

# PRODUCING ACTIVATED CARBONS FROM PINECONES VIA CHEMICAL ACTIVATION

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## Abstract

The objective of this study is to investigate the effects of three different chemical impregnation and activation temperatures on the textural and chemical properties of the activated carbons prepared from pinecones. For this purpose KOH, H<sub>3</sub>PO<sub>4</sub> and ZnCl<sub>2</sub> were chosen as the chemicals and relatively low ratios of chemical agent/biomass were used. TG and DTG curves of biomass samples were identified. Burn-off values were calculated and it was found that pinecones impregnated with KOH gave the lowest burn-off values such as 52%, 57% and 59% for the activation temperatures of 600, 700, and 800°C respectively. Surface characteristics of all products were determined using N<sub>2</sub> adsorption isotherms and surface areas were calculated by using BET equation. The results showed that activated carbons have micro porous structure and these results were corrected with SEM photographs. FTIR spectra, C, H and N contents and pH of all products and raw material were determined. To determine the effectiveness of products for adsorption processes, adsorption of nickel from aqueous solutions were tested. The results showed that producing activated carbons by simple chemical activation techniques from pinecone seems to be an alternative method for evaluation of biomass samples.

## Introduction

Activated carbon is a high porosity material and it is generally produced from coals or lignocellulosic materials in two ways: physical or chemical activation at high temperatures. Chemical activation of different lignocellulosic materials has been studied during recent years. Different chemical agents can be used for activation processes, i.e. H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, KOH, NaOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, ZnCl<sub>2</sub> and etc. [Carrott, P.J.M., 2006; Evans, M.J.B. et al., 1999; Hayashi, J. et al., 2000] Moreno-Castilla, C. Et al., have studied chemical activation of olive residues to produce activated carbons. When KOH and H<sub>3</sub> PO<sub>4</sub> were used as activating agent, results indicate that the chemical activation with KOH at 800°C, in an inert atmosphere, yielded activated carbons with the highest surface area and more developed micro, meso and macroporosity.

The emphasis of this study is to investigate the proper conditions for producing activated carbons with microporous surface structure in an economical way. Cheap precursor sample, a forestry residue, pine cone, is selected as the raw material and three different chemicals are used for precursor preparation. Activation is applied at three different final temperatures to investigate the effect of final temperature on surface morphology. Adsorption of Nickel from aqueous solutions was also studied to investigate if produced activated carbons could be used for metal removal processes.

## Experimental

Pine cone samples used in this study were collected from Eskisehir in Turkey. The raw material was ground to obtain particles with a size of 0.425<D<sub>p</sub><1.25 mm. A typical proximate and ultimate analysis results of pine cone sample are given in Table 1.

Three chemicals, namely H<sub>3</sub>PO<sub>4</sub>, KOH and ZnCl<sub>2</sub>, were used as activating agents. Pine cone was mixed with the activating reagent and water. The mixture was then waited for 24 hours at room temperature and they were dried in an oven at 105°C to prepare the precursors for pyrolysis experiments.

Thermogravimetric analyses of all precursors (TGA) have been performed using a LINSEIS Thermowaage L81 thermogravimetric analyser coupled with differential thermal analyser (DTA). About 10 mg of samples was placed in an Al<sub>2</sub>O<sub>3</sub> crucible without lid and heated to 1000°C under nitrogen gas flow with a heating rate of 10°C/min.

Activation experiments were performed in a fixed-bed stainless steel reactor. 30 grams of each precursor was heated till activation temperatures of 600, 700 and 800°C. Once the activation temperature was reached, heating period stopped and nitrogen gas was used again while the reactor was allowed to cool down to room temperature naturally. The degree of burn-off (carbon loss) achieved was calculated from:

$$\text{burnoff}(\%) = \left( \frac{w_i - w_{ac}}{w_i} \right) \times 100$$

where,  $w_i$  = mass of initial precursor fed to the reactor (g) and  $w_{ac}$  = mass of activated carbon produced (g).

