area [m^2/g] 400 °C	BET surface area [m^2/g] 500 °C	Total pore volume [cm^3/g] 400 °C	Total pore volume [cm^3/g] 400 °C
10 %	0.5	349		256	180	0.160	0.096
10 %	1	217	249		172		0.096
10 %	2	244	461				
20 %	0.5	256	261				
			230 (450°C)		116 (450°C)		0.063 (450°C)
20 %	1	194	178	69		0.038	
			149 (450°C)		91(450°C)		0.049 (450°C)
20 %	2	237	267				
			179 (450°C)				
40 %	0.5	172	256	54		0.029	
40 %	1	126	330	60		0.035	
40 %	2	198	151		3.8		0.006

Already at the low conditions of suphate concentration, impregnation ratio and temperature (10% sulphate concentration, 0.5 impregnation ratio and 400 ºC), high iodine number is obtained in comparison with the iodine number of the carbons activated at harder conditions.



4. Conclusions

Impregnation ratio, activation temperature and acid concentration during activation influence the properties of the obtained activated carbons. In general harder activation conditions increase the size of the pores in the carbons and so the adsorption capacity. But if the activation conditions are too hard, the adsorption capacity decrease.

Depending of the precursor, it is necessary to adjust the impregnation ratio, activation temperature and acid concentration in order to optimize the adsorption of liquid (Iodine number) and gas (Ammonia), respectively. The results also confirm that the different precursor optimize the adsorption on different areas of usage.

Carbons, activated using phosphoric acid, from Cuban pine have higher iodine number than those from Swedish pine from Iggesund. The highest iodine number was obtained using high acid concentration (40 -50 wt %) and an activation temperature of 400ºC.

The highest ammonia adsorption was achieved through preparing Swedish pine from Iggesund with an acid concentration of 30 wt %, an impregnation ratio of 2 and an activation temperature of 500ºC. Almost the same result was however obtained by an acid concentration of 50 wt %, an impregnation ratio of 1 and an activation temperature of 400ºC. At higher activation temperatures a lower acid concentration can be used.

When choosing a method for preparation of chemically activated carbon it very much depends on the precursor specimen, the usage area and the activation conditions (acid concentration, impregnation ratio and activation temperature). Clearly the Cuban wood specimen would have better usage in liquid purification and the Swedish wood specimen would have better usage in gas purification.

In the process of choosing a method one should also have in mind that the reason why society prefer to activate carbon chemically is that the activation process doesn´t demand as high activation temperature as in other activation techniques like physical activation. Another important issue is to avoid using too much chemicals since it is often corrosive and damaging to the environment.

The activated carbons produced using zinc sulphate show higher ammonia adsorption when temperature is increased from 400^{0}C to 500 ^{0}C using low sulphate concentration (10 % wt). At 400^{0}C, activated carbons with good ammonia adsorption can be produced using a sulphate concentration of 20 to 40 % wt.

The CCl4 adsorption was highest at a temperature of 400 ^{0}C, 10 wt % sulphate concentration and impregnation ratio 2. The adsorption of carbon tetrachloride on the produced activated carbon is lower than the adsorption of ammonia

Already at the low conditions of acid concentration, impregnation ratio and temperature (10% sulphate concentration, 0.5 impregnation ratio and 400 ºC), high iodine number is obtained. The highest iodine number has been obtained in activated carbons produced at 500 ^{0}C, 10 wt % sulphate concentration and impregnation ratio 2. The second highest value was obtained in activated carbons prepared at 400 ^{0}C, 10 wt % sulphate concentration and impregnation ratio 0.5, which are the lowest temperature, lowest sulphate concentration and the lowest impregnation ratio. This might be a motivation to try to milder the conditions even more to see when the trend turns around.

The obtained surface area and pore volume are low. The highest surface area was obtained in carbons activated using low concentration of sulphate (10% wt) and low impregnation ratio (0.5).

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