



## Cadmium removal using activated pine bark

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**Abstract:** *In this study we activated pine barks (*Pinus nigra*) by using NaOH and this activated material used for the removal of Cd(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, zeta potential and surface area analyses were examined for the determination of surface properties changes after activation. Maximum adsorption capacity was 50 mg g<sup>-1</sup> at pH 7 and with a 240-min contact time (for 35 mg L<sup>-1</sup> initial concentration and a 2.5 g L<sup>-1</sup> 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, cadmium, 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 & Dursun, 2006). Human uptake of heavy metals takes place mainly through food chains. Cadmium pollution occurs in many industrial wastewaters such as those produced by electroplating, battery industry, pigment and photoconductor productions, plastic stabilizer and fertilizer industry. 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 Cd leads to damage of kidney and renal system, skeletal deformation (Itai-itai), cardiovascular diseases and hypertension (Oliver, 1997). Therefore, the removal of excess Cd 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 & 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.

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

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adsorbent and to increase adsorption capacity (Argun *et al.*, 2007; Horsfall *et al.* 2006; Argun, 2007; Taty-Costodes *et al.* 2003). In this study, we extensively studied the modification of a natural adsorbent (pine bark) with NaOH reagent for Cd 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 Cd(II) used in this study ( $1000 \text{ mg L}^{-1}$ ) was prepared by dissolving CdSO<sub>4</sub> salt in twice-distilled water. Concentrations of the metal solutions ranged from 1 to  $150 \text{ mg L}^{-1}$ . 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). Zeta potential measurements were conducted using a *Zetameter* (Nano ZS, Malvern Inst., UK) equipped with a microprocessor unit. The surface area of the bark was measured by "three point" N<sub>2</sub> gas adsorption method using Quantachrome surface analyzer (Model Autosorb-1, Boynton, Beach, FL). A thermal stirrer (ZHWY-200B, ZHICHENG Analytical Co., Ltd) was used for the batch experiments. The metal solution was filtered through 0.45- $\mu\text{m}$  membrane filters after settling and it was then analyzed using ICP-AES (Vista AX CCD Simultaneous ICP-AES, Varian, Australia). Chemical 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 then 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 then 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 + lignin) 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 (Anon., 1994) 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 hours.

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 2h.

## 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). Probably, some components of the pine bark like abietic acid were dissolved in alkali condition, and adsorbent porosity was increased with this application. NaOH solution may also react with phenolic constituents of barks, and may be phenoxy anions occur.



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

From Table 3 it could be also concluded that all phenolic compounds did not completely extracted during the chemical process. However, they may be explained with the conversion to less soluble species of phenolic compounds or they reacted with the modificant and reticulated within modified barks. Results of chemical and physical analyses of bark properties were given in Table 1 and Fig. 1. During the activation processes, ratio of lignin was increased, but ratios of cellulosic, hemicellulosic and extractive materials were decreased. Chemical modifications dominantly decreased cellulosic and hemicellulosic constituents from bark due to their solubility were more than lignin. Also chemical structures of cellulose and hemicellulose have more affinity to react and dissolve in this chemical modificant. This change is beneficial, because previous researches have demonstrated that heavy metals may be adsorbed by lignin better than by cellulose and hemicellulose (Gaballah and Kilbertus, 1998). The BET specific surface areas and zeta potentials of raw bark and activated barks are comparable, indicating that the activated barks are generally have greater values.