For the characterization of activated carbons proximate and elemental analyses were performed. Moisture, volatile matter and ash contents of the products were determined according to ASTM. Elemental analyses were performed with Carlo Erba 1108 Elemental Analyser. Nitrogen isotherms were determined at 77 K using a Quantachrome Autosorb-1 instrument after degassing the produced activated carbons at 150°C until outgassing was completed. BET equation was used for surface area calculations. Total pore volumes were determined at relative volumes of about 0.95.

Adsorption experiments were held at room temperature with activated carbons produced from KOH impregnated pine cone at 600, 700 and 800°C (ACK600, ACK700 and ACK800). Three sets of experiments were performed; first part was to investigate the effect of adsorbent amount to metal removal. In the second part, metal concentration was the parameter for nickel removal and for the last part effect of contact time was investigated. Adsorbent amounts were chosen to be between 0.025 and 0.6 mg, and 10 ppm nickel nitrate solution was the aqueous media. For different concentrations were tested, 5, 10, 25 and 50 ppm. And residence time of maximum 180 min was waited for the last group of experiments.

## Results and Discussion

Proximate and ultimate analysis results of pine cone sample are given in Table 1. Pine cone contains little amount of ash and this makes it more favorable for thermal processes.

Figure 1 a-d shows TG and DTG curves of raw and pretreated pinecone samples. The chemistry of biomass is very complicated. But, generally it is assumed that biomass has three major constituents; hemicellulose, cellulose and lignin according to the mass loss curve. It is known from previous studies that thermal decomposition of hemicellulose and cellulose have the first (150-350°C) and second weight-loss (275-350°C) steps for lignocellulosic materials after the initial weight loss (30-150°C) associated with the moisture loss. However, lignin undergoes gradual decomposition over a wide temperature interval (275-500°C) [Apaydin-Varol, E. et al., 2006]. Raw pine cone gives a typical thermal degradation curve having its maximum peak at about 268°C which corresponds to the presence of cellulose. Figures 1 b, c and d are for pretreated pine cone samples and from those figures it can be seen that impregnation with three different agents had great effect on thermal degradation. All agents shifted the second mass loss peak to lower temperatures when compared with raw material. Previous experiments performed with original, raw H<sub>3</sub>PO<sub>4</sub>, KOH and ZnCl<sub>2</sub> showed that; in Figure 1-b, last peak at about 873°C is due to phosphorous; in Figure 1-c, 4<sup>th</sup> mass loss occurring at 854°C is due to KOH and in Figure 1-d last peak at 565°C is due to the presence of zinc chloride thermal degradations. Having this knowledge, it can be said that pre-treatment fastens thermal degradation of pine cone samples via effecting the final degradation temperature and therefore pyrolysis time.

Burn off values for activation of impregnated pine cone samples calculated by the equation given above is given in Table 2. Higher activation temperatures lead to higher burn off percentages for all impregnations. But except for KOH impregnation, others gave similar percentages.

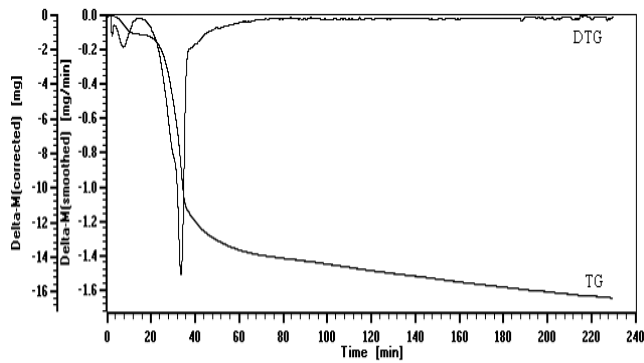
Proximate analysis was applied to activated carbons and Table 3 gives the results for ash, C, H, N, O contents, pH values and surface properties of activated carbons obtained at three different temperatures. As the temperature is raised from the lowest activation temperature to highest, carbon content of ZnCl<sub>2</sub> impregnated activated carbons is increased sharply from about 67.7% to 94.8%. However, for the other activated carbons, opposite situation is occurred, i.e. the increase in temperatures decreased the carbon content. This may be due to the increment of ash content of the products with respect to temperature increment.

