# REMOVAL OF $Pb^{+2}$ IONS FROM AQUEOUS SOLUTIONS BY ACTIVATED CARBONS PRODUCED FROM PEANUT SHELLS

*Ayşe Eren Pütün, Dept. of Chemical Engineering, Anadolu University, Eskisehir, Turkey*
*Esin Apaydın Varol, Dept. of Chemical Engineering, Anadolu University, Eskisehir, Turkey*
*Ersan Pütün, Dept. of Material Science and Engineering, Anadolu University, Eskisehir, Turkey*

## Abstract

This study involves physical activation of an agricultural waste, peanut shell, to produce activated carbons and adsorption of lead ion from aqueous solutions with these carbons. The activation method contains two steps, first one being pyrolysis and the second one being activation. Final pyrolysis temperature and heating rate were chosen as 550$^{o}$C and 10$^{o}$C/min respectively and nitrogen is used as the sweeping gas. After obtaining chars, activation was applied to the temperatures of 600, 700 and 800$^{o}$C with a dwell time of 0.5 hour. Steam and carbon dioxide were used as the activation agents during the dwell time. For characterisation elemental analysis was applied to the raw material, char and activated carbons. To figure out the changes in the structure of the raw material and activated carbons scanning electronic microscopy SEM was conducted. Surface areas of all activated carbons were calculated by BET equation. FT-IR spectra of raw material and products were obtained to analyse functional groups. For the adsorption experiments, three groups of experiments were performed to investigate the effects of amount of adsorbent, initial concentration of the aqueous solution and adsorption time.

## Introduction

Activated carbon is an extremely porous material with a large surface area, and typically produced from organic precursors such as coconut shells, palm-kernel shells, wood chips, sawdust, corncob and seeds. Activated carbons have several important uses including solution purification, removal of tastes and odours from domestic and industrial water supplies, fats and oils, chemicals and pharmaceuticals and in the waste treatments. It is also useful for purification of gases, liquid phase recoveries and separation processes. Activated carbons can generally be produced in two different ways: *i*) chemical activation, *ii*) physical activation. For physical activation, generally resulting char from pyrolysis process is allowed to react with carbon dioxide or steam at higher temperatures such as 900-1200$^{o}$C to produce more porous structures, activated carbons. Carbonization of the raw material with the addition of activating agents such as zinc chloride, potassium sulphide and phosphoric acid is chemical activation. For commercial production both types of activation techniques are widely used [Bonelli, P.R. et al., 2001; El-Hendawy, A.N.A. et al., 2001; Lua, A.C. et al., 2004].

Adsorption is the most studied property of activated carbons and heavy metal removal from aqueous solutions takes attention for many years. Lead is a soft, heavy, toxic material and it is used in building construction, lead-acid batteries, bullets, and etc. Being a heavy metal lead is potent neurotoxin which accumulates in soft tissues and bone over time [Ozer, A., 2007; Singh, K.K. et al., 2006].

This study involves the production of activated carbon from peanut shells via physical activation and testing it if it could be used as adsorbent for $Pb^{+2}$ removal from aqueous solutions.

## Methods

***Preparation of activated carbon***

Air dried peanut shell samples was grounded and sieved to have particle size of $0.425<D_p<1.25$ mm The proximate analysis of the raw material yielded, moisture 8.1 %, volatile matter 67.8 %, ash 3.5 %, and fixed carbon 20.6 %. Pyrolysis - activation experiments were performed in a stainless steel reactor details of which were given somewhere else [Pütün A.E. et al., 2004]. 30 grams of ground peanut shell was placed in the reactor and heated at a constant rate to the pyrolysis final temperature. According to previous experiments that were performed with many other biomass samples, pyrolysis parameters such as final pyrolysis temperature, heating rate and nitrogen flow rate were chosen to be 550$^{o}$C, 10$^{o}$C/min and 50cm$^{3}$/min respectively [Pütün, A.E. et al., 2002; Pütün A.E. et al., 2004]. After pyrolysis, the reactor was cooled down to room temperature with nitrogen flow naturally. After obtaining char, with the same heating rate and nitrogen gas flow rate, char was subsequently re-heated till activation temperatures of 600, 700 and 800$^{o}$C. Once the activation temperature was reached, nitrogen gas in the reactor was changed to steam or carbon dioxide for 30 minutes keeping the temperature constant. After activation, nitrogen was used again while the reactor was allowed to cool down to room temperature naturally. Produced activated carbons are nominated as follows:

