

Adsorption of Heavy Metal Ions onto Chemically Oxidized *Ceiba pentandra* (L.) Gaertn. (Kapok) Fibers

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The physico-chemical properties of kapok fibers were altered via the combination processes of chlorite-periodate oxidation, in order to assess their efficacy as a heavy metal adsorbent. The chemically-oxidized kapok fibers were found to harbor a certain amount of polysaccharides, together with lowered lignin content. This alteration in lignin characteristics was clearly confirmed via FTIR and NBO yield. Moreover, chemically oxidized kapok fibers retained their hollow tube shape, although some changes were noted. The chemically oxidized kapok fibers evidenced elevated ability to adsorb heavy metal ions with the best fit for the Langmuir adsorption isotherm model. Three cycles of adsorption-desorption were conducted with in-between regeneration steps. Our experimental results indicated that chemically oxidized kapok fibers possessed excellent adsorption characteristics, and the modified kapok fibers could be completely regenerated with almost equimolar diluted sodium hydroxide. Pb, Cu, Cd and Zn ions evidenced adsorption rates of 93.55%, 91.83%, 89.75%, and 92.85% on the chemically oxidized kapok fibers. The regeneration efficiency showed 73.58% of Pb, 71.55% of Cu, 66.87% of Cd, and 75.00% of Zn for 3rd cycle with 0.0125N NaOH

Key words : adsorption, chlorite-periodate oxidation, heavy metal ions, kapok fiber

The presence of heavy metals in water bodies for human consumption and in industrial wastewater has become a cause of great concern, and this has resulted in a need for the development of several new materials with potential for the removal of heavy metal from such waters [Kumar *et al.*, 2000]. Ion exchange fiber, which has proven to be one of the most useful tools for the removal of heavy metals from wastewater, has attracted a great deal of attention in recent years, due to the large specific surface area and high adsorption rate of this material. There are many types of fibers or modified fibers, including polyester, polyacrylonitrile, polypropylene, and so on, which have thus far been used for the adsorption of heavy metal ions, or to enrich trace amounts of heavy metals from aqueous solution [Wei *et al.*, 2005].

All of these techniques make possible moderate to

efficient heavy metal removal. However, as the result of their ready availability and cost effectiveness, biological waste materials including starch [Wing *et al.*, 1974; Wing *et al.*, 1978; Wing *et al.*, 1981; Marani *et al.*, 1980; Marani *et al.*, 1981 and Rayford *et al.*, 1979], straw [Changeng, 1991], saw-dust [Srivastava *et al.*, 1986], peat moss [Sharma and Forster, 1993], sugar cane pulp [Sharma and Forster, 1994], coconut hulls [Pino *et al.*, 2006; Tan *et al.*, 1993], sheep manure waste [Kandah, 2001], groundnut shell and sawdust [Shukla and Pai, 2005a], jute fiber [Shukla and Pai, 2005b], activated carbon fiber [Park and Kim, 2005], thiol cotton fiber [Yu *et al.*, 2001], as well as other materials, have attracted the attention of investigators into adsorption and ion exchange removal [cited in Kumar *et al.*, 2000].

Kapok fiber, which is traditionally used as fiberfill in pillows, quilts, and some soft toys, is quite fine (ca. 8~10 μm diameter), and has a homogeneous hollow tube shape, with a wall thickness of ca. 0.8~1.0 μm . In addition, this material is significantly hydrophobic, and

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does not become wet in water, as the result of its high surface tension ($7.2 \times 10^{-4} \text{ N cm}^{-1}$ at 20°C against air) and chemical characteristics, including a high ratio of syringyl/guaiacyl units (4~6) and a high level of acetyl groups (13.0%) as compared with normal plant cell walls (about 2~4%) [Hori *et al.*, 2000].

In the present study, we utilized chemically oxidized kapok fibers for the adsorption of heavy metal ions, including Pb, Cd, Cu, and Zn, from aqueous solutions. In order to alter the hydrophobicity of this material to hydrophilicity, we conducted a series of chemical modifications on the kapok fibers, most notably oxidative treatments with NaClO_2 for lignin degradation and NaIO_4 for sugar degradation. In this study, characterization of the effects of chemical oxidation treatments on kapok fiber in the context of heavy metal ion adsorption behaviors was tried. We also estimated the Langmuir and Freundlich adsorption isotherms. Heavy metal ion adsorption was also investigated, and the regeneration of the chemically oxidized kapok fibers have been assessed.

Materials and Methods

Kapok fibers. Kapok [*Ceiba pentandra* (L.) Gaertn.] fibers were obtained from the Union of Myanmar, and were sequentially extracted by boiling in diethyl ether and alcohol-benzene (1 : 2, v/v) for 24 hours using a Soxhlet extractor. This impurity sample was used as a control sample for chemical analyses. All analyses were conducted in triplicate.

