Removal of heavy metal ions using chemically modified adsorbents

Mehmet Emin ARGUN[*], Şükrü DURSUN

Dept. of Environmental Engineering, Engineering & Architecture Faculty, Selcuk University, 42031 Konya, TURKEY

Abstract

In this article, chemical modification methods and its enhancement affect on the adsorption capacity of wood based adsorbents for treatment process has been investigated. HCl, H_2SO_4, HNO_3, NaOH, KOH, acetone, ethanol, chloroform, H_2O_2, Fenton reaction, polymerization, tetra ethylene glycol, diethyl ether, and glycol were used to modification process. Maximum adsorption capacities were obtained by modification of NaOH (98 %), KOH (96 %), HCl (85 %), Fenton (94 %), polymerization (94 %), tetra ethylene glycol (97 %), and diethyl ether (95 %). These modifications decreased soluble organic compounds of wood materials leading to increase in chemical oxygen demand (COD) of water. Adsorption capacities of adsorbents were increase quietly as a result of modification with increase in active surfaces of adsorbents. These adsorbents are suitable for industrial effluent treatment containing cadmium and lead ions. It is important to note that the adsorption capacities of the adsorbents presented in this paper vary, depending on the characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate.

Keywords: Heavy metal; modification; adsorption; removal efficiency

1. Introduction

Environmental pollution and its harmful effect on ecology have been studied intensively during last decade years. Problems of the pollutants removal from wastewater were increased with fast industrialization. These waste waters are produced 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.

The most widely used methods for removing heavy metals are chemical or electrochemical precipitation, both of which pose a significant problem in terms of disposal of the precipitated wastes [Özdemir *et. al.*, 2005; Meunier *et. al.*, 2006], and ion-exchange treatments, which do not appear to be economical [Pehlivan & Altun, 2006]. It has been reported that some aquatic plants

---

[*]Corresponding author: *E-mail address: argun@selcuk.edu.tr Tel: +90 332 223 2057Fax: +90 332 241 0635*

[Keskinkan *et. al.* 2004], wood materials [Shukla *et. al.*, 2002; Argun, in Press], agricultural byproducts [Chuah *et. al.*, 2005], clay [Márquez *et. al.*, 2004], natural zeolite [Erdem *et. al.*, 2004], turba (partially decomposed vegetable matter) [Twardowska & Kyziol, 2003; Ho *et. al.*, 1995], microorganisms [Bai & Abraham, 2002], and other low-cost adsorbents [Dakiky *et. al.*, 2002] have the capacity to adsorb and accumulate heavy metals. Adsorption capacities ranged from 1.51 to 270 mg g^{-1} for Cd(II) and from 3.19 to 425 mg g^{-1} for Pb(II) (Table 1). Although the use of aquatic plants, microorganisms, and wood-based materials such as sawdust and bark increases the COD of water, modification of these adsorbents decreases this problem [Bai & Abraham, 2002]. However, problems with the aforementioned solutions make it necessary to develop easily available, inexpensive, and equally effective alternatives for wastewater treatment.

Table 1: Heavy metal removal capacities (mg g^{-1}) for various methods, and cost comparisons.

Material	Sources	Cu^{2+}	Ni^{2+}	Cr^{6+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Capacity per unit cost (mg US\$$^{-1}$)[a]
Chemical precipitation (NaOH)	Meunier et. al., 2006	9.5	9.6		8.0	7.9	6.2	99, 100, 85, 83, 65
Ion exchange resin (Dowex 50W)	Pehlivan and Altun, 2006	146	138	–	425	154	270	608, 575, 1770, 640, 1124
Ceratophyllum demersum	Keskinkan et. al. 2004	6.2		–	44.8	14.0	–	NA
Modified pine bark	Argun et. al., 2005	–	20.6	–	–	–	–	NA
Natural zeolite	Erdem et. al., 2004	8.9	–	–		8.5	–	NA
Rhizopus nigricans	Bai and Abragam, 2002	–		46.2	–	–	–	NA
Wool	Dakiky et. al., 2002	–	–	41.2	–	–	–	NA
Olive cake	Dakiky et. al., 2002	–	–	33.4	–	–	–	NA
Activated carbon	Üçer et. al., 2006	2.23	–	–	–	1.23	1.51	15, 9, 10
Maple sawdust	Yu et. al., 2001	1.79	–	–	3.19	–	–	NA
Sphagnum moss peat	Ho et. al., 2000	12.4	7.54	–	12.3	–	–	NA
Modified oak sawdust	Argun et. al., 2006	3.22	3.29	1.70	–	–	–	2450, 2500, 1294
Modified pine bark (NaOH)	In this study				11.9		11.2	3132, 2950

NA: Not available

[a] Order of costs matches the order of the ions, from left to right.

