

MECHANISM OF CADMIUM ION REMOVAL BY BASE TREATED JUNIPER FIBER

Soo-Hong. Min, J. K. Park

Department of Civil and Environmental Engineering, University of Wisconsin-Madison, USA

James S. Han, Eun Woo. Shin

USDA-Forest Service Forest Products Laboratory, Madison, WI., USA

SUMMARY

Pinyon juniper, *Juniperus Monosperma*, is a small-diameter and underutilized (SDU) lignocellulosic material. Evaluated were efficacy of base-treated juniper fiber (BTJF) sample for cadmium (Cd^{2+}) sorption and the viability of juniper fiber as a sorbent for the removal of Cd^{2+} from water. Fourier Transform Infrared Spectroscopy (FTIR) analysis indicated that carboxylate ion is a major functional group responsible for Cd^{2+} sorption and the apparent ideal sodium hydroxide (NaOH) concentration for the base treatment was approximately about 0.5 M. From the batch sorption isotherm test, it was found that equilibrium sorption data were better represented by the Langmuir model than by the Freundlich model. After the base treatment, despite a decrease in specific surface area from 0.2864 to 0.2450 m^2/g , the maximum Cd^{2+} sorption loading, Q_{max} , was greatly improved from 9.18 to 29.54 mg/g. A pseudo-second order kinetic model, assuming that the sorption follows the Langmuir equation, fitted well for the sorption of Cd^{2+} onto BTJF. Alkalinity of treatment was the major parameters influencing the kinetics of the sorption reaction. The BTJF could be an inexpensive and an efficient sorbent for the removal of heavy metals in storm water runoff due to a rather strong heavy metal (Cd^{2+}) binding ability and fast kinetics.

Key words: cadmium, juniper, saponification, Fourier transform infrared (FTIR) spectroscopy, isotherms, kinetics.

1. INTRODUCTION

Cadmium ion (Cd^{2+}) is one of the main heavy metal pollutants in storm water runoff, has been classified as a very toxic heavy metal that can cause serious damage to kidneys and bones [1]. However, all conventional methods of heavy metals removal such as chemical precipitation, ion exchange, reverse osmosis and adsorption on activated carbon are expensive and are not suitable for low concentration, large volume waste streams such as storm water runoff.

Lignocellulosics, one of the low cost unconventional sorbents, have been examined for potential use as inexpensive heavy metal removal sorbents [2]. However, their ion exchange or adsorption capacities were lower than other sorbents. Due to this drawback, chemical modifications have been attempted to various lignocellulosic fibers with different chemicals [3]. Recently, some scientists chose a simple and low cost base treatment (saponification) process to increase heavy metal removal capacity of lignocellulosic fibers [4,5]. Tiemann *et al.* (1999)[4], using X-ray absorption spectroscopic analysis (XANES and EXAFS), revealed that the carboxyl group played an important role in the binding of heavy metals. However, there have been few studies on the optimum base (NaOH) concentration chemical modification.

Pinyon Juniper, *Juniperus Monosperma*, was selected as an appropriate Cd^{2+} sorbent because it has relatively high heavy metal sorption capacity compared to other lignocellulosic fibers [6]. Also, juniper is a small-diameter and underutilized (SDU) material, Juniper woodland, concentrated in the South Western United States, covers approximately 60 million acres of land. Over the years, large areas of range land have become overgrown with these trees [7].

In this study, Fourier Transform Infrared Spectroscopy (FTIR) was employed to quantify the carboxylic group which is a major functional group presumably responsible for the removal of Cd^{2+} and to pinpoint the degree of

alkalinity of substrate to maximize Cd^{2+} removal and at the same time to minimize the exudation of the extractives from the sample during the NaOH treatment process. In addition, a series of batch sorption tests were performed to investigate parameters that could affect Cd^{2+} sorption reaction on the sorbents and to evaluate the viability of BTJF as a sorbent for the removal of Cd^{2+} from water.