**Table 1.** Properties of pine cone

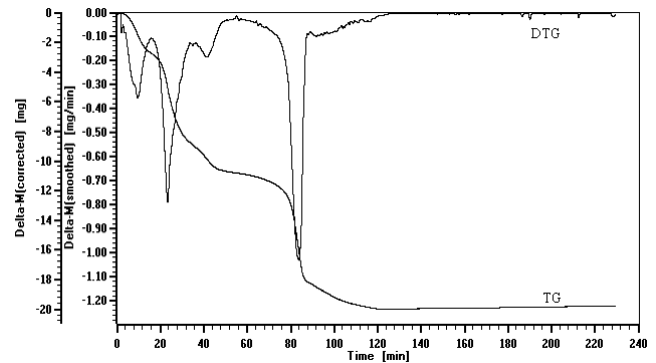
Analysis	wt. %		Element	wt. %
Moisture	8.83		Carbon	56.47
Ash	1.40		Hydrogen	6.55
Volatile matter	71.66		Nitrogen	0.37
Fixed carbon	18.11		Oxygen (by difference)	36.61

**Table 2.** Burn off values of activation processes at different temperatures

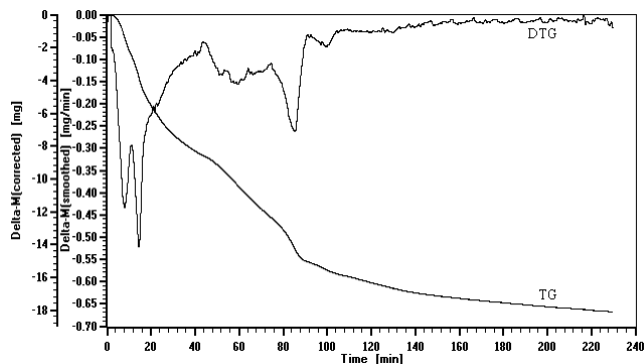
Activation temperature (°C)		600	700	800
Burn off %	H <sub>3</sub> PO <sub>4</sub> impregnated	54.0	66.4	73.0
	KOH impregnated	52.2	57.2	58.8
	ZnCl <sub>2</sub> impregnated	58.8	68.0	73.7



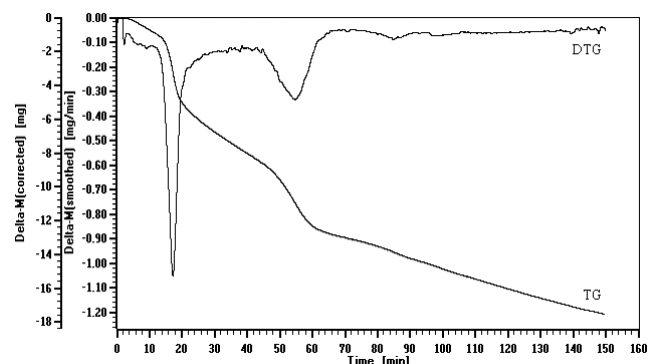
(a) Thermal behaviour of pine cone sample