Barks are wood based materials which are produced in large quantities at sawmills as a solid waste. These materials contain primarily lignin and cellulose. Interest in the use of bark as an adsorbent has been stimulated by the good results that have been obtained [Gaballah and Kilbertus, 1998]. In this context, pine (*Pinus nigra*) bark is particularly interesting in Turkey because of its high availability and low cost; pine bark costs can be negligible and costs increased a little with

modification such as; 6 $/kg for HCl modification, 9 $/kg for HNO_3 modification, 7.4 $/kg for H_2SO_4 modification, 9 $/kg for HNO_3 modification, 3.84 $/kg for NaOH modification, 33.4 $/kg for acetone modification, 31.2 $/kg for chloroform modification, 60 $/kg for TEG modification, 24 $/kg for DEE modification, 68.75 $/kg for G modification. However other treatment methods are more expensive than modified pine barks mentioned, for example ~US\$96 kg^{-1} for NaOH (a chemical precipitation agent; EMD Chemicals Pellets (ACS) 500 g; US\$48.47), US\$390 kg^{-1} for ion-exchange resins (Dowex(r) 50WX8-100 ion-exchange resin 500 g; US\$195.30), and ~US\$145 kg^{-1} for activated carbon (Charcoal, Activated Coconut, EMD Chemicals 500 g; US\$77.40) [www1.fishersci. com]. In addition, it is a renewable resource, and does not need to be regenerated after it has been used to capture the metals.

However, some components of wood based materials such as phenolic groups of cellulose, hemicellulose, polysaccharides and tannins are also likely to create a high COD in the wastewater. Thus, our goal in the present study was to determine whether modified wood materials would have an acceptable adsorption efficiency for removing Cu(II), Ni(II), and Cr(VI) and would thus offer an effective and economical alternative to more expensive treatments.

2. Materials and Methods

2.1 Adsorbents and reagents

The adsorbents (*Pinus nigra*) were obtained from their own natural resources. Structural analyses of this material were performed using the Yaşar's method [Yaşar, 1999] (Table 2). All the chemical compounds used to prepare the reagent solutions were of analytic grade (Merck, Whitehouse Station, NJ). The stock solutions of the two metals used in this study (1000 mg L^{-1}) were prepared by dissolving weighed quantities of $CdSO_4$ and $PbCl_2$ salts in twice-distilled water. 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_3. After we selected the optimal pH, we only tested one pH value in all subsequent adsorption tests.

2.2 Instruments

A Gallenkamp thermal stirrer was used for the batch experiments (ZHWY-200B, ZHICHENG Analytical Co., Ltd). The metal solution was filtered through 0.45-μm membrane filters after settling (Millipore Corp., Bedford, Mass.). It was then analyzed using an inductively coupled plasma spectrometer (Optima 4300DV ICP, Perkin-Elmer, Boston, MA). The pH measurements

were performed with digital ion analyzer with a combination electrode (Multi 340i, WTW, Weilheim Germany).

Table 2. Structural analyses of the pine bark samples (wt. % daf)[a] and COD created by bark before and after modification.

Adsorbent	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Extractives[b] (%)	COD (mgO$_2$ L^{-1})
Raw bark	32.7	41.5	22.8	3	1800
HCl modification	32.5	38.2	26.8	2.5	90
NaOH modification	28.5	36	33.2	2.3	35.4
CHCl$_3$ modification	29.8	37.5	30.2	2.5	57.4
Fenton modification	32.0	37.5	28.2	2.3	88
Polymer modification	32.5	40.0	24.8	2.7	95
TEG modification	32.2	37.7	27.6	2.5	88
DEE modification	31.5	37.2	29.1	2.2	86
Glycol modification	32.6	40.5	24.2	2.7	107

[a] daf: dry and ash free.

[b] Alcohol–benzene extractives.

2.3 Preparation and modification of adsorbents

The adsorbent used in this study was pine bark with a range of particle sizes. In accordance with ASTM Method D4749 [ASTM, 1994]. We sieved the barks through a range of sieves, and used only the particles that passed through a 0.25-mm mesh in our study. The sieves were shaken for approximately 15 min, and then the separated particles were stored. After sieving, the adsorbents were heated in an oven at 80–85 ^{o}C for 2 h.

For the modification process, acids, bases, organic solvents, polymerization, and Fenton reaction were 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. First, previously determinated modificant solutions were prepared. An accurately weighed (± 0.001 g) 25-g sample of oven-dried bark was washed several times with distilled water to remove any particles adhering to the surface and any water-soluble particles, then was oven-dried again at 85°C. Following this operation, individual bark samples were poured into 500-mL conical flasks containing 250 mL of modificant solution, and then were shaken at 200 rpm for 4 h at 50°C. The mixture was left overnight, and then was filtered to remove the sorbent, which was washed several times with distilled water to provide neutral pH. The adsorbents were then oven dried at 85°C for 2 h. The maximum removal efficiency by this material (i.e., the sample that showed the greatest weight

increase as a result of adsorption of the metals) was used to select that would be used in subsequent modification of the bark**.**

2.3.1 Modification with acids and bases

First 0.1 N HCl, HNO$_3$, and H$_2$SO$_4$ acid solutions and 1 N NaOH and KOH base solutions were prepared and then modification carried out according to above mentioned methods.