Reagents. Standard stock solutions (1,000 mg/L) of heavy metal ions (sulfates of Pb, Cu, Cd, and Zn) were prepared by dissolution of them in the corresponding reagents of GR or AR grade. On use, the stock solutions were successively diluted (0, 100, 200, 300, 400, and 500 mg/L). Other reagents used in the experiments were of GR or AR grade.

The modification of kapok fiber by chemical oxidation. The kapok fibers (25 g) were treated four times with NaClO_2 (10 g) and concentrated acetic acid (2 mL) for 1 hour at $70\text{--}80^\circ\text{C}$ in order to break the phenolic compounds, particularly the lignins [Chung *et al.*, 2003]. Periodate oxidation was conducted on the NaClO_2 treated kapok fibers in order to introduce the aldehyde groups to polysaccharides [Kim and Kuga, 2002]. Kapok fibers (20 g) after the first NaClO_2 treatment were suspended in 2.1 liters of H_2O , coupled with 15 mL of acetic acid and 75 g of NaIO_4 . The mixture was gently stirred for 10 minutes at ambient temperature, and allowed to stand in darkness for 7 days with constant stirring. After the reaction was complete, ethylene glycol (17.5 mL) was added in order to decompose the excess NaIO_4 , and washed with

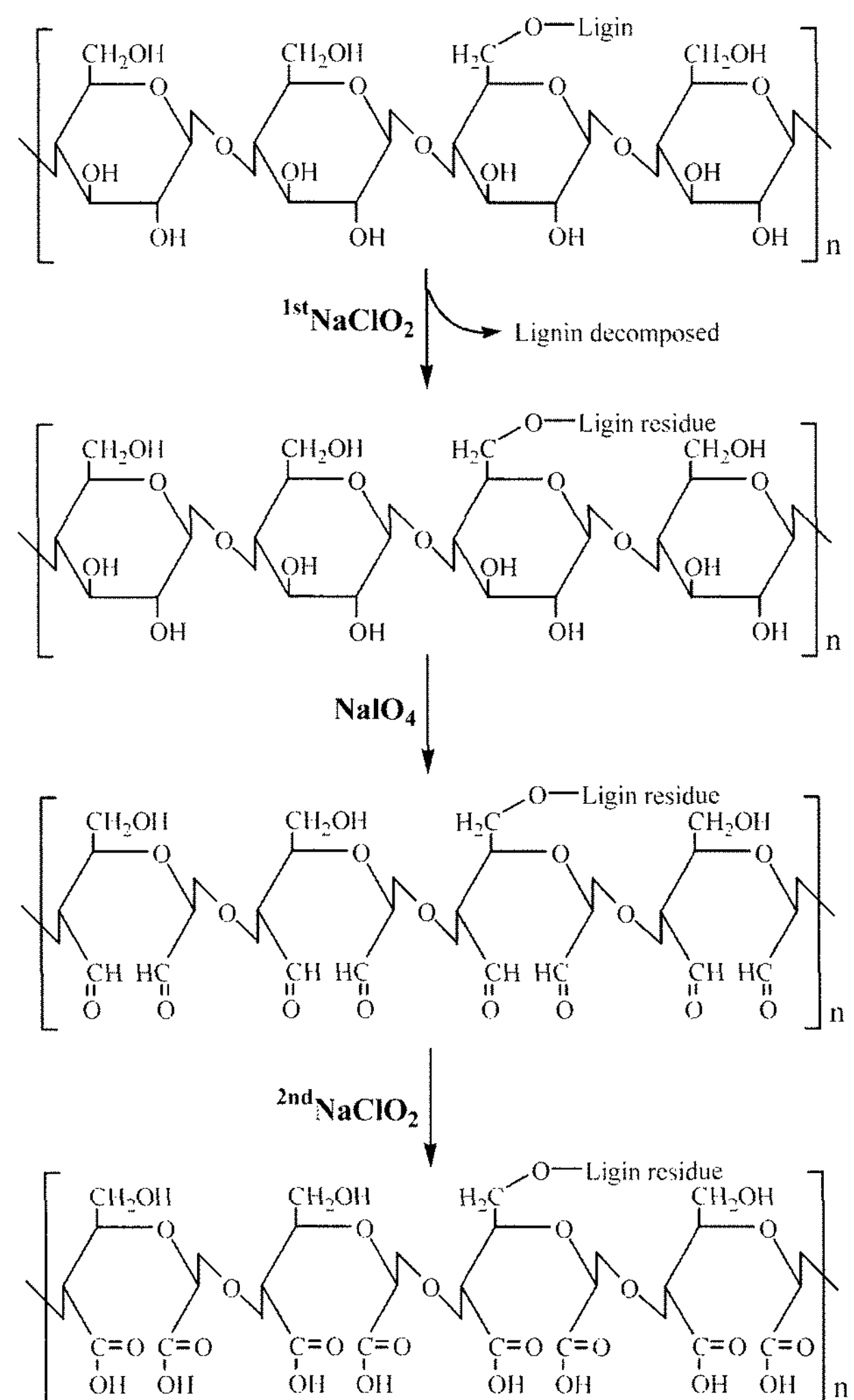


Fig. 1. Scheme of chlorite-periodate oxidation process on kapok fibers.

deionized water via repeated decantation (first treatment) [Fukagawa *et al.*, 1992]. This was followed by the treatment of the NaClO_2 - NaIO_4 treated kapok fibers with NaClO_2 for 10 minutes at $70\text{--}80^\circ\text{C}$ in order to introduce the carboxyl groups (second treatment) [Kim and Kuga, 2002]. After this, the materials were washed thoroughly in acetone (Fig. 1). These kapok fibers were dried overnight over P_2O_5 in a vacuum oven at 40°C .

