



## **Activation of pine bark surface with NaOH for lead removal<sup>#</sup>**

M. Emin ARGUN\*, Şükrü DURSUN

*Selçuk University, Engineering & Architecture Faculty, Department of Environmental Engineering, 42003 Konya, TURKEY*

Accepted 15 April, 2007

**Abstract:** In this study we activated pine barks (*Pinus nigra*) by using NaOH and this activated material used for the removal of Pb(II) ions from aqueous solutions. Chemical activation and its enhancement effect of adsorption capacity for treatment process have been investigated in this article. FT-IR analyses were examined for the determination of surface properties changes after activation. Maximum adsorption capacity was 49 mg/g at pH 8 and with a 180-min contact time (for 35 mg/L initial concentration and a 2.5 g/L solid-to-liquid ratio) These modification processes also decreased soluble organic compounds from pine barks leading to increase in chemical oxygen demand of water. Adsorption capacities of adsorbents increased quietly as a result of modification according increase of adsorbent surface activity.

**Keywords:** Activation, lead, bark, removal, NaOH.

### **Introduction**

Environmental pollution and its harmful effect on habitat have been studied intensively during last decades. The pollutants removal difficulties from wastewater were increased with increasing industrialization. These wastewaters are produced in large volumes and must be absolutely treated before discharge. Heavy metals are very harmful for humans, animals and plants. Global and local agencies have therefore established certain limits on the quantities of heavy metals being discharged into environment. Trace metals if transported towards the ecosystem may enter the human body through inhalation of dust, consumption of contaminated drinking water and aquatic livings, direct ingestion of soil, and consumption of animal foods and food plants grown in metal-contaminated soil (Oliver, 1997; Karatas and Dursun, 2006). Human uptake of heavy metals takes place mainly through food chains. Lead pollution occurs in many industrial wastewaters such as those produced by acid battery manufacturing, metal plating and finishing, ammunition, PbEt<sub>4</sub> manufacturing, ceramic and glass industries. This heavy metal is not biodegradable and its presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings. Excessive human intake of Pb causes to disruption of the biosynthesis of haemoglobin, rise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of nervous systems, brain damage, diminished learning abilities of children (Oliver, 1997). Lead is also known carcinogen. Therefore, the removal of excess Pb ions from wastewater is essential to protect human and environmental health.

The most widely used methods for removing heavy metals are chemical or electrochemical precipitation (Lai and Lin, 2003; Ozdemir et al., 2005) and ion exchange treatment (Cardoso et al., 2004). It has been reported that some aquatic plants (Axtell et al., 2003), agricultural by-products (Argun et al., 2005; Chuah et al., 2005; Murathan et al., In Press), clay (Márquez et al., 2004), zeolite (Erdem et al., 2004), turba (Ho et al., 1995) and microorganisms (Li et al., 2004) have the capacity to adsorb and accumulate heavy metals.

\* Corresponding author: e-mail: [argun@selcuk.edu.tr](mailto:argun@selcuk.edu.tr), Tel: +90-332-2232058; Fax: +90-332-2410635.

<sup>#</sup> This study has been presented at SEGM-2007 conference.

Tree barks are produced in large quantities at sawmills as a solid waste. It basically contains lignin, cellulose and tannin. Some components of barks, such as phenolic groups of lignin, polysaccharides and tannins, have stained the treated water and greatly increased COD. Several modification techniques have been studied to reduce organic components of natural adsorbent and to increase adsorption capacity (Argun et al., 2007; Horsfall et. al. 2006; Argun and Dursun, 2006; Taty-Costodes et. al. 2003). In this study, we extensively studied the modification of a natural adsorbent (pine bark) with NaOH reagent for Pb removal which was intended to benefit of the NaOH destroying effect on organic components in barks.