2. MATERIALS AND METHODS

2.1 Materials

Pinyon juniper trees, *juniperous monopeuna*, were randomly collected from New Mexico, bark and wood were chipped together, and then ground to pass through a 3-mm screen using a Wiley Mill. An aliquot of 250 mL of 1 M NaOH solution was added to 500 mL Erlenmeyer flask containing 20 g of juniper powder and agitated for 30 min (BTJF1-30 min) and 24 hrs (BTJF1-1 day), respectively. The excess alkaline solutions were decanted, and the media were washed continuously with distilled water until the pH of the washed water became less than 8. Finally, the Base-Treated Juniper Fiber (BTJF) samples were air-dried at an ambient temperature over 3 days and then ground to pass through a 0.66-mm screen for homogenization.

2.2 Surface Area Measurement

The specific surface area of juniper fiber and BTJFs was measured by BET method [8] using an ASAP 2010 Accelerated Surface Area and Porosimetry System (Micrometries®, USA) with nitrogen gas as the analysis gas.

2.3 FTIR Analysis

Milled samples were sieved through a 0.18-mm sieve and then dried overnight at 105°C. Samples were pulverized with oven-dried KBr and pressed into pellets. FTIR spectra were collected on a Mattson Galaxy 5020 (Mattson instruments, Madison) using 64 scans between 400 to 4000 cm^{-1} , triangular apodization and a resolution of 4 cm^{-1} . In order to compare one spectrum to another, spectra were baseline corrected at 840,2000, and 4000 cm^{-1} . Then, peak absorbances were measured from the baseline.

2.4 Sorption Isotherm Model

Batch sorption isotherm experiments were conducted as follow. Various concentrations of Cd^{2+} solutions were prepared by serial dilution of standard 1,000 mg/L Atomic Adsorption Spectrophotometer (AAS) reference solution between 0 to 200 mL/L. The mixtures of 0.2 g BTJF samples with 50 mL of Cd^{2+} solutions of various concentrations were shaken at 150 rpm for one day at 25°C. The mixtures were taken out from the shaker and the solutions were filtered by pore size 0.45- μm membrane filters using syringes. Then, measured for dissolved Cd^{2+} concentration and Ca^{2+} concentration which was released from polysaccharide by means of Inductively-Coupled Plasma (ICP) emission (ICP: Jobin Yvon, Ultima ICP-AES). The final concentration (C_e) mg/L measured differs according to the different C_o . The uptake capacity (q_e) which is the amount of Cd^{2+} sorbed at equilibrium (mg/g) was calculated by mass balance between C_o and C_e . Because q_e of BTJF1-1 day constant in the pH range of 4 to 7, the whole pH of influent and effluent solutions of the following isotherm and kinetic experiments were remained in that range [9].

A characteristic of Langmuir isotherm is that the loading of sorbate onto the sorbent approaches a limiting value, Q_{max} , as the concentration increases. This corresponds to monolayer coverage of the adsorbent surface with a Langmuir constant, b , related to the free energy of adsorption:

$$q_e = \frac{bQ_{max}C_e}{1 + bC_e} \quad (1)$$

where b is Langmuir constant (L/g) and Q_{max} is maximum adsorbate loading (g- adsorbate/g adsorbent).

The Freundlich isotherm is empirical and used for heterogeneous surface energies:

$$q_e = KC_e^{1/n} \quad (2)$$

where K (L/mg), a measure of sorption capacity, and $1/n$, a measure of sorption intensity, are Freundlich constants. To obtain the best estimate of all constants for the Langmuir isotherm and Freundlich isotherm, data were fitted with nonlinear regressions using a least squares fitting program (Origin 7.0, Microsoft).

2.5 Sorption Kinetic Model

The kinetic experiment was performed by the following method. Four or 10 g of media were mixed in the predetermined concentrations of Cd^{2+} solution vigorously with a magnetic stirrer throughout the experiment. The pH ranged from 4.2-4.6 and the temperature of the solution was 25°C. After the media were mixed in the solution, each 8 mL of filtered sample was collected at proposed time intervals then analyzed for metal elements with the ICP.

Because all the correlation coefficients of the pseudo second order rate model gave the best fit compared with other kinetic models, k of sorption was determined from the pseudo second order rate equation. This model assumed that the sorption follows the Langmuir equation [10].