Chemical analyses. Klason lignin levels were gravimetrically determined via TAPPI standard T-222om-88, and the neutral sugars in a sulfuric acid hydrolysate were analyzed as their alditol acetates, using myoinositol as an internal standard, with a Shimadzu GC-18A system (Tokyo, Japan) equipped with a flame-ionization detector [Chung *et al.*, 2003]. The chemical structure of lignin was determined via alkaline nitrobenzene oxidation (NBO), in accordance with the procedure described by Iiyama and Lam (1990), with some modification. In brief, cell wall residues (40 mg) were placed in a 10 mL stainless steel

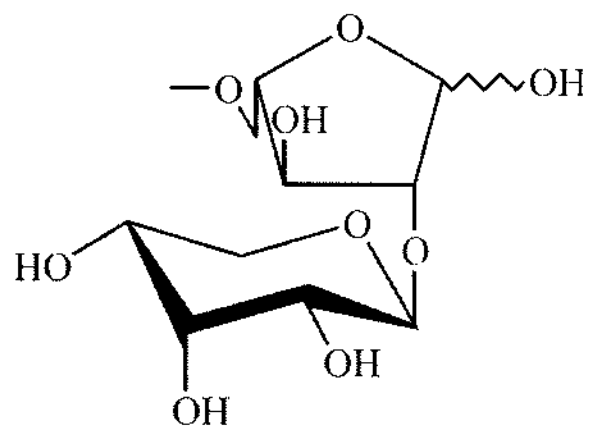


Fig. 2. Structure of β -D-xylopyranosyl unit.

reactor with 4 mL of 2 M NaOH and 0.25 mL of nitrobenzene. The products were quantified, using 3-ethoxy-4-hydroxybenzaldehyde (0.1 mL of a 5 mg/mL) as an internal standard, with a Shimadzu GC-18A (Tokyo, Japan) gas chromatograph (NB-capillary column: 25 m \times 0.25 mm id) equipped with a flame-ionization detector. The injector and detector temperatures were 280°C. The column temperature was maintained at 150°C for 10 minutes, then elevated to 250°C at 5°C min⁻¹, and maintained for 5 minutes at 250°C.

FTIR spectral analysis and scanning electron microscopy (SEM). A standard pellet (13 mm diameter) was prepared by pressing the sample (ca. 1 mg) in KBr (200 mg) in an evacuated die. The FTIR spectra of the unmodified and modified kapok fibers were recorded on a KBr disc on a FTIR Bruker Tensor 37 (Germany) at a resolution of 4 cm⁻¹, with 64 scans. SEM was utilized to determine the morphology of the kapok fibers. After the chemical treatments, the kapok fibers were immersed in glutaraldehyde overnight, then dehydrated using a graded series of ethanol (50%, 75%, 95%, and 100%) for 10 min each, and finally freeze-dried. The fibers were sputter-coated with gold for 2 minutes at 20 mA, and imaged using a Hitachi 2400 scanning electron microscope (Tokyo, Japan). Micrographs were taken of random areas of each scaffold at 15 kV with a magnification of between 2,000 and 5,000 \times .

The adsorption-desorption studies. From the first treatment and the second treatment kapok samples as described above 2.3, the second treatment kapok fiber was utilized in the adsorption-desorption experiment. The adsorption-desorption study and regeneration of adsorbents for the chemically oxidized and unmodified kapok fibers have been previously described by Shukla and Pai (2005). One gram of the materials was shaken at 30°C in a flask containing 50 mL of the heavy metal ion solutions at each concentration, for a predetermined equilibrium time of 150 min. The material was then filtered, and the residual solution was analyzed for the estimation of heavy metal ion concentrations, using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu, ICPS-7500). All experiments were repeated five times, and blank experiments were also conducted in

order to ensure that no adsorption occurred on the walls of the apparatus used. More details regarding the adsorption isotherms of Langmuir and Freundlich for the chemically oxidized and unmodified kapok fibers have been described by Pino *et al.* (2006). In order to explain the observed phenomena more clearly, the Freundlich isotherm model was also employed. However, it provides no information regarding the monolayer adsorption capacity, unlike the Langmuir model (Aksu and Kutsal, 1990; Veglio and Beolchini, 1997; Donmez *et al.*, 1999; Matheickal *et al.*, 1999; McKay *et al.*, 1999) (cited in Pino *et al.*, 2006). In the adsorption-desorption experiment conducted to assess the re-use possibility of kapok fiber, the adsorption isotherm experiment, and the concentration of the heavy metal ions was found to be 100 mg/L. Following the adsorption experiments, the heavy metal ions from each of the loaded materials were desorbed by shaking with 50 mL of 0.20 N HCl at 30°C for 150 minutes. The modified materials after the desorption of heavy metal ions were washed thoroughly with de-ionized water, and were treated with 50 mL of 0.5 g/L of NaOH solution for 60 min. This was followed by an additional washing with de-ionized water, drying, and reusing for the adsorption studies. The experiment was also conducted without NaOH treatment [Shukla and Pai, 2005b).