2.3.2 Modification with organic solvents

Organic solvents were used for the modification process. At first, each organic solvents were prepared as 25 % solutions. After then acid modified barks were exposed to related organic solvents during 4 hour at 50°C. The mixture was left overnight, then was filtered to remove the sorbent, which was washed several times with distilled water to provide neutral pH. Other procedures are same as mentioned above.

2.3.3 Modification with polymerization

Pine bark was grafted with polyacrylamide using the procedure described by Shigetomi *et al.* (1980). About 25.0 g sawdust was immersed in 250 ml aqueous solution containing 2.5 g N,N^1-methylenebisacrylamide and 1.5 g potassium peroxydisulphate. To the mixture then 7.5 g acrylamide was added and this was stirred vigorously at 70°C. The polymerized product was then washed with water and dried at 80°C. Other procedures are same as mentioned above.

2.3.4 Modification with Fenton reactions

Fenton's reagents were also used for the modification process. At first, Fenton's reagents solutions, which Fe^{2+}/H$_2$O$_2$ ratio of 0.01 to 10, were prepared. An accurately weighed and oven dried 25 g of bark materials separately were poured into 500 ml conical flask containing 250 ml Fenton's reagents solutions and stirred with 200 rpm for 4 hour at pH 3. In this content, the Fe^{2+}/H$_2$O$_2$ ratio of maximum removal efficiency obtained was chosen as the required ratio (0.01) for the modification.

3. Results and Discussion

3.1 Use of acids for modification

Acids were 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 (Chemical Oxygen Demand). Table 3 shows that removal efficiencies were obtained 85% and 88 % with HCl modification, 76 % and 76 % with H_2SO_4 modification and 75% and 77 % with HNO_3 modification for Cd (II) and Pb (II) respectively. It was concluded that adsorption efficiency decreased with the strength of the acidity. For the adsorption of heavy metal cations, adsorbent surfaces must be charged negatively. Although acid modification decreased the organic content of adsorbent and increased porosity, positively charged surfaces with hydrogen ions prevented to extra increase of adsorption. Eq. 1 was more dominant than Eq. 2 in the solution for the existence of H^+ ions like explained above.

$$Ar\text{-}OH^- + H^+ = Ar\text{-}OH_2 \tag{1}$$
$$Ar\text{-}OH^- + M^{2+} = Ar\text{-}O\text{-}M + H^+ \tag{2}$$

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

3.2 Use of bases for modification

Bases were used same purposes like acid modification. However bases were also increase adsorption efficiency due to negatively charged hydroxyl anions. Hydroxyl ions charge adsorbent surfaces negatively according to Equation 3 and metal cations adsorbed on the surface (Equation 4). NaOH solution reacts with phenolic constituents of barks and occurs phenoxy anions.

$$ArOH + NaOH = ArO^-Na^+ + H_2O \tag{3}$$
$$2ArO^- + M^{+2} = Ar_2O_2M \tag{4}$$

where, *Ar* is the phenolic groups of lignin and tannin, and *M* represents metal ions.
Removal efficiencies were obtained as 98 % and 99 % with NaOH modification and 96 % and 98 % with KOH modification for Cd (II) and Pb (II) respectively (Table 3).

3.3 Use of organic solvents for modification

Bark contents such as polymeric lignin dissolves in organic solvents more easily than water. Solvation is effected by the intermolecular forces such as, hydrogen bonding, ion-dipole forces,

dipole-dipole forces, dipole-induced dipole forces, electron pair donor-electron pair acceptor interactions, solvophobic interactions etc. (Reichard, 1988). Acetone, ethanol, chloroform, formaldehyde, tetra ethylene glycol, diethyl ether and glycol were used for this purpose. They can break off the polymeric constituents of barks such as tannin, lignin and cellulose and so prevent the elution of phenolic compounds that would stain the treated water. Among bark extractives, polar materials (tannins, polyphenols, glycosides) are generally three to five times as abundant as nonpolar constituents (fats, waxes, terpenes, steroids, etc.). While some of these chemicals have polar groups such as acetone, ethanol, and glycol; others have non-polar groups such as chloroform, tetra ethylene glycol, and diethyl ether. From Table 3 it was observed that non-polar solvents increased adsorption efficiency more than polar solvents. This may be explained with the interaction of non-polar solvents and non-polar constituents of barks such as tannin, fats, and waxes (like solves like). Non-polar constituents of bark do not increase adsorption and extracted of them will increase active surface percent while interference of COD to water will decrease. However, polar constituents such as cellulose, phenols, simple sugars, starch and simple amino acids were extracted with polar solvents. Modification with polar solvents will decrease adsorption capacity because of polar constituents of bark increase adsorption capacity. Removal efficiencies were obtained as 65.5% and 69% with acetone modification, 61 % and 63 % with ethanol modification, 82 % and 85 % with chloroform modification, 97 % and 98 % with TEG modification, 95 % and 97 % with DEE modification, and 90 % and 94 % with G modification for Cd(II) and Pb(II) respectively.