(c) Thermal behaviour of KOH impregnated pine cone



(b) Thermal behaviour of H<sub>3</sub>PO<sub>4</sub> impregnated pine cone

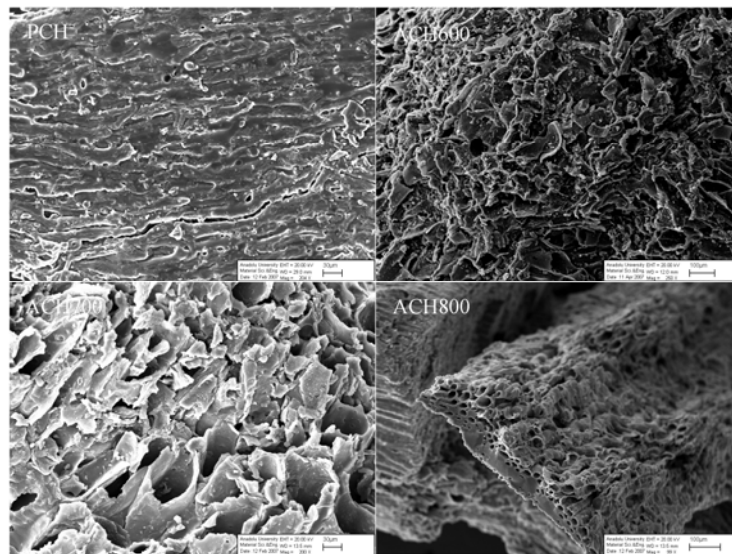


(d) Thermal behaviour of ZnCl<sub>2</sub> impregnated pine cone

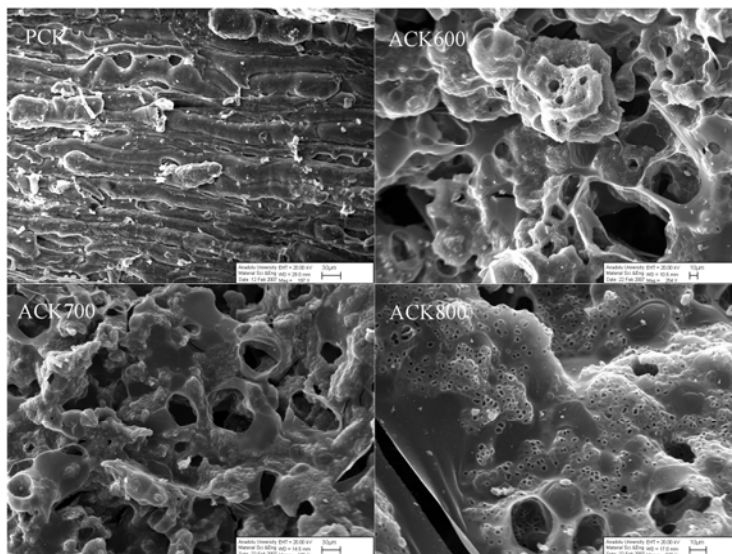
Figure 1 a-d. TG and DTG curves for raw and impregnated pine cone samples

Table 3. Properties of produced activated carbons

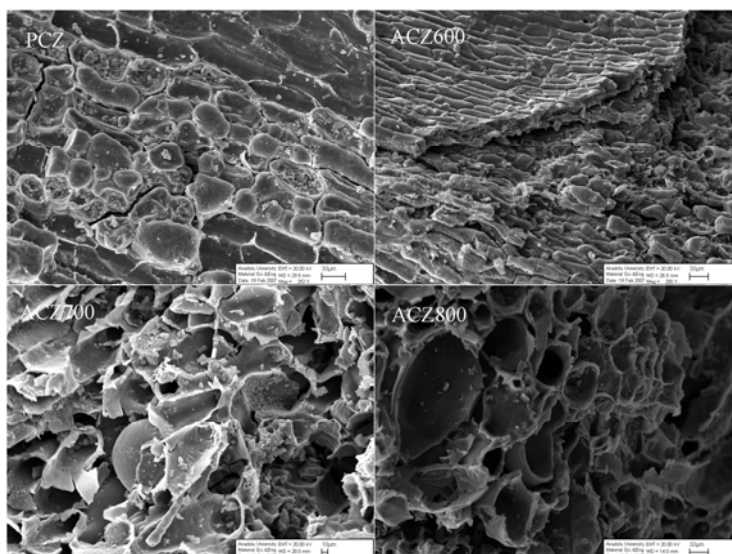
		H <sub>3</sub> PO <sub>4</sub> impregnated			KOH impregnated			ZnCl <sub>2</sub> impregnated		
Temperature (°C)		600	700	800	600	700	800	600	700	800
Proximate analysis	Moisture %	-	-	-	-	-	-	-	-	-
	Ash %	1.93	6.64	14.99	3.18	4.18	5.15	1.2	1.4	0.8
	Bulk density (kg/m <sup>3</sup> )	321.4	316.5	310.2	90.7	86.2	80.0	224.4	222.1	217.4
	pH	2.54	2.7	4.18	8.15	8.1	7.1	4.67	4.87	4.59
Elemental analysis (%)	C	70.1	77.8	74.4	93.1	80.9	75.1	67.7	94.6	94.8
	H	1.1	0.8	0.8	0.7	0.6	0.5	1.1	1.2	0.7
	N	0.9	1.1	1.4	1.2	1.1	0.8	1.3	1.5	0.9
	O (by difference)	27.9	20.3	23.4	5.0	17.4	23.6	29.9	2.7	3.6
	S <sub>BET</sub> (m <sup>2</sup> /g)	1377	1240	1166	695	998.8	1142	1292.4	1302	1219.6
	V <sub>total</sub> (cm <sup>3</sup> /g)	0.754	0.644	0.568	0.324	0.498	0.4996	0.571	0.526	0.5696
	V <sub>micro</sub> (cm <sup>3</sup> /g)	0.585	0.53	0.49	0.273	0.386	0.452	0.518	0.491	0.5215
	S <sub>micro</sub> (m <sup>2</sup> /g)	1256	1150	1105	665.4	951.1	1125	1273	1199	1280
	S <sub>external</sub> (m <sup>2</sup> /g)	12	90	61	29.3	47.7	15.6	18.97	20.2	21.97
	r <sub>average</sub> (Å)	21.9	20.78	19.48	18.66	19.94	17.5	17.67	17.25	17.5