Results and Discussion

Characteristics of the modified kapok fibers. The yields of cell wall residues (CWR) remaining after each of the chemical treatments are shown in Table 1. The NaClO₂ and NaIO₄ treatments removed the lignins and modified some of the polysaccharides, respectively. Therefore, the remaining CWR decreased gradually, and the significant decrease in the amount of cell wall materials was observed after the first NaClO₂ treatment. As had been expected, the lignin contents were reduced dramatically after NaClO₂ treatment, to 2.6% from 20.9% (control), due to delignification by NaClO₂. This result

Table 1. Residual yields and lignin contents after chemical treatments

Treatments	Yield (mg)	Lignin (%)
Kapok fiber	1,000	20.7 \pm 1.5
Alcohol benzene extraction (1 : 2)	970.6 \pm 44.6	20.9 \pm 1.6
1 st NaClO ₂	824.4 \pm 40.4	2.6 \pm 0.3
NaIO ₄	750.5 \pm 39.8	-
2 nd NaClO ₂	234.8 \pm 7.5	-

-: not able to be determined. All data are the means \pm S.D. of triplicate experiments.

Table 2. The results of nitrobenzene oxidation (NBO) after chemical treatments (unit: mg/g of cell wall residues)

CWR	H	HA	V	VA	S	SA	Total
Control	0.7±0.0	0.1±0.0	10.3±0.3	1.0±0.1	59.5±3.0	7.0±0.3	78.4±3.0
1 st NaClO ₂	0.2±0.0	ND	2.4±0.0	1.5±0.2	4.6±0.1	1.7±0.1	10.5±0.2
NaIO ₄	0.3±0.0	1.3±0.1	1.7±0.0	1.7±0.1	7.9±0.2	1.8±0.0	4.6±0.3
2 nd NaClO ₂	0.2±0.0	ND	0.8±0.1	0.6±0.0	0.1±0.0	ND	1.0±0.1

CWR: cell wall residues, H: *p*-hydroxybenzaldehyde, HA: *p*-hydroxybenzoic acid, V: vanillin, VA: vanillic acid, S: syringaldehyde, SA: syringic acid, ND: not detected. All data are the means±S.D. of triplicate experiments.

Table 3. Neutral sugar composition of kapok fiber after chemical treatments (unit: mg/g of cell wall residues)

CWR	Rha	Ara	Xyl	Man	Glc	Gal	Total
Control	0.4±0.1	0.4±0.0	21.2±0.0	0.4±0.1	33.7±0.6	0.9±0.2	56.9±0.8
1 st NaClO ₂	0.5±0.1	0.5±0.1	28.7±1.1	1.1±0.1	46.9±4.2	1.3±0.3	79.0±3.3
NaIO ₄	1.2±0.1	0.1±0.0	9.6±0.4	ND	3.0±0.2	0.1±0.1	13.9±1.6
2 nd NaClO ₂	0.7±0.2	0.1±0.0	6.9±0.1	ND	15.9±0.4	0.2±0.1	23.6±0.2

CWR: cell wall residues, Rha: rhamnose, Ara: arabinose, Xyl: xylose, Man: mannose, Glc: glucose, Gal: galactose, -: not detected. All data are the means±S.D. of triplicate experiments.

was verified by observations of the total alkaline nitrobenzene oxidation (NBO) yield. The total NBO yield was reduced to 10.5 mg/g of CWR in the first NaClO₂ treated sample, while the control sample, showed the yield of 78.4 mg/g of CWR (Table 2). The lignin contents in the NaIO₄ and second NaClO₂ treated samples could not be determined via conventional methods, including the acetyl bromide and Klason methods, due to co-existence of high amounts of interfering compounds derived from oxidation treatments [Jin *et al.*, 2003]. However, we were able to postulate that those samples should harbor negligible amounts of lignin, since the NBO yield was low. In general, NBO provides for the qualitative and quantitative determinations of the building units of lignin [Iiyama and Lam, 1990]. Lignins from *Angiospermae* and *Gymnospermae* yield syringaldehyde and vanillin as major products of NBO, with maximum yields of approximately 50% and 30%, on the basis of the lignin content, respectively [Chen, 1992]. Therefore, the total yields of the NBO products, 4.6 mg/g of CWR in the NaIO₄ treated sample, and 1.0 mg/g of CWR in the second NaClO₂ sample, suggest that the lignin contents of those samples are obviously negligible.