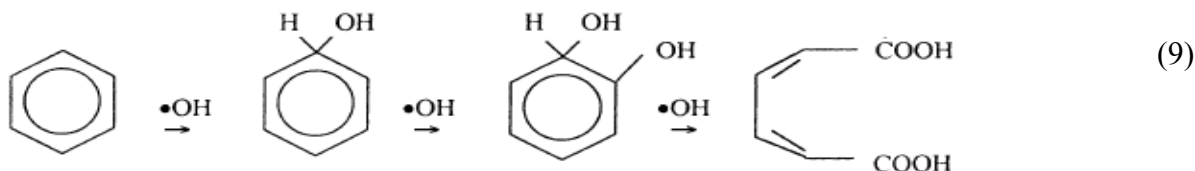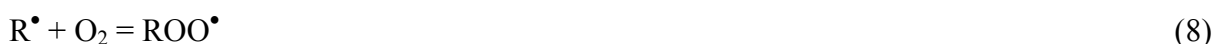### 3.4 Use of polymerization for modification

In most chelating adsorbents, the functional groups with the donor atoms are attached to polymeric matrices that are fixed as part of a three-dimensional network held by cross-linking compounds (Sengupta et al., 1991). Optimization of arrangement and distribution of immobilized ligands in the carrier to control the affinity of chelating adsorbents for a particular metal has been the concern of past researches on this field (Melby, 1975; Warshawsky, 1986).

In this research we have applied graft polymerization to modify barks for heavy metal adsorption. Graft polymerization has been a favorite method for surface modification of polymers for a variety of end uses (Iwakura et al., 1966; Ikada et al., 1995). Adsorption of ions, including toxic heavy metals, is one application that has been explored in detail (Navarro et. al., 1999; Saito et al., 1991). The process involves the generation of free radicals on suitable polymeric matrices and then allowing these free radicals to serve as macro-initiators for the polymerization of monomers containing complexing agents onto the matrix. For our initial procedure, graft polymerization was

not directly used. Instead, a two stage modification scheme was conducted (Iwakura et al., 1966). At first stage acid modification were processed to remove of soluble organics which leads to color. Secondly, product was grafted with polyacrylamide to improve adsorption capacity. Polymerized pine bark had an adsorption capacity of 94 % for Cd(II) and 97 % for Pb(II) as shown in Table 3 while COD relase to water was 95 mg/L.

3.5 Use of Fenton for modification

Ferrous iron and hydrogen peroxide are commonly known as Fenton's reagent. Hydrogen peroxide and ferrous ions are usually more stable in a strong acid. However, if hydrogen peroxide is added to an aqueous system containing an organic substrate and excess ferrous ions in a strong acid, a complex redox reaction (Ahn et. al.,1999; Neyens and Baeyens, 2003) as in Eqs. 5–8, and Eq. 9 will occur:

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + HO^{\bullet} \tag{5}$$

$$RH + HO^{\bullet} = H_2O + R^{\bullet} \tag{6}$$

$$R^{\bullet} + H_2O_2 = ROH + OH^{\bullet} \tag{7}$$

$$R^{\bullet} + O_2 = ROO^{\bullet} \tag{8}$$

(9)

Hydroxyl radicals (oxidation potential: 2.8 V) are stronger oxidants than ozone and H_2O_2. The Fenton reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic constituents of bark (Neyens and Baeyens, 2003). A great potential of Fenton reaction among advanced oxidation methods has drawn more and more attention. The Fenton reaction has also several important advantages such as a short reaction time among all advanced oxidation processes, iron and H_2O_2 are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easily to run and control. Fenton reactions mentioned above destroyed complex organics and phenolic structures of barks, which leads to COD and color, and increased active surfaces for adsorption. The removal efficiencies for Cd(II) and Pb(II) by Fenton modified barks were obtained as 94 % and 96 % respectively.