AC-C6, AC-C7, AC-C8: Activated carbon produced under carbon dioxide atmosphere at final temperatures of 600, 700 and 800 $^{o}$C

AC-S6, AC-S7, AC-S8: Activated carbon produced under steam atmosphere at final temperatures of 600, 700 and 800 $^{o}$C

Elemental analysis was applied to char and produced activated carbons using Carlo Erba 1108 Elemental Analyser. pH of the activated carbons were determined as follows: 0.5 grams of each material was weighed in stoppered glass tubes and 20 ml of hot distilled water was added. It was agitated using a magnetic stirrer keeping the temperature about 100$^{o}$C. After 20 minutes, the mixture was filtered and pH of the filtrate was measured. Characterizations of the activated carbons and char were determined by nitrogen adsorption at 77 K with the help of Quantachrome Autosorb 1. The surface areas were calculated from nitrogen adsorption isotherms by using Brunauer-Emmett-Teller equation. FT-IR spectra of raw material, char and activated carbons were recorded between 4000 and 400 cm-1 using a Bruker Tensor 27 Fourier Transform Infrared Spectrometer. Dried KBr was used to prepare pellets from samples.

***Lead adsorption procedure***

Batch experiments were conducted to investigate the effect of adsorbent amount, lead concentration and contact time on adsorption of lead on produced activated carbons and char at room temperature. A stock solution of 1000 ppm was prepared from lead (II) nitrate using deionised water. For the first group of experiments; 6 different amounts of adsorbents are held together with 50 ml of 10 ppm $Pb^{+2}$ solutions for 1 hour. 5, 10, 25 and 50 ppm of lead solutions were prepared for the second group of experiments, which are held out with 0.1 grams of adsorbents for 1 hour. In order to ascertain the effect of contact time, 50 ml of 10 ppm $Pb^{+2}$ solutions were used with 0.1 grams of adsorbent. After filtration, the metal concentration in the filtrates was determined by Atomic Absorption Spectrometry using a Varian Absorption Spectrometer.

## Results and Discussion

***Preparation of activated carbon***

When commercial production of activated carbon is aimed, high yields of products after activation steps must be achieved. Final temperature is an important parameter on activated carbon product yields. The increase in activation temperature leads to a great decrease in activated carbon yield. Generally temperatures higher than 800$^{o}$C are preferred for activated carbon production, but since burn off degrees increase with temperature, 800$^{o}$C was chosen to be the maximum final temperature for this study.

Elemental analysis results of char and activated carbons are given in Table 1. Carbon content of activated carbons produced under carbon dioxide atmosphere are higher then that of steam atmosphere. This shows that steam is a more active agent then carbon dioxide, it reacts with the char and removes carbon more then carbon dioxide leaving high amounts of ash behind.

Figure 1 gives the surface areas of all activated carbons. It is surprising that having a lower carbon-higher ash content, AC-S8 gave the highest surface area. The size distribution of micropores of an activated carbon is one of the important factors determining its quality and applicability. t-plot calculations showed that activated carbons have a high microporous structure. The microstructures of the carbons are also observed by SEM images given in Figure 2. It can be seen from figure that raw material, peanut shell, already has a porous structure and activating it helps to increase the microporous structure.