The changes in the amounts and composition of monosaccharides differed substantially between the chemically treated samples and the control sample (Table 3). The total amounts of neutral sugars in the first NaClO₂ treated sample increased in proportion to the lignin loss, and the quantity of xylose (9.6 mg/g of CWR) was relatively high in the NaIO₄ treated sample, as compared with the amount of glucose (3.0 mg/g of CWR). This result indicates that the CWR after NaIO₄ treatment

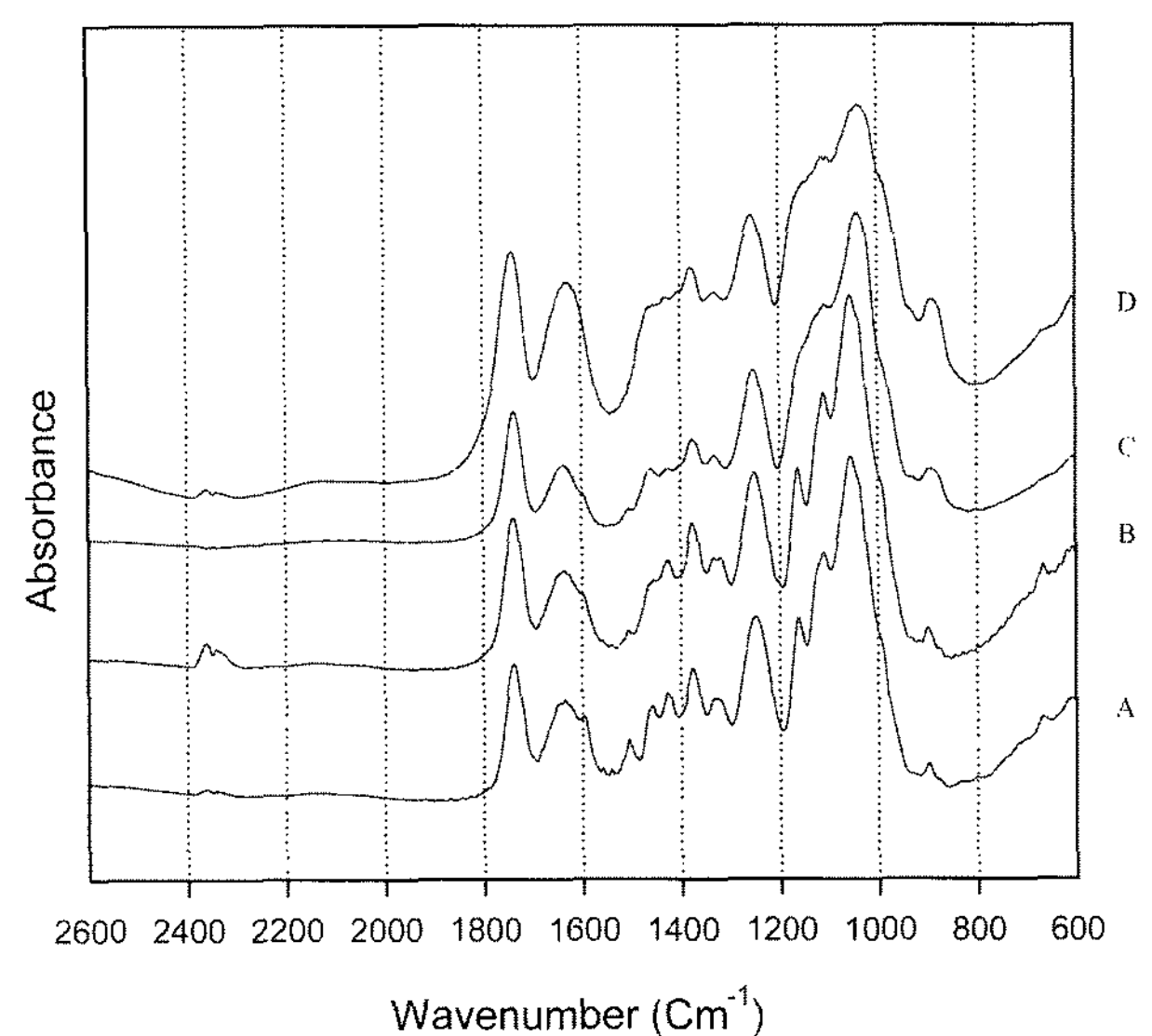


Fig. 3. FTIR spectra of kapok fibers. A, control; B, after 1st NaClO₂ treatment, C, after NaIO₄ treatment; D, after 2nd NaClO₂ treatment.

would contain NaIO₄ resistant xylose residues, such as β-D-xylopyranosyl units [Wende and Fry, 1997].