Table 3: The effect of modification processes on pine barks for increasing adsorption capacity (bark dose: 2.5 g/L; shaking speed: 200 rpm; contact time: 60 min.)

| Modification processes	Initial metal ion conc. (mg/L)		Final metal ion conc. (mg/L)		Removal (%)		COD (mg/l)		qe (mg/g)		pH_i	pH_e
	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}		
Raw bark (RB)	28	30	8.39	8.4	**70**	**72**	1820		7.8	8.6	7	6
RB + 1 N HCl	28	30	4.14	3.6	**85.2**	**88**	90	88	9.54	10.6	6	3
RB + 0.1 N H$_2$SO$_4$	28	30	6.75	7.2	**75.8**	**76**	95	95	8.5	9.12	5	3
RB + 0.1 N HNO$_3$	28	30	7.0	6.9	**75**	**77**	95	93	8.4	9.24	5	3
RB + 0.1 N NaOH	28	30	0.08	0.3	**98**	**99**	35.4	35.2	11.2	11.9	7	6.2
RB + 0.1 N KOH	28	30	0.84	0.66	**96**	**97.8**	35	35	10.9	11.7	7	6
RB + %25 Acetone	28	30	9.65	9.3	**65.5**	**69**	75.4	75	7.3	8.3	5	2
RB + %50 Acetone	28	30	10.72	10.5	**61.7**	**65**	76	75	6.9	7.8	5	2
RB + %25 Acetone + 1N HCl	28	30	9.32	9	**66.69**	**70**	82	80	7.5	8.4	5	2
RB + %25 Acetone + 1N HCl + 0.1 N NaOH	28	30	0.087	0.45	**98**	**98.5**	48.4	48	11.2	11.8	5	3
RB + %25 Acetone + 0.1 N NaOH	28	30	2.71	1.8	**90.3**	**94**	88	85	10	11.3	7	5
RB + 0.1 N NaOH + %25 Astn	28	30	0.02	0.03	**99.9**	**99.9**	35	35	11.2	12	7	6
RB + %50 Ethanol	28	30	10.88	11.1	**61.11**	**63**	21	21	6.85	7.6	7	7
RB + %50 H$_2$O$_2$	28	30	12.10	12	**56.74**	**60**	53.8	53.8	6.4	7.2	4	4
RB + 4M CHCl$_3$	28	30	5.01	4.5	**82**	**85**	57.4	57.4	9.2	10.2	7	6.6
RB + Fenton (Fe/ H$_2$O$_2$=0.01)	28	30	1.68	0.6	**94**	**98**	88	88	10.5	11.7	5	3
RB + Pol	28	30	1.65	0.9	**94**	**97**	95.3	95	10.5	11.6	6.5	6
RB + %25 TEG	28	30	0.71	0.6	**97**	**98**	88	88	10.9	11.8	7.5	7
RB + %25 DEE	28	30	1.28	0.9	**95**	**97**	86	85	10.7	11.6	7.5	7
RB + %25 G	28	30	2.80	1.8	**90**	**94**	107	105	10	11.3	7.5	7
Activated Carbon	28	30	4.83	3.6	**83**	**88**	45	42	9	10.6	7	6
Zeolite	28	30	0.21	0.3	**99**	**99**	25	25	11	11.9	7	6
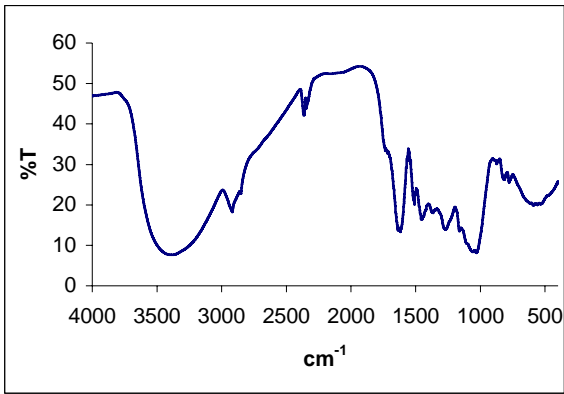
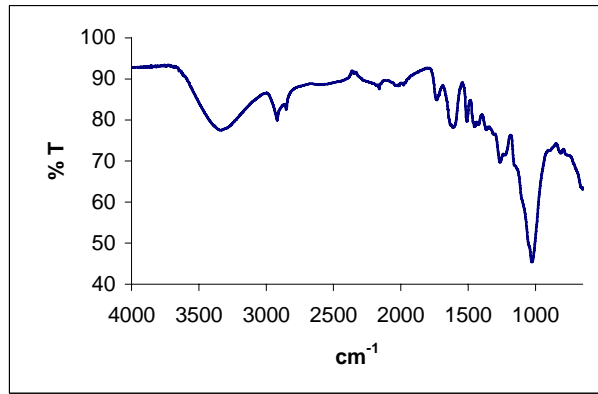**Fig. 1:** ATR spectrum of raw pine bark.

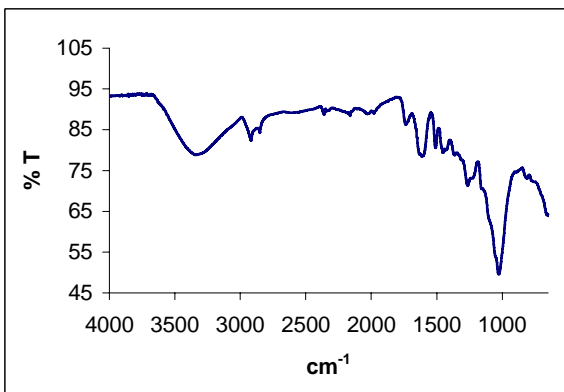**Fig. 2:** ATR spectrum of TEG treated pine bark.