**Table 1:** Chemical and physical analyses of the pine bark sample (oven dry and ash free)

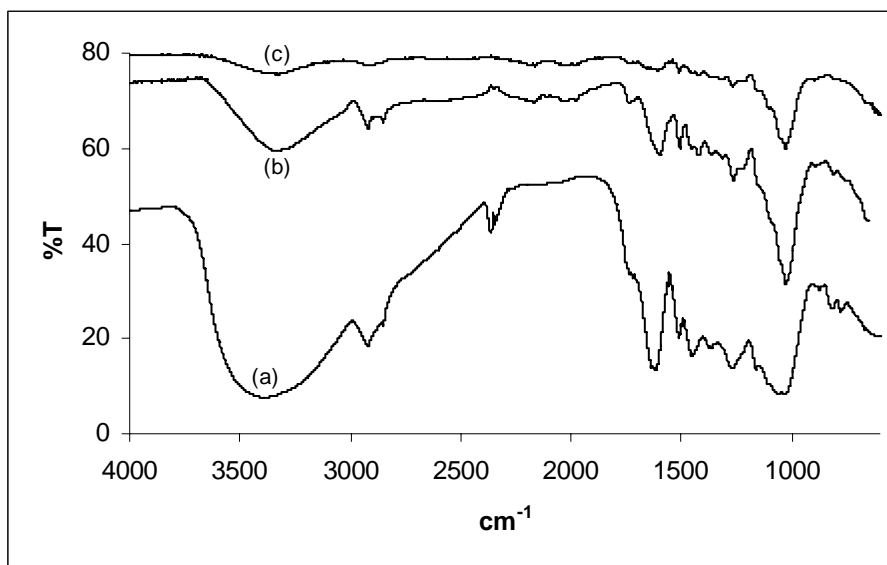
Pine bark types	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Extractives <sup>a</sup> (%)	Zeta potential (mV)	Surface area (m <sup>2</sup> /g)
Raw bark	32.7	41.5	22.8	3.0	-13.9	1.41
NaOH activated	28.5	36	33.2	2.3	-31.6	3.15

The comparisons of the FTIR spectra of native and modified barks were given in Figure 1. The band at 3700–3200 cm<sup>-1</sup> is O-H and C-O stretching of polymeric compounds especially polysaccharides (cellulose); 2962–2853 cm<sup>-1</sup> interval is symmetric vibration of CH<sub>2</sub> especially alkenes, 1740–1610 cm<sup>-1</sup> is stretching vibration of COO and C=O, 1650–1500 cm<sup>-1</sup> band interval is bend vibration of C=C (aromatic skeletal mode of lignin), 1423–1417 cm<sup>-1</sup> is of phenolic O-H and C-O stretching of carboxylates, 1350–1200 cm<sup>-1</sup> band interval is vibration of carboxylic acids, 1150–1000 cm<sup>-1</sup> is vibration of C-O-C and O-H of polysaccharides, 1000–500 cm<sup>-1</sup> band interval is C-H and C-C bend vibration and halogenated compounds' (C-X) stretching vibration. FTIR spectrums show that bark constituents mainly composed of polymeric O-H, 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

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

The effect of pH on the adsorption of Cd(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 Cd ions at higher pH values. At

pH lower than 8, Cd(II) ions were the dominant species; Cd(OH)<sub>2</sub> was present at pH higher than 8 (Gaballah & Kilbertus, 1998). Under acidic conditions, the NAB surface will be completely covered with H<sup>+</sup> ions and the Cd(II) ions cannot compete with them for adsorption sites. However, with increasing pH, the competition from the hydrogen ions decreases and the positively charged Cd(II) ions can be adsorbed at the negatively charged sites on the adsorbent. The optimum adsorption (9.6 mg g<sup>-1</sup>) was at a pH of 7 with a 90-min contact time, a 2.5 g L<sup>-1</sup> solid-to-liquid ratio, and an initial heavy metal concentration of 35 mg L<sup>-1</sup>. Based on these results, the divalent Cd was bound to active surfaces on the adsorbent by O<sup>2-</sup> ions and released H<sup>+</sup> into the solution, thereby decreasing the pH (Gaballah & Kilbertus, 1998).



**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 Cd(II) adsorption.

#### ***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 180 min: 89%. However, the equilibrium (maximum) value was attained at around 4 h with adsorption rate of 99%. The removal efficiency did not change considerably with increasing contact time after equilibrium had been reached.

#### ***Effect of Cd(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 240 min. Therefore, the Cd adsorption capacities at pH 7 were calculated by means of Langmuir isotherm (Argun et. al., 2007) for 240 min contact time. The resulting adsorption isotherms for the NAB used in this study are shown in Figure 4 (a) and (b). The maximum adsorption capacity based on the Langmuir isotherm was obtained 50 mg/g.