**Table 1.** Elemental analysis results and bulk densities for char and activated carbons

| Substance | % C | % H | % N | % O+Ash (by difference) | Bulk density (kg/m$^3$) |
|---|---|---|---|---|---|
| Char | 84.53 | 1.8 | 0.95 | 12.72 | 148 |
| AC-C6 | 87.31 | 1.21 | 1.05 | 10.43 | 163 |
| AC-C7 | 88.65 | 0.62 | 0.78 | 9.95 | 183 |
| AC-C8 | 90.71 | 0.41 | 0.79 | 8.09 | 140 |
| AC-S6 | 88.05 | 1.36 | 0.91 | 9.68 | 143 |
| AC-S7 | 82.76 | 0.6 | 0.61 | 16.03 | 138 |
| AC-S8 | 78.54 | 0.39 | 0.38 | 20.69 | 121 |

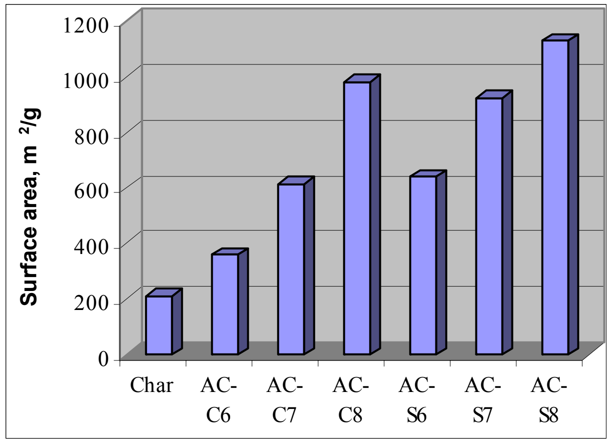


**Figure 1.** BET surface areas of char and activated carbons

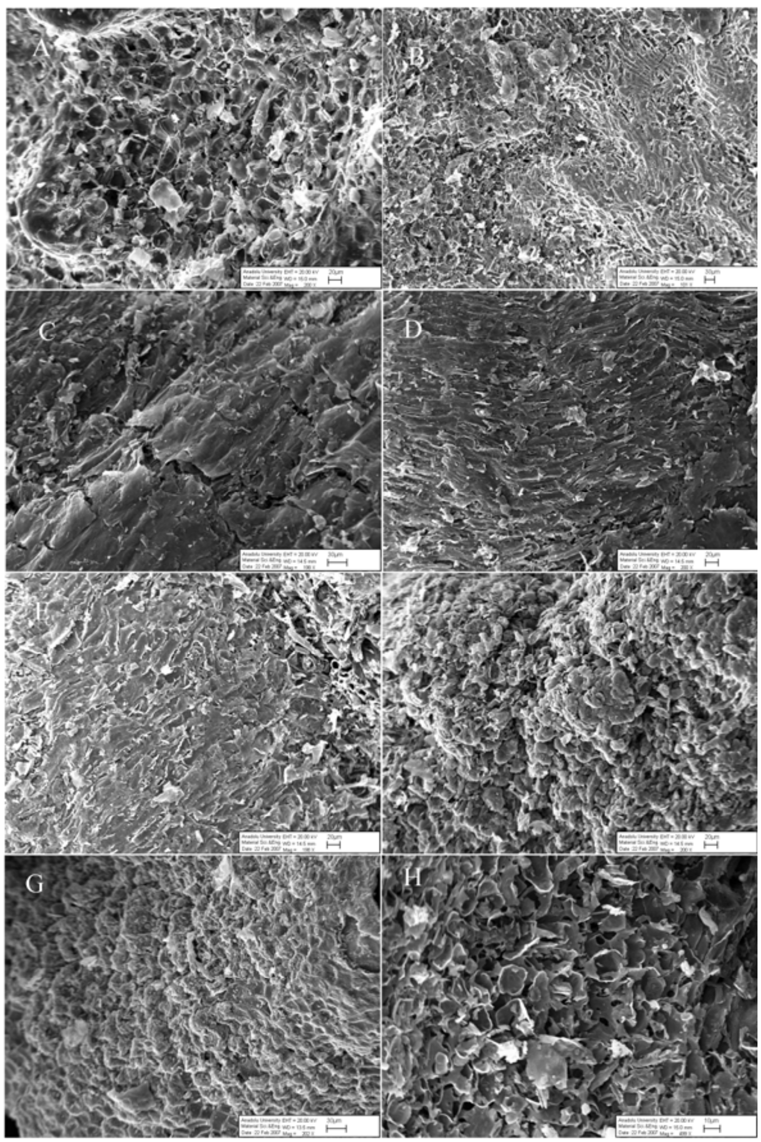


**Figure 2.** SEM images of A) Peanut shell, B) Char, C) AC-C6, D) AC-S6, E) AC-C7, F) AC-S7, G) AC-C8, H) AC-S8

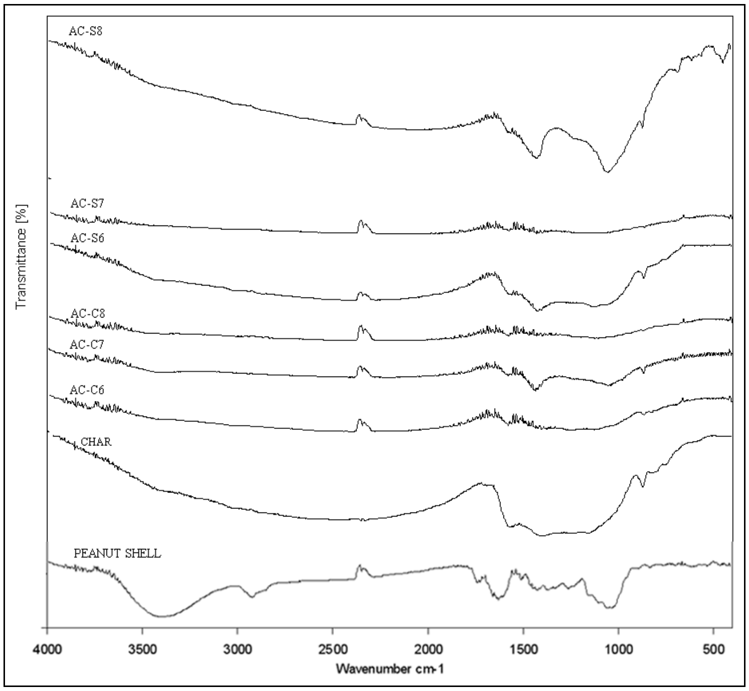


**Figure 3.** FT-IR spectra of produced char and activated carbons

Produced char and activated carbons at three different temperatures and under carbon dioxide and steam atmospheres were characterized by infrared spectroscopy (Figure 3). The spectra are roughly very similar for the char and AC-S6. Also the spectra of carbon dioxide activated carbons at 600, 700 and 800$^oC$ show similarities. The bands at about 3450-3150 $cm^{-1}$ represent O-H vibrations in hydroxyl groups and N-H vibrations. The presence of aliphatic hydrogen (C-H) vibrations appears with a band between 2930 $cm^{-1}$ only for peanut shell. Stretching vibrations between 1650-1450 $cm^{-1}$ indicate the presence of C=C vibrations. Olefinic C=C vibrations show intensities around 1600 $cm^{-1}$.

***Adsorption***

Activated carbon has an extraordinarily large surface area and pore volume that gives it a unique adsorption capacity. Commercial products range between 300-2000 $m^2$/g, and some surface areas are as high as 5000 $m^2$/g. This advantage makes activated carbons important adsorbents for many purification or filtration processes.

There are many factors affecting adsorption capacity of an activated carbon. The pH of the aqueous media has been identified as the most important variable. This is partly due to the fact that hydrogen ions themselves are strong competing sorbates and partly that solution pH influences the chemical specification of metal ions [Villaescusa I. et al., 2004].

pH values of activated carbons produced from peanut shells via physical activation range between 9.5 and 10.3 showing that carbons have basic property. Figure 1 gives the metal removal vs. absorbent amount. Increasing the amount of adsorbent decreases metal removal. Singh, K.K. et al., have studied lead removal using maize bran at different pH values and they showed that optimum pH for lead removal is 6.5. pH values higher then 6.5 influenced formation of metal oxides, instead of adsorption. For the experiments carried out with peanut shell based activated carbons, larger amounts of activated carbons increased the pH of the aqueous media and due to this fact metal removal percentage is decreased.