IR spectra and scanning electron micrograph. The FTIR spectra of the control and modified kapok fibers are shown in Fig. 3. The most significant difference in the FTIR spectra among kapok samples is the change in the characteristics of the phenolic compounds, particularly lignin, owing to the degradation of the majority of phenolic compounds by NaClO₂. The presence of strong peaks at 1730 cm⁻¹ has been assigned to carboxylic acids, and the spectrum of the second NaClO₂ treated sample was more

straightforward for the O-H, C-H, and C=O stretching vibration at 1620 cm^{-1} than was observed in other samples. Obviously, the components of the aromatic skeletal vibration at 1320 cm^{-1} , 1420 cm^{-1} , 1510 cm^{-1} , 1591 cm^{-1} were either significantly decreased or absent. In addition, 1150 cm^{-1} , which has its origin in aromatic C-H, was almost completely absent in the first NaClO_2 treated sample, together with an appreciable decrease in intensity observed in the NaIO_4 treated sample. The absorption band at 880 cm^{-1} , which is assigned to a hemiacetal structure originating from cellulose, was found to have increased gradually with each of the treatments. In addition, the combination C-H elongation and CH_2 deformation in carbohydrate became apparent around $2380\text{--}2280\text{ cm}^{-1}$ after the first NaClO_2 treatment [Faix, 1992; Kim *et al.*, 2004; Roggo *et al.*, 2004]. This is probably attributable to the change in the absolute amount of total sugar, from 56.8 mg/g of CWR (control) to 79.0 mg/g of CWR (first NaClO_2 treated sample). All FTIR spectra were consistent with the results of chemical analyses, as shown in Tables 1–3. The morphological alterations in the kapok fibers shown in Fig. 4 after chemical treatments were observed with scanning electron microscopy (SEM). Although distorted hollow shape and rough surfaces were observed the characteristic fine hollow shape was still maintained in all of the modified kapok fiber samples. These results led us, therefore, to conclude that the chemically modified kapok fibers retained a high water holding capacity.

Adsorption isotherms. Adsorption is a mass transfer operation involving the contact of solids with either liquids or gases, followed by mass transfer from the fluid