The kinetic rate equations can be written as follows [10].

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad \text{-----} \quad (3)$$

where q_t is the amount of Cd^{2+} sorbed at time t (mg/g) and k is the equilibrium rate constant of the second order sorption (g/mg·min).

The initial sorption rate, h (mg/g·min), is defined as:

$$h = kq_e^2 \quad \text{-----} \quad (4)$$

The q_e and h values were determined from a plot of t/q_t against t .

3. RESULTS AND DISCUSSION

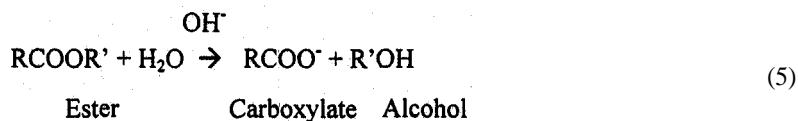
3.1 Carbohydrate composition and characteristics of the juniper fibers

	Sample				
^a Composition (%)	BTJF1-1 day	Juniper	Bark	Sapwood	Hearwood
Klason lignin	34.8	36.5	35.3	36.1	39.9
Arabinan	2.76	2.76	2.81	1.01	1.09
Galactan	3.61	3.25	2.15	2.71	3.19
Rhamnan	0.44	0.49	0.49	0.23	0.26
Glucan	30.10	26.65	23.73	36.31	31.97
Xylan	6.56	5.92	5.04	7.55	7.29
Mannan	5.20	4.65	3.52	5.38	5.47
Total carbon	48.7	43.7	37.7	53.2	49.3
Total yield	83.7	80.5	73.8	89.3	89.2
^b q_e (mg/g)	19.76 ± 0.23	7.84 ± 0.68	9.58 ± 0.04	1.14 ± 0.88	3.36 ± 0.62
Surface area (m ² /g)	0.2450	0.2864			

^a Experimental procedures based on references: [11].^b Mean and standard deviation of three determinations.

3.2 FTIR Analysis

FTIR analysis was performed to confirm the carboxyl group as the major Cd^{2+} removal functional group of BTJF and to determine the ideal NaOH concentration in the saponification process. The idea of saponification to increase the cation sorption capacity of wood fiber is that saponified ester groups in the wood fiber produce carboxylate which can bind cations as shown in the following Eq. (5)[4]:



The major peak assignments are described below. The region below 1550 cm^{-1} is the 'fingerprint region' and the absorption cannot clearly be assigned to any particular vibration because they correspond to complex interacting vibration systems. The region between 1800 and 3500 cm^{-1} presents two major peaks centered at about 3420 cm^{-1} (the H-bonded OH group) and at 2921 cm^{-1} (the C-H stretching of the CH_2 groups). The region between 1500 and 1800 cm^{-1} is a special range to evaluate the degree of saponification since this presents the carbonyl and double bond region [12-14].

For the FTIR experiment, juniper samples were treated with different concentrations of NaOH solutions for 30 min. The concentrations of NaOH solutions were 0, 0.05, 0.20, 0.30, 0.50, and 1.00 M, respectively. The FTIR spectra of various NaOH treated juniper fiber samples are shown in Fig.1 (A). Though major peak (wave number) shift is not observed in Fig.1 (A), differences of peak height are observed in the range between 1500 and 1800 cm^{-1} . In Fig. 1 (B), all spectra were set at the base line equally and then, this range was magnified to investigate this region more closely. In this range, there are two peaks centered at 1620 and 1737 cm^{-1} . According to the literature [12-15], the peak wavenumber of the ester group and carboxyl acid groups in the organic compounds is approximately 1740 cm^{-1} while the peak wavenumber of the carboxylate ion groups is about 1620 cm^{-1} . Barker and Owen (1999) [16] assigned carboxyl groups a peak number of 1737 cm^{-1} for juniper, *Juniperus virginiana*, and Brown *et al.* (2001) [17] assigned a peak number of 1620 cm^{-1} as a carboxylate. These peak numbers are identical to the numbers in this study. Therefore, it can be concluded from Fig. 1 that the peak at 1737 cm^{-1} is attributed to the absorption of carboxylic groups except carboxylate in the BTJFs while the peak at 1620 cm^{-1} corresponds to the absorption of the carboxylate. Meanwhile, the pK_a of the weak carboxyl group and of the strong carboxyl group in base treated sugar beet pulp is 6.10 and 4.6, respectively [5]. Since all juniper fibers in the study were treated with NaOH solutions in which the pH was at least 12.5 and then neutralized to pH 8 as well as pH of untreated juniper fiber was approximately 8, it is clear that all the non-esterified carboxylic groups are in the form of carboxylate,