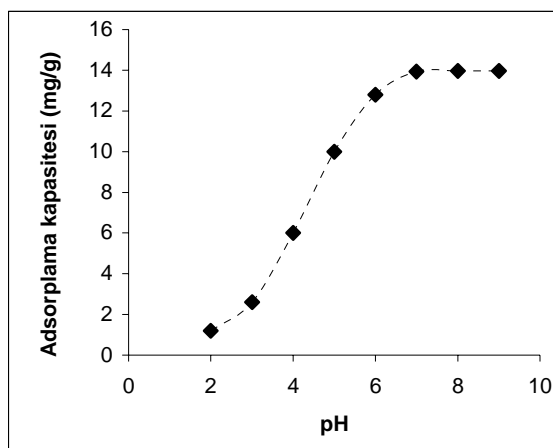


Figure 2: Effect of pH on the removal of Cd(II)

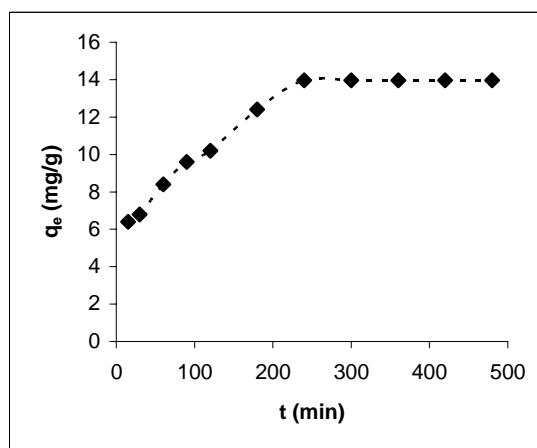
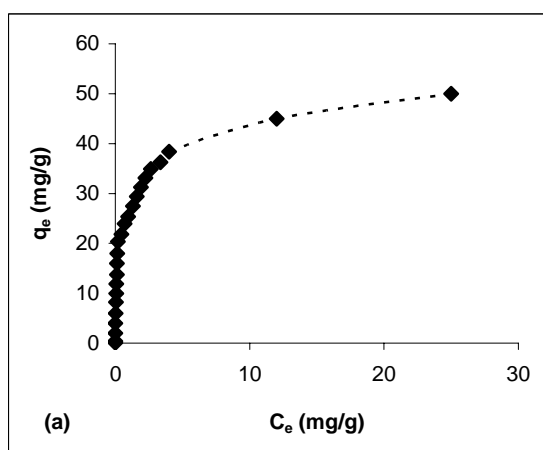
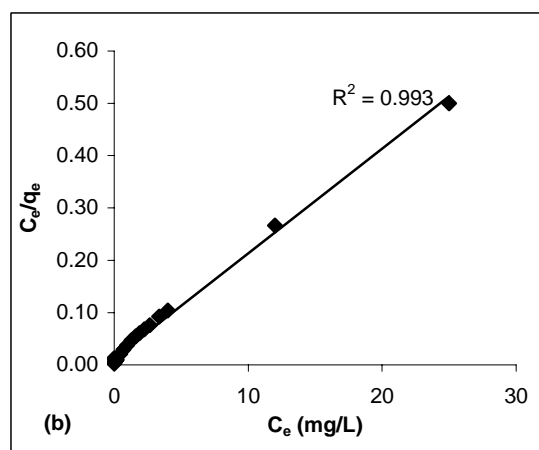


Figure 3: Effect of contact time on the removal of Cd(II)



(a)



(b)

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

## Conclusion

In this study, NaOH was used for activating the bark surface and therefore enhance its removal efficiency for Cd(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 Cd(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 Cd(II) concentrations of the solution clearly affect the removal efficiency. The maximum Cd(II) removal by the NAB was obtained at pH 7 with the adsorption capacity of 50 mg g<sup>-1</sup>.

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