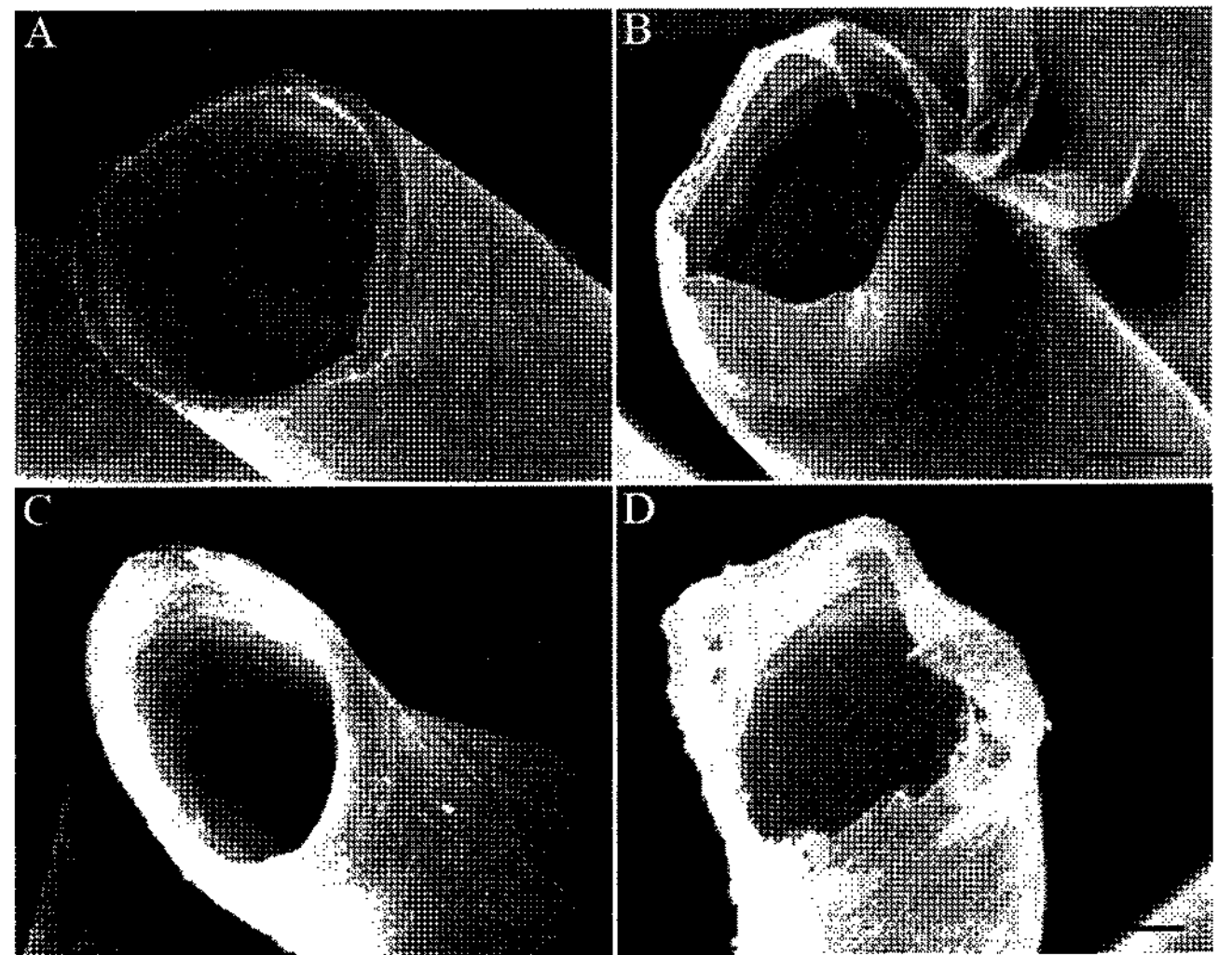


Fig. 4. SEM micrographs of kapok fibers. A, control; B, after 1st NaClO_2 treatment, C, after NaIO_4 treatment; D, after 2nd NaClO_2 treatment. (Ba=5 μm)

phase to the solid phase. Classical adsorption models (Langmuir and Freundlich) were employed in this study in order to describe the equilibrium between adsorbed heavy metal ions in the solid phase and heavy metal ions in solution at constant temperature [Kandah, 2001]. Fig. 5 shows the adsorption isotherms of Pb, Cu, Cd, and Zn on unmodified and chemically oxidized kapok fibers. The application of the Langmuir model to the experimental equilibrium isotherm data yields two parameters; the maximum uptake, Q_0 , and a constant related to the energy of adsorption, b , whereas Freundlich treatment provided the parameters, n , which is indicative of bond energies