## **Material and Methods**

### ***Adsorbents and reagents***

The activated pine tree (*Pinus nigra*) bark with NaOH reagent was used in this study and named as NaOH Activated Bark (NAB). The adsorbent was obtained from the Demir Corporation sawmill in Turkey's Konya city. All the chemical compounds used to prepare the reagent solutions were of analytic reagent grade (Merck, Whitehouse Station, NJ). The stock solution of Pb(II) used in this study (1000 mg/L) was prepared by dissolving PbCl<sub>2</sub> salt in twice-distilled water. Concentrations of the metal solutions ranged from 1 to 100 mg/L. Before mixing these solutions with the adsorbent, we created test solutions with pH values ranging from 2 to 9 (to permit a determination of the optimal pH for adsorption) by adding 0.1 M NaOH or 0.1 M HNO<sub>3</sub>. After we selected the optimal pH, we only tested one pH value in all subsequent adsorption tests.

### ***Instruments and characterization of the adsorbent***

Infrared spectra of bark samples in solid phase were performed using a Fourier transform infrared spectrometer (Spectrum 2000 Explorer, Perkin-Elmer, USA). A thermal stirrer (ZHWHY-200B, ZHICHENG Analytical Co., Ltd) was used for the batch experiments. The metal solution was filtered through 0.45- $\mu$ m membrane filters after settling and it was then analyzed using ICP-AES (Vista AX CCD Simultaneous ICP-AES, Varian, Australia). Structural analyses of this material were applied using following procedures. Two different oven-dried 0.5 g pine bark samples extracted with alcohol-benzene separately and than they were oven dried again. For lignin determination, one of the extractive-free bark samples were exposed to hydrolysis with 72% H<sub>2</sub>SO<sub>4</sub> solution under boiling condition for three times and than oven dried. Other extractive-free bark, firstly delignified by acidified NaClO<sub>2</sub> solution and holocellulose separated from solution. After than NaOH extraction was applied to remind material and separated oven dried material was named as cellulose. The difference between extractive-free barks and separated cellulose is named as hemicellulose. The pH measurements were performed with digital ion analyzer with a combination electrode (Multi 340i, WTW, Weilheim, Germany).

### ***Preparation and modification of adsorbents***

The adsorbent was made of NaOH activated pine bark materials at variable particle sizes. In accordance with the ASTM Method D4749 (ASTM, 1995) the milled particles were sieved for approximately 15 min and then the separated particles were stored. After the sieving, the adsorbent was heated in an oven at 80 – 85°C for 2 hour.

For the activation process, NaOH reagent was used to increase the proportion of active surfaces and to prevent the elution of tannin compounds that would stain the treated water and that greatly increase COD. An accurately weighed and oven dried 25 g of bark materials separately were poured into 500 ml conical flask containing 250 ml 0.1 N NaOH reagent solution and stirred with 200 rpm. After then, the solution was filtered and barks were taken and washed for several times with distilled water. Then the adsorbent was oven dried at 85°C for 2 hour.

## Result and Discussion

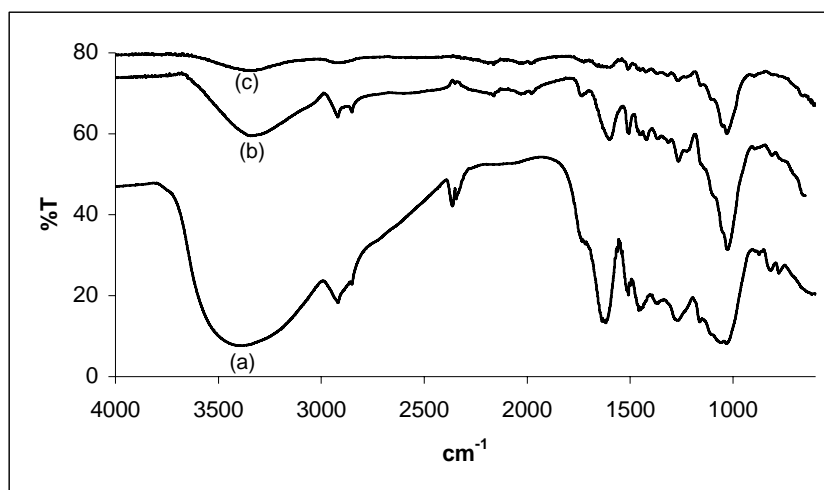
### Effect of modification

Sodium hydroxide was used to increase the proportion of active surfaces and to prevent the elution of tannin compounds that would stain the treated water and that greatly increase COD. Sodium hydroxide solution was increase adsorption efficiency due to increase of negatively charged hydroxyl anions. Hydroxyl ions charge adsorbent surfaces negatively according to Equation 1, and metal cations are adsorbed on the surface (Eq. 2). NaOH solution reacts with phenolic constituents of barks, and occurs phenoxy anions.



where, *Ar* is the functional groups of bark and *M* represents metal ions.