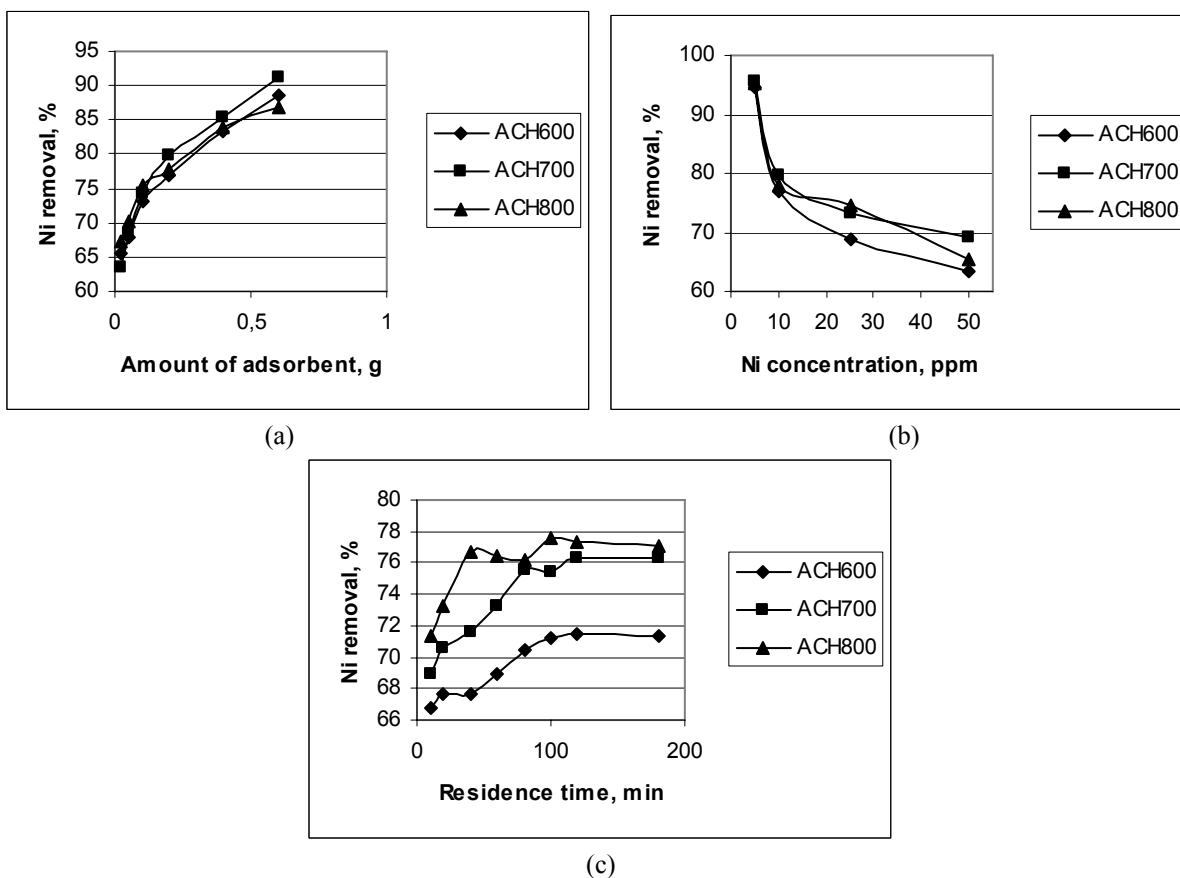
**Figure 2.** SEM micrographs of activated carbons produced from phosphoric acid impregnated pine cone