Figure 2 gives the results for the second group of adsorption experiments that were made for investigating the effect of concentration of metal ions in the solutions. There is a sharp decrease on metal removal with increasing the concentration.

A series of experiments were performed at different contact times with the activated carbons. The removal of lead was found to be ranging between 64 and 81 % when contact time was 100 min. Equilibrium was reached about 100 and 120 minutes for all activated carbons.

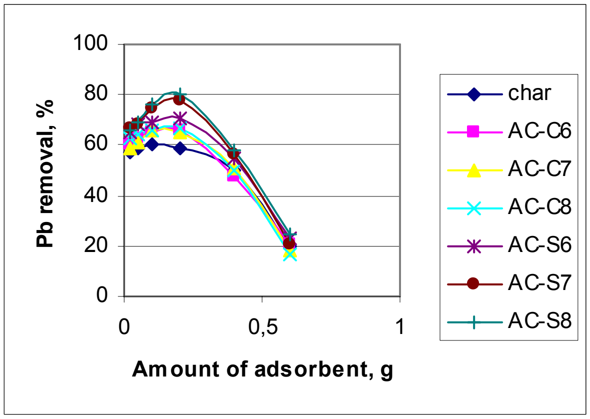


**Figure 4.** Effect of adsorbent amount on $Pb^{+2}$ adsorption

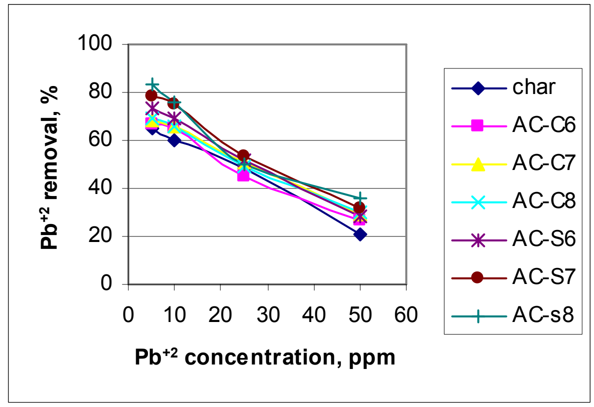


**Figure 5.** Effect of concentration on $Pb^{+2}$ adsorption

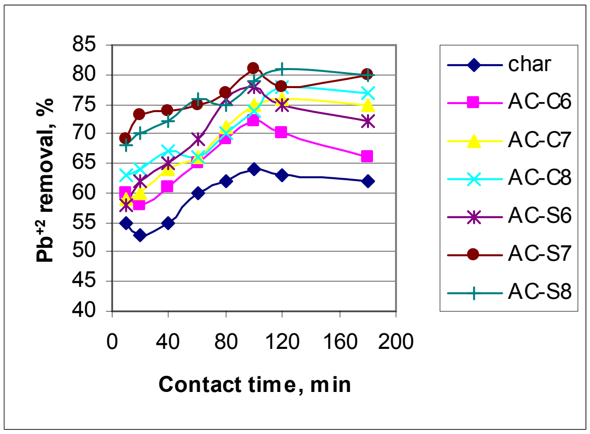


**Figure 6.** Effect of contact time on $Pb^{+2}$ adsorption

## Conclusion

Studies on the preparation (pyrolysis + physical activation) and characterisation of active carbons from peanut shell are given in this paper. The effect of activation temperature on burn off degrees and quality of produced activated carbons had been investigated when steam or carbon dioxide were used as the activating agents. According to the results it can be said that peanut shell could be a proper biomass sample for producing activated carbons.

Adsorption experiments showed that pH of the adsorbent strongly influenced removal of lead from aqueous solutions by increasing the pH of the solution.

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