The comparisons of the FTIR spectra of native and modified barks were given in Figure 1. The band at 3700–3200  $\text{cm}^{-1}$  is O-H and N-H stretching of polymeric compounds; 2962–2853  $\text{cm}^{-1}$  interval is symmetric vibration of  $\text{CH}_2$  especially alkenes, 1740–1610  $\text{cm}^{-1}$  is stretching vibration of COO, C-O, 1650–1500  $\text{cm}^{-1}$  band interval is bend vibration of N-H, 1423–1417  $\text{cm}^{-1}$  is of phenolic O-H and C-O stretching of carboxylates, 1350–1200  $\text{cm}^{-1}$  band interval is vibration of C-N of peptidic bond of proteins, 1233  $\text{cm}^{-1}$  band is vibration of carboxylic acids, 1150–1000  $\text{cm}^{-1}$  is vibration of C-O-C and O-H of polysaccharides, 1000–500  $\text{cm}^{-1}$  band interval is Si-H bend vibration and halogenated compounds' (C-X) stretching vibration. FTIR spectrums show that bark constituents mainly composed of polymeric O-H and N-H groups, phenolic O-H and carboxylate groups and O-H groups of polysaccharides. It has been known that all these groups have affinity of heavy metal adsorption.



**Figure 1:** Infrared spectra of pine bark samples. Symbols in the figures are (a), Raw pine bark; (b), NaOH activated pine bark before adsorption; (c), NaOH activated pine bark after adsorption.

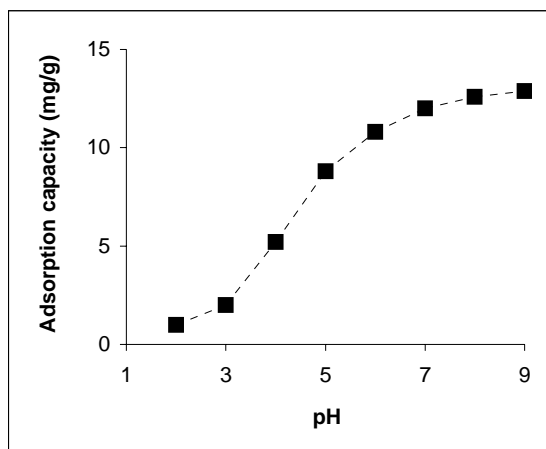
### Effect of pH on Pb(II) removal

The effect of pH on the adsorption of Pb(II) by the NAB is presented in Figure 2. The pH of the aqueous solution was an important parameter that controlled the adsorption process. Adsorption capacity of adsorbent increased remarkably with increasing pH values up to 7, and then increase rate was slower until pH 9 due to precipitation of Pb ions at higher pH values. At pH lower than 8, Pb(II) ions were the dominant species;  $\text{Pb}(\text{OH})_2$  was present at pH higher than 8 (Gaballah and Kilbertus, 1998). Under acidic conditions, the NAB surface will be completely covered with  $\text{H}^+$  ions and the Pb(II) ions cannot compete with them for adsorption sites.

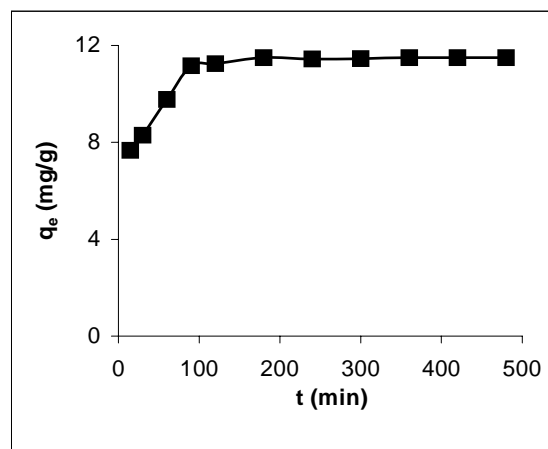
However, with increasing pH, the competition from the hydrogen ions decreases and the positively charged Pb(II) ions can be adsorbed at the negatively charged sites on the adsorbent. The optimum adsorption (12.6 mg/g and 90% removal) was at a pH of 8 with a 90-min contact time, a 2.5 g/L solid-to-liquid ratio, and an initial heavy metal concentration of 35 mg/L. Based on these results, the divalent Pb was bound to active surfaces on the adsorbent by  $O^{2-}$  ions and released  $H^+$  into the solution, thereby decreasing the pH (Gaballah and Kilbertus, 1998):