**Figure 3.** SEM micrographs of activated carbons produced from potassium hydroxide impregnated pine cone



**Figure 4.** SEM micrographs of activated carbons produced from zinc chloride impregnated pine cone



**Figure 5.** (a) Nickel removal using phosphoric acid impregnated pine cone based activated carbons, effect of adsorbent amount, (b) Nickel removal using phosphoric acid impregnated pine cone based activated carbons, effect of metal concentration, (c) Nickel removal using phosphoric acid impregnated pine cone based activated carbons, effect of contact time

Figures 2, 3 and 4 give SEM micrographs of produced activated carbons. The structure of activated carbons looks like a wavy surface, with many micropores. These micropores provide superb conditions for adsorption processes. When compared with raw materials activated carbons seem to have more porosity giving larger surface areas. The surface properties given in Table 3 also correct these SEM micrographs. All produced activated carbons have great microporous surface areas, whereas only a little portion of the total area comes from meso or macro pores. Also, it can be seen from the table that activated carbon produced from  $ZnCl_2$  impregnated pine cone at  $700^\circ C$  has the highest surface area of  $1302 \text{ m}^2/\text{g}$  and activated carbon produced from  $H_3PO_4$  impregnated pine cone at  $600^\circ C$  has the highest surface area of  $1377 \text{ m}^2/\text{g}$ .

Adsorption capacity depends mostly on physical and chemical characteristics of the activated carbon, adsorbate, concentration of the adsorbate in aqueous solution, characteristics of liquid phase (temperature, pH and etc.) and residence time. Previous studies for Ni adsorption on different activated carbons showed that at pH 5.5 maximum removal efficiency was reached [Kobya, M. et al., 2005; Liu, C.C. et al., 2005]. Figure 5-a, b, c gives the results for adsorption experiments that were held with activated carbons produced from phosphoric acid impregnated pine cone samples at 600, 700 and  $800^\circ C$  (ACH600, ACH700, ACH800) having the largest surface areas with respect to other carbons. pH of the stock solution and solutions after filtration was measured and seen that there is no net change. The effect of adsorbent amount on removal efficiency when Ni concentration was 10 ppm was studied and results are given in Figure 5-a. It is obvious that the higher the amount of adsorbent, the higher the removal efficiency. After then, to investigate effect of Ni concentration on adsorption efficiency, 0.2 grams of adsorbent was introduced with 5, 10, 25 and 50 ppm of Ni solutions for 1 hour. Adsorption efficiency is about 95 % for 5 ppm solutions for all activated carbons, Figure 5-b. 10, 20, 40, 60, 80, 100, 120 and 180 minute contact times were tested for Ni removal (Figure 5-c). A sharp increase is seen for removal efficiency till 100 minute residence time. After then, there is a slight increase in removal capacity, indicating that equilibrium is reached.

## Conclusion

Results obtained indicate that chemical activation of pine cone with  $\text{H}_3\text{PO}_4$ , KOH and  $\text{ZnCl}_2$  produced activated carbons with higher BET surface area and much better developed porosity. Although burn off values increase at higher temperatures, the quality of the products improved. As a result, it can be said that since produced activated carbons have large surface areas and microporous structure they can be utilized as adsorbents for metal removal from solutions.

## References

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