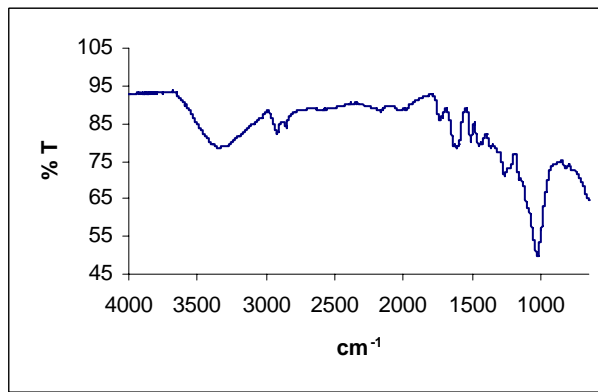**Fig. 3:** ATR spectrum of DEE treated pine bark.
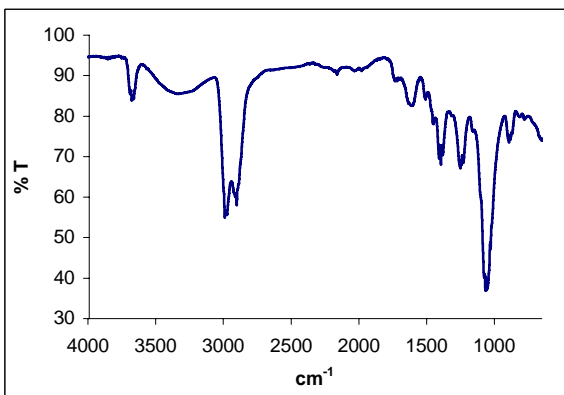

Fig. 4: ATR spectrum of G treated pine bark.

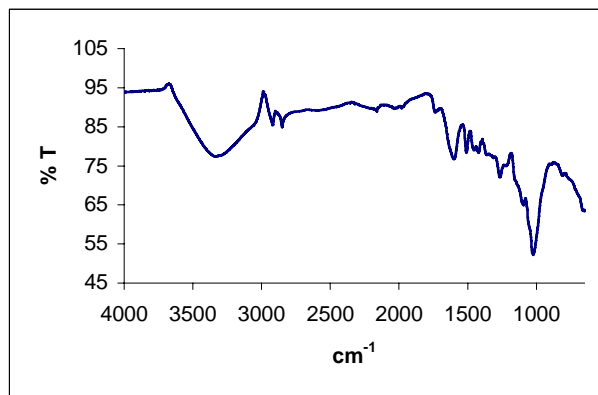**Fig. 5:** ATR spectrum of polymer treated pine bark.
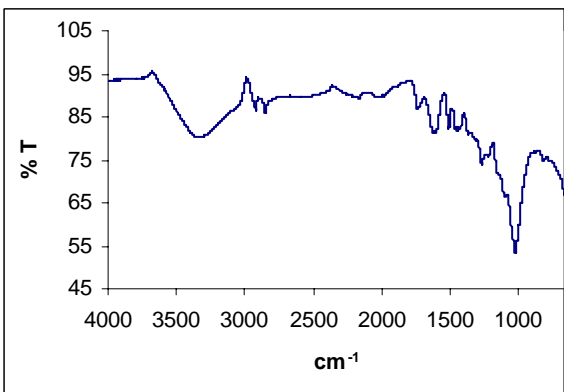

Fig. 6: ATR spectrum of HCl+NaOH treated pine bark.

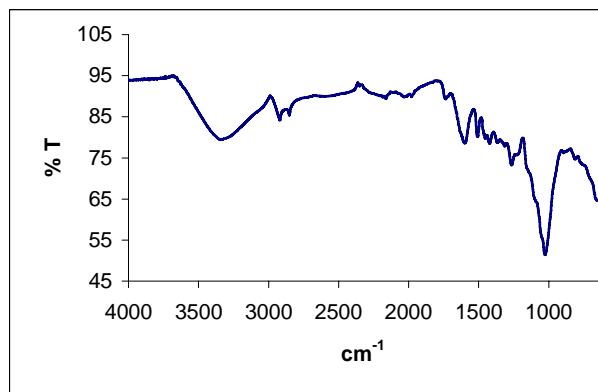**Fig. 7:** ATR spectrum of NaOH+H_2SO_4 treated pine bark.

Fig. 8: ATR spectrum of NaOH treated pine bark.