#### ***Effect of contact time***

For a fixed concentration of heavy metals and a fixed adsorbent mass, the retention of heavy metals increased with increasing contact time. Figure 3 shows that the adsorption rate initially increased rapidly, and that the optimal removal efficiencies were reached within about 90 min: 96%. However, the equilibrium (maximum) value was attained at around 3 h with adsorption rate of 99%. The removal efficiency did not change considerably with increasing contact time after equilibrium had been reached.



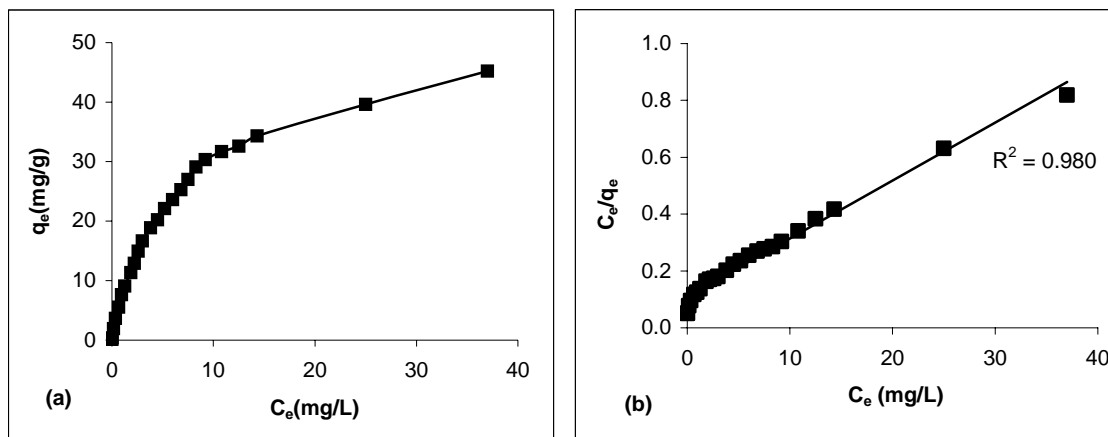
**Figure 2:** Effect of pH on the removal of Pb(II).



**Figure 3:** Effect of contact time on the removal of Pb(II)

#### ***Effect of Pb(II) concentration and determination of maximum adsorption capacity***

Adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption systems since they indicate how the metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of increasing metal concentration. When an adsorbent and metal ion solution is placed in contact, the concentration of metal ions on the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a defined distribution of metal ions between the solid and liquid phases. As can be seen in Fig 3, the minimum contact time between solid and liquid phase required to achieve the process equilibrium is 180 min. Therefore, the Pb adsorption capacities at pH 8 were calculated by means of Langmuir isotherm (Argun et. al., 2007) for 180 min contact time. The resulting adsorption isotherms for the NMB used in this study are shown in Figure 4 (a) and (b). The maximum adsorption capacity based on the Langmuir isotherm was obtained 49 mg/g.



**Figure 4:** (a) Effect of Pb(II) concentration on adsorption capacity of NMB, (b) The linearized Langmuir isotherm for adsorption of Pb(II) by NAB

## Conclusion

In this study, NaOH was used for activating the bark surface and therefore enhance its removal efficiency for Pb(II) ions in comparison to raw bark. It was clearly established that NaOH is an effective method for activation of natural adsorbent. This paper also presents the results of equilibrium and isotherm of the sorption process for removing Pb(II) ions from aqueous solution. NaOH modification decreased the released COD concentration of the bark to acceptable level for wastewater. Operational parameters such as pH, contact time, and initial Pb(II) concentrations of the solution clearly affect the removal efficiency. The maximum Pb(II) removal by the NAB was obtained at pH 8 with the adsorption capacity of 49 mg/g.