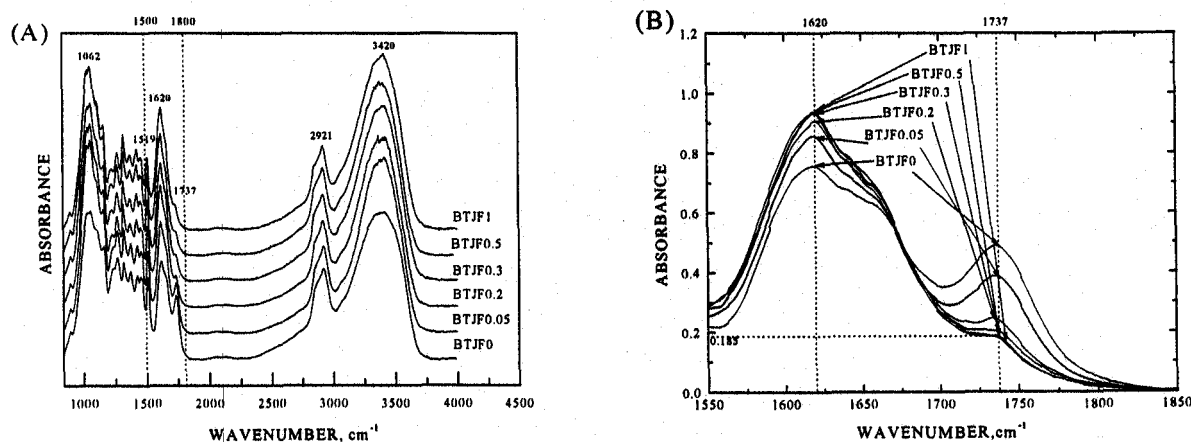


Fig.1. (A) FTIR spectra of 0,0.05,0.2,0.3,0.5, and 1.0 M of NaOH treated juniper (B) FTIR spectra of the carbonyl group region from 1550 to 1850 cm^{-1} .

In order to quantify the relative changes in the spectral intensities of the carboxyl group in the juniper fibers which were treated by different concentrations of NaOH, the peak ratios of 1620 cm^{-1} (carboxylate) and 1737 cm^{-1} (ester) were calculated. Fig. 2 (A) shows that both 1620/1737 (carboxylate/ester) ratio and q_c increased as the NaOH concentration for the base treatment increased. Figure 2 (B) shows a linear relationship between 1620/1737 and q_c . This result is explained by the saponification process (see Eq. (5)). Hydroxyl ions from NaOH convert the ester in the juniper fiber to carboxylate which can bind Cd^{2+} . Thus, as high concentrations of NaOH are used for the base treatment, the amount of ester in the juniper fiber is reduced while the amount of carboxylate is increased. In addition, since no ester group which can convert to carboxylate was left when initial NaOH concentrations were higher than 0.5 M, both 1620/1737 ratio and q_c values were hardly increased in the range (see Fig. 2 (A)). From this data, it can be concluded that the ideal NaOH concentration for this base treatment is about 0.5 M.