3.6. Properties of bark

The comparisons of the ATR spectra of native, modified barks were given in Figs. 1–12. The band at 3700–3000 cm^{-1} is O-H and N-H stretching and 3400-3200 cm^{-1} is stretching of polymeric compounds; 2962-2853 cm^{-1} interval is symmetric vibration of CH$_2$ especially alkenes, 1740–1610 cm^{-1} is stretching vibration of COO, C-O, 1650-1500 cm^{-1} band interval is bend vibration of N-H, 1423–1417 cm^{-1} is of phenolic O-H and C-O stretching of carboxylates, 1350-1200 cm^{-1} band interval is vibration of C-N of peptidic bond of proteins, 1233 cm^{-1} band is vibration of carboxylic acids, 1150–1000 cm^{-1} is vibration of C-O-C and O-H of polysaccharides, 1000-500 cm^{-1} band interval is Si-H bend vibration and halogenated compounds' (C-X) stretching vibration. ATR spectrums also shows 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.
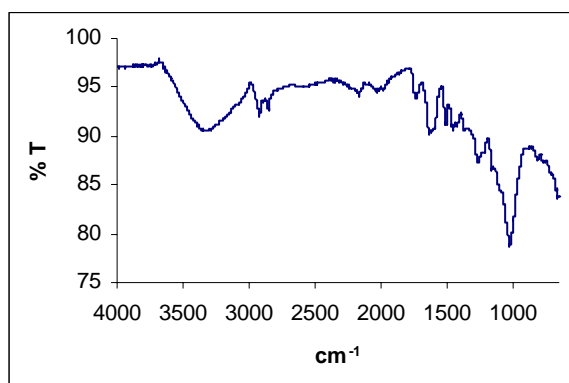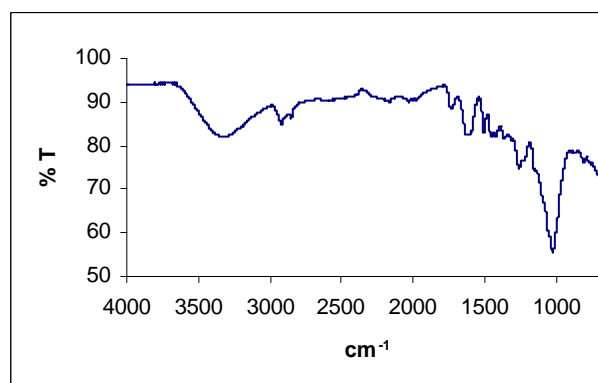

Fig. 9: ATR spectrum of acetone treated pine bark.
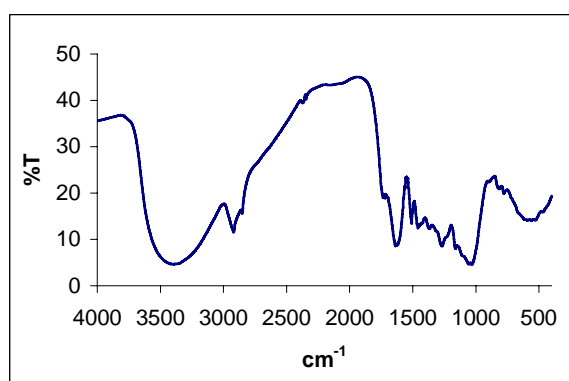

Fig. 10: ATR spectrum of CHCl$_3$ treated pine bark.

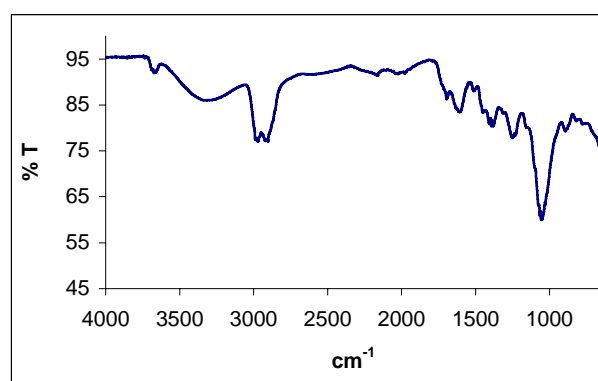**Fig. 11:** ATR spectrum of Fenton treated pine bark.

Fig. 12: ATR spectrum of H$_2$O$_2$ treated pine bark.

4. Conclusions

The present study clearly establishes that pine bark is an effective adsorbent for Cd(II) and Pb(II) removal from aqueous solutions. The results obtained show that the sorption of lead is higher than that of cadmium. Moreover, both sorption capacity and sorption rate are strongly dependent on

the modification method, initial concentration in heavy metals, initial pH of solution, and bark concentration.

It was observed that modification of bark was applicable and decreased some constituents of bark which leading to increase in COD. Optimum modification processes were designated with the use of NaOH (98 %), KOH (97 %), HCl (85.2 %), Fenton (94 %), polymerization (94 %), tetra ethylene glycol (97 %), and diethyl ether (97 %).

It can be concluded that the use of bark as an adsorbent may be an alternative to more costly materials such as activated carbon and ion exchange for the treatment of liquid wastes containing metal ions. Moreover, the rapid uptake allows considering carrying out the sorption of heavy metals on column filled with this bark because the contact time between the metal solution and the adsorbent is generally short in this process.