**Acknowledgements:** The authors thank the Selcuk University Research Found (BAP) for its financial support of the work undertaken here (Project no: 07701113), that this paper has been derived from a part of Ph.D. thesis of M. Emin ARGUN.

## References

- American Society for Testing and Materials, Method D4749, 1994. Standard Test Method for Performing the Sieve Analysis of Coal and Designating Coal Size, USA.
- Argun, M.E., Dursun, Ş., Özdemir, C., Karatas, M., 2007. Heavy metal adsorption by oak sawdust: thermodynamics and kinetics. *J. Hazard. Mater.* 141, 77-85.
- Argun, M.E., Dursun, Ş., 2006. Removal of heavy metal ions using chemically modified adsorbents. *J. Int. Environ. Appl. Sci.* 1, 27-40.
- Argun, M.E., Dursun, Ş., Gür, K., Özdemir, C., Karatas, M., Dogan, S., 2005. Nickel adsorption on the modified pine tree materials. *Environ. Technol.* 26, 479-488.
- Axtell, N.R., Sternberg, S.P.K., Claussen, K., 2003. Lead and nickel removal using *Microspora* and *Lemna minor*. *Bioresour. Technol.* 89, 41-48.
- Cardoso, V.A., de Souza, A.G., Sartoratto, P.P.C., Nunes, L.M., 2004. The ionic exchange process of cobalt, nickel and copper(II) in alkaline and acid-layered titanates. *Colloid. Surface A: Physicochem. Eng. Aspects.* 248, 145-149.
- Chuah, T.G., Jumariah, A., Azni, I., Katayon, S., Thomas Choong, S.Y., 2005. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. *Desalination* 175, 305-316.
- Erdem, E., Karapinar, N., Donat, R., 2004. The removal of heavy metal cations by natural zeolites. *J. Colloid. Interf. Sci.* 280, 309-314.

- Gaballah, I., Kilbertus, G., 1998. Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks. *J. Geochem. Explor.* **62**, 241-286.
- Ho, Y.S., Wase, D.A.J., Forster, C.F., 1995. Batch nickel removal from aqueous solution by sphagnum moss peat. *Water. Res.* **29**, 1327-1332.
- Horsfall, M., Abia, A.A., Spiff, A.I., 2006. Kinetic studies on the adsorption of Cd<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions from aqueous solutions by cassava (*Manihot sculenta* Cranz) tuber bark waste. *Bioresource Technol.* **97**, 283–291.
- Karatas, M.; Dursun, S., 2006. Heavy metal contamination in drainage system of Konya city in Turkey. *J. Int. Environ. Appl. Sci.* **1**(1-2), 54-62.
- Lai, C.L., Lin, S.H., 2003. Electrocoagulation of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication. *Chem. Eng. J.* **95**, 205-211.
- Li, Q., Wu, S., Liu, G., Liao, X., Deng, X., Sun, D., Hu, Y., Huang, Y., 2004. Simultaneous biosorption of cadmium (II) and lead (II) ions by pretreated biomass of *Phanerochaete chrysosporium*. *Sep. Purif. Technol.* **34**, 135-142.
- Márquez, G.E., Ribeiro, M.J.P., Ventura, J.M., Labrincha, J.A., 2004. Removal of nickel from aqueous solutions by clay-based beds. *Ceram. Int.* **30**, 111–119.
- Murathan, A., Gürü, M., Alicilar, A., In Press. Production of appropriate adsorbent from oak valonia for the adsorption of copper II from aqueous solution. *Fresen. Environ. Bull.*
- Oliver, M.A., 1997. Soil and Human Health: a review. *Eur. J. Soil Sci.* **48**, 573-592.
- Özdemir, C., Karatas, M., Dursun, S., Argun, M.E., Dogan, S., 2005. Effect of MnSO<sub>4</sub> on the chromium removal from leather industry wastewater. *Environ. Technol.* **26**, 397-400.
- Taty-Costodes, V.C., Fauduet, H., Porte, C., Delacroix, A., 2003. Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*. *J. Hazard. Mater.* **B105**, 121–142.