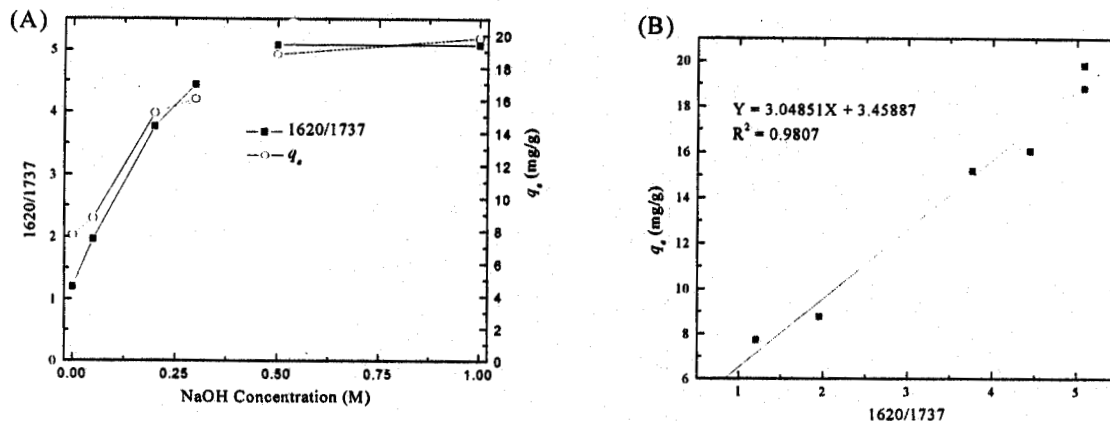


Fig. 2. (A) 1620/1737 and q_c values in different initial concentrations of NaOH
(B) 1620/1737 versus q_c values.

3.3 Sorption Isotherms

Sorption equilibria and sorption kinetics are two important physicochemical aspects of the sorption process as a unit operation.

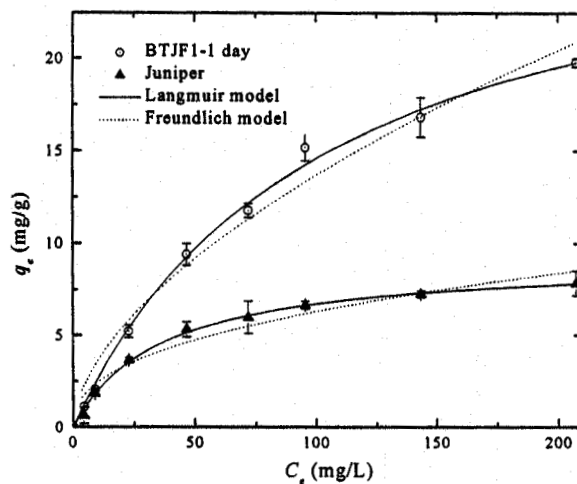


Fig.3. Langmuir and Freundlich isotherms for the sorption of Cd^{2+} onto Juniper and BTJF1-1 day.

Table 2. Isotherm constants for Cd²⁺ adsorbed onto juniper and BTJF1-1 day

Sorbent	Freundlich isotherm			Langmuir isotherm		
	<i>1/n</i>	<i>K</i> (L/mg)	Correlation coefficient, R ²	<i>Q_{max}</i> (mg/g)	<i>b</i> (L/g)	Correlation coefficient, R ²
Juniper	0.413	0.943	0.938	9.175	0.027	0.997
BTJF	0.579	0.952	0.974	29.537	0.010	0.997

Figure 3 shows the observed points of Cd²⁺ sorbed capacity, *q_e*, of juniper and BTJF1-1 day in various effluent Cd²⁺ concentrations *C_e* in relation to the curves calculated from the constants in Table 2. The R² numbers in Table 2 show that the Langmuir isotherm model yielded a better fit than the Freundlich isotherm model in the sorption of Cd²⁺ onto both juniper and BTJF1-1 day fibers.