References

Ahn D.H., Chang W.S., Yoon T.I. (1999). Dyestuff wastewater treatment using chemical oxidation, physical adsorption and fixed bed biofilm process. Process Biochemistry 34, 429–439.

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 S., Özdemir C., Karatas M. (2006). Heavy metal adsorption by modified sawdust: Thermodynamics and kinetics. J. Hazard. Mater. In Press.

Argun M. E., Removal of heavy metal ions using chemically modified adsorbents, *PhD. Thesis*, Selçuk University Graduate School of Natural and Applied Science, Selçuklu-Konya, Turkey, In Press.

Argun M.E., Dursun S., Gür K., Özdemir C., Karatas M., Dogan S. (2005). Nickel adsorption on the modified pine tree materials, Environ. Technol. 26, 479-488.

Bai R.S., Abraham T.E. (2002). Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. Water Research 36, 1224–1236.

Chuah T.G., Jumasiah 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.

Dakiky M., Khamis M., Manassra A., Mer'eb M. (2002). Selective adsorption of chromium VI in industrial wastewater using low-cost abundantly available adsorbents. Adv. Environ. Res. 6, 533-540.

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., Mckay G., (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Res. 34, 735-742.

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.

https://www1.fishersci.com

Ikada Y., Zhang J., Kato K., Uyama Y. (1995). Surface graft polymerization of glycidyl methacrylate onto polyethylene and the adhesion with epoxy resin. J. Polym. Sci. Part A Polym. Chem. 33, 2629-2638.

Iwakura Y., Kurosaki T., Uno K., Imai Y. (1964). Reactive fiber. II. Chemical reactivities of cellulose fiber grafted with glycidyl methacrylate. J. Polym. Sci. Part C Polym. Symp. 0(4), 673-698.

Keskinkan O., Goksu M.Z.L., Basibuyuk M., Forster C.F. (2004). Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*). Bioresour. Technol. 92, 197-200.

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.

Melby R.L. (1975). Polymers for selective chelation of transition metal ions. J. Am. Chem. Soc. 97(14), 4044-4051.

Meunier N., Drogui P., Montané C., Hausler R., Mercier G., Blais J.-F. (2006). Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. J. Hazard. Mater., *In Press*.

Navarro R.R., Sumi K., Matsumura M. (1999). Improved metal affinity of chelating adsorbents through graft polymerization. Wat. Res. 33(9), 2037-2044.

Neyens E., Baeyens J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. J. Hazard. Mater. 98(1-3), 35-50.

Özdemir C., Karatas M., Dursun S., Argun M.E., Dogan S. (2005). Effect of $MnSO_4$ on the

chromium removal from leather industry wastewater. Environ. Technol. 26, 397-400.

Pehlivan E., Altun T. (2006). The study of various parameters affecting the ion exchange of Cu2+, Zn2+, Ni2+, Cd2+, and Pb2+ from aqueous solution on Dowex 50W synthetic resin. J. Hazard. Mater. B134, 149-156.

Reichard C. (1988). Solvents and solvent effects in organic chemistry. H.F. Ebel (ed.), VCH, Weinheim, Germany.

Saito K., Iwata H., Furusaki S. (1991). Adsorption characteristics of an immobilized metal affinity membrane. Biotechnol. Prog. 7, 412-418.

Sengupta A.K., Zhu Y,. Hauze D. (1991). Metal (II) ion binding onto chelating exchangers with nitrogen donor atoms: some new observations and related implications. Environ. Sci. Technol. 25, 481-488.

Shukla A, Zang Y.H., Dubey P., Margrave J.L., Shukla S.S. (2002). The role of sawdust in the removal of unwanted materials from water. J. Hazard. Mater. 95, 137-152.

Twardowska I., Kyziol J. (2003). Sorption of metals onto natural organic matter as a function of complexation and adsorbent–adsorbate contact mode. Environ. Int. 28, 783-791.

Üçer A., Uyanik A., Aygün Ş.F. (2006). Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon. Separation and Purification Technology 47, 113–118.

Warshawsky A. (1986). Modern research in ion exchange. In Ion Exchange: Science and Technology, ed. A. E. Rodriguez. NATO ASI Series, Martinus Nijho. Publishers, Boston, MA, pp. 67-116.

Yaşar S. (1999). Beurteilung der technologischen Qualität von Cellulose, Hemicellulosen und Lignin bei *Miscanthus* 'Giganteus' und *Cannabis sativa* L. Dissertation der Universität für Bodenkultur Wien.

Yu B., Zhang Y., Shukla A., Shukla S.S., Dorris K.L. (2001). The removal of heavy metals from aqueous solutions by sawdust adsorption—removal of lead and comparison of its adsorption with copper. J. Hazard. Mater. B84, 83–94.