Table 3. Reported Cd²⁺ sorption capacities for various sorbents

Sorbent	<i>q_e</i> (mg/g)	<i>Q_{max}</i> (mg/g)	Source
BTJF1-1 day	-	29.5	This study
Juniper	-	9.18	This study
Walnut shell	1.5	-	[18]
Activated carbon	11.1	-	[19]
Geothite	-	3.08	[20]
Acid-treated bentonite	-	4.11	[21]
Sphagnum moss peat	-	5.8	[22]
Seaweeds			
<i>Ascophyllum andosum</i>	67	-	[23]
<i>Sargassum natans</i>	-	100	[24]
Chitosan powder	420	-	[25]

The sorption capacities of various sorbents tested by other researchers are summarized in Table 3 along with the results obtained in this study. Cadmium ion sorption to BTJF1-1 day with the maximum sorption capacity of BTJF1-1 day was greater than these sorbents except for seaweeds and chitosan. However, biomass such as seaweed has a tendency to easily collapse and swell, which prevents successful use in sorption columns [24]. Also, Hsien and Rorrer (1995) [26] noted two major limitations of chitosan: its solubility in acidic solution and its non-porosity.

3.4 Sorption Kinetics

The kinetic data of BTJF1-1 day and juniper are shown in Fig.4. After the base treatment, the *q_e* value increased from 3.770 to 8.409 mg/g, the *h* value increased from 0.802 to 9.756 mg/g-min, and the *k* value increased from 0.054 to 0.137 g/mg-min. The *k* value of BTJF1-1 day was approximately 2.5 times greater than that of juniper. This implies that the base treatment on juniper not only increases Cd²⁺ removal capacity but also increased the Cd²⁺ removal kinetics.

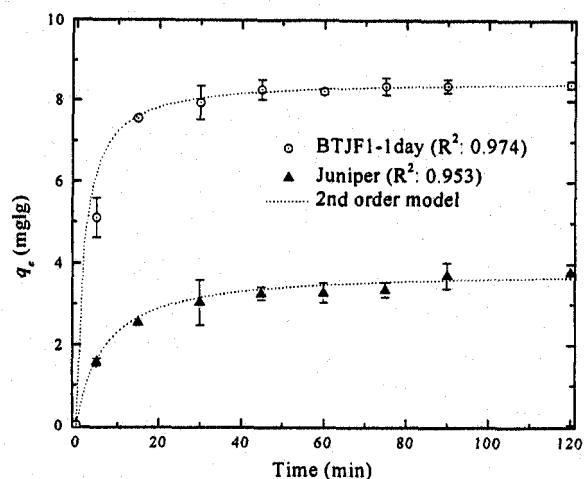


Fig.4. Cd²⁺ removal capacity versus time for juniper and BTJF1-1 day at 25°C, 40 mg- Cd²⁺/L, and 4 g-sorbent/L.

4. CONCLUSIONS

1. Carboxylate ion which was produced by saponification reaction during the base-treatment was a major functional group responsible for the Cd²⁺ sorption. The optimum NaOH concentration to maximize Cd²⁺ removal and to minimize the exudation of the extractives during the NaOH treatment process is about 0.5 M.
2. The Langmuir theory was found to represent the sorption of Cd²⁺ onto both raw juniper fiber and BTJF better than the Freundlich model. Based on this model, the base treatment raised Q_{max} about 3.2 times.
3. A pseudo-second order kinetic model has been fitted for the sorption of Cd²⁺ onto BTJF. The kinetics and initial sorption rate of Cd²⁺ onto BTJF were much faster than that of the control juniper sorbent.

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6. REFERENCES

1. Volesky B. (1990) *Biosorption of heavy metals*. CRC Press, Boca Raton, FL.
2. Friedman M. and Waiss A. C. Jr. (1972) Mercury uptake by selected agricultural products and by-products. *Environ. Sci. Technol.* **6**, 457-458.
3. Morita M., Higuchi M. and Sakata I. (1987) Binding of heavy metal ions by chemically modified woods. *J. Appl. Polym. Sci.* **34**(3), 1013.
4. Tiemann K. J., Gardea-Torresdey, J. L., Gamez, G., Dokken, K. and Sias, S. (1999) Use of X-ray absorption spectroscopy and esterification to investigate Cr(III) and Ni(II) ligands in alfalfa biomass. *Enviro. Sci. Technol.* **33**(1), 150-154.
5. Reddad Z., Gerente, C., Andres, Y., Ralet, M. C., Thibault, J. F. and Le Cloirec, P. (2002) Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. *Carbohydr. Polym.* **49**(1), 23-31.
6. Han J. S. (1999) Stormwater filtration of toxic heavy metal ions using lignocellulosic materials: selection process, fiberization, chemical modification and mat formation. *2nd Inter-regional conference on environment-water* 99.
7. LeVan-Green, S. L. and Livingston, J. (2001) Exploring the uses for small-diameter trees. *Forest. Prod. J.* **51**(9), 10-21.

8. Brunauer S. (1945) The Absorption of gases and vapors. Vol. 1. Princeton University Press, Princeton, NJ.
9. Min S. H. (2001) Mechanisms of cadmium removal by base treated juniper fiber, *M.S. Thesis*, University of Wisconsin-Madison.
10. Ho and McKay (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Wat. Res.* **34**(3), 735-742.
11. Davis M.W. (1998) A rapid modified method for compositional carbohydrate analysis of lignocellulosics by HPAEC/PAD. *J. Wood Chem. & Technol.* **18**(2), 235-252.
12. Chatjigakis A. K., Pappas, C., Proxenia, N., Kalantzi, O., Rodis, P. and Polissiou, M. (1998) FTIR spectroscopic determination of the degree of esterification of cell wall pectins from stored peaches and correlation to textural changes. *Carbohydr. polym.* **37**(4), 395-408.
13. Pappas C., Rodis, P., Tarantilis, P. A. and Polissiou, M. (1998) Prediction of the pH in wood by diffuse reflectance infrared Fourier transform spectroscopy. *Carbohydr. polym.* **53**(7), 805-809.
14. Inbar Y., Chen, Y. and Hadar, Y. (1989) Solid-state C-13 nuclear magnetic-resonance and infrared-spectroscopy of composted organic-matter *Soil Sci. Soc. Am. J.* **53**(6), 1695-1701.
15. Roeges N.P.G. (1994) *A Guide to the complete interpretation of infrared spectra of organic structures.* Wiley & Sons, NY.
16. Barker B and Owen, N. L. (1999) Identifying softwoods and hardwoods by infrared spectroscopy *J. Chem. Educ.* **76** (12), 1706-1709.
17. Brown P., Gill, S., Allen, S. J. (2001) Determination of optimal peat type to potentially capture copper and cadmium from solution. *Water Environ. Res.* **73** (3), 351-362.
18. Orhan Y. and Büyükgüngör H. (1993) The removal of heavy metals by using agricultural waste. *Water Sci. Technol.* **28**(2), 247-255.
19. Larsen V. J. and Schierup H. H. (1981) The use of straw for removal of heavy metal from wastewater. *J. Envir. Qual.* **10**(2), 188-193.
20. Johnson B. B. (1940) Effect of pH, temperature and concentration on the adsorption of cadmium on goethite. *Enviro. Sci. Technol.* **24**(1), 112-118.
21. Pradas E, G., Sánchez M. V., Cruz F. C., Viciano M. S. and Pérez M. F. (1994) Adsorption of cadmium and zinc from aqueous solution on natural and activated bentonite. *J. Chem. Tech. Biotechnol.* **59**(3), 289-295.
22. McLelland J. K. and Rock C. A. (1988) Pretreating landfill leachate with peat to remove metals. *Water, Air Soil Poll.* **37**(1-2), 203-215.
23. Volesky B. and Prasetyo I. (1994) Cadmium removal in a biosorption column. *Biotechnol. Bioeng.* **43**(11), 1010-1015.
24. Holan Z. R., Volesky B. and Prasetyo I. (1993) Biosorption of cadmium by biomass of marine algae." *Biotechnol. Bioeng.* **41**(8), 819-825.
25. Rorrer G. L., Hsien T.-Y. and Way J. D. (1993) Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from waste water. *Ind. Eng. Chem. Res.* **32**(9), 2170-2178.
26. Hsien T. Y. and Rorrer G. L. (1995) Effects of acylation and crosslinking on the material properties and cadmium ion adsorption capacity of porous chitosan beads. *Separ. Sci. Technol.* **30** (12), 2455-2475.

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