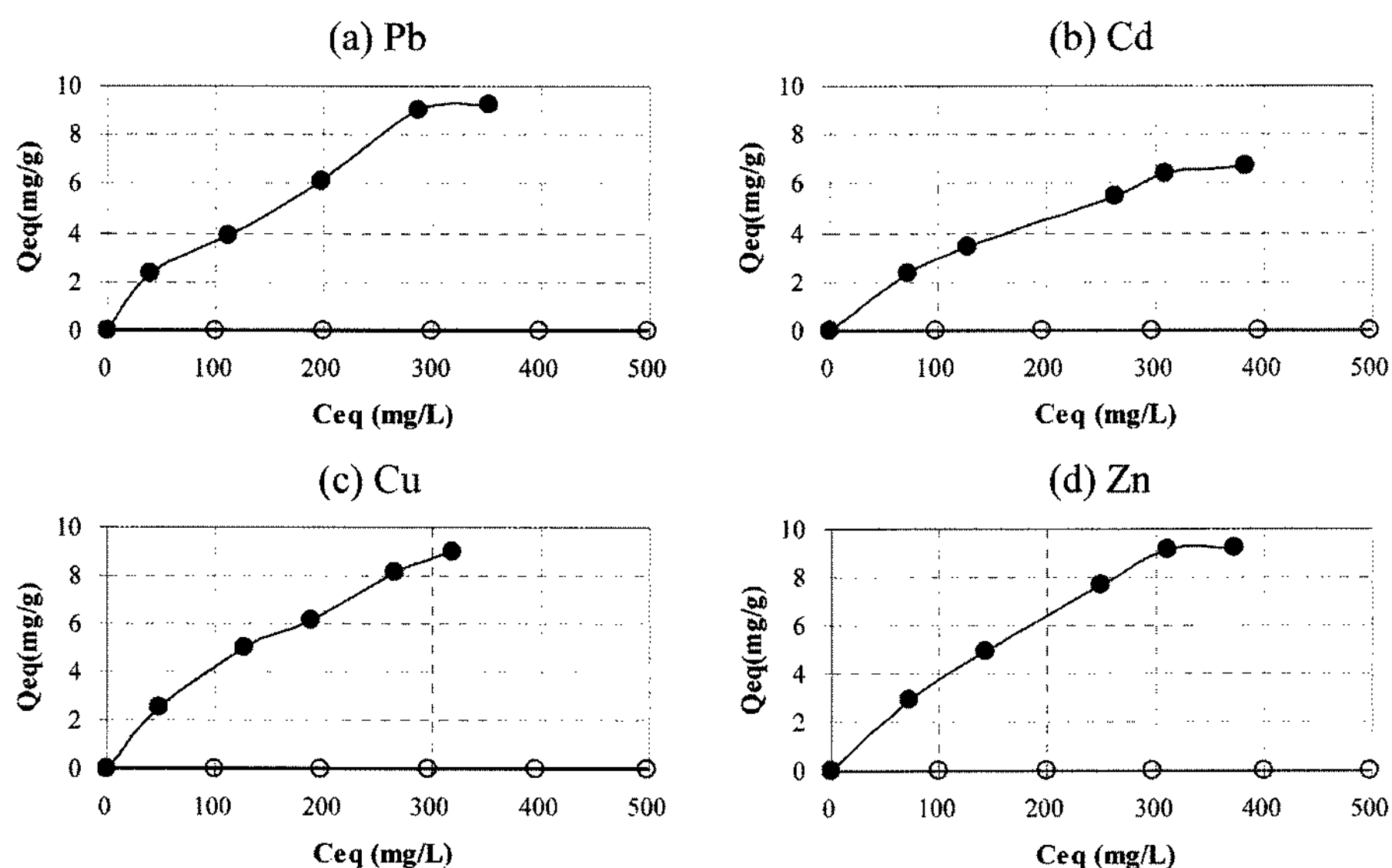
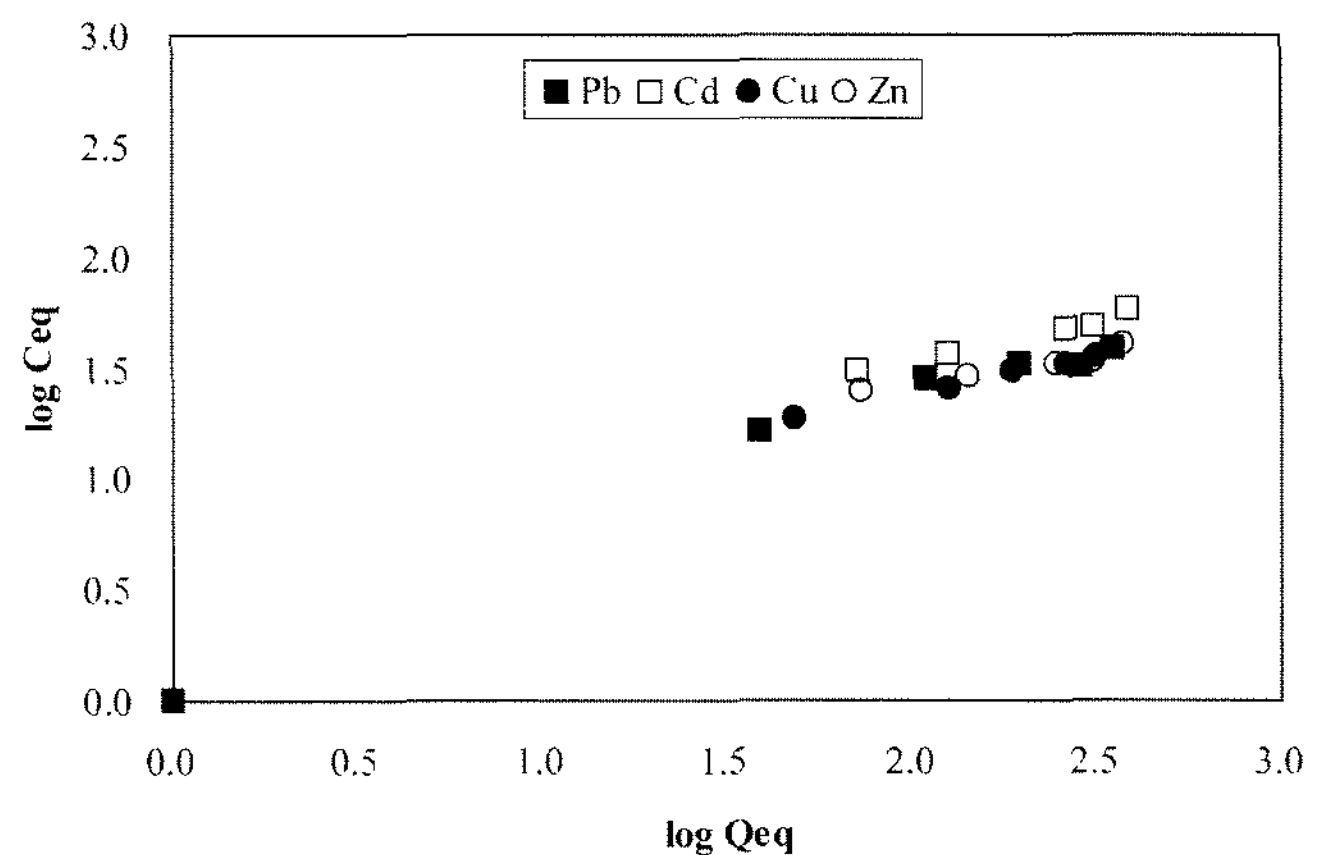


Fig. 5. Langmuir plot for the adsorption of heavy metal ions on different kapok fibers. ○: unmodified kapok fiber, ●: chemically oxidized kapok fiber.

Table 4. The parameters extracted from the Langmuir and Freundlich treatments for the adsorption of different metal ions onto chemically oxidized kapok fibers

Metal ions	R^2 values		Q_0 (mg/g)	b (l/mg)	n	K_f
	Langmuir	Freundlich				
Pb	0.969	0.871	38.46	0.0317	1.6013	1.18
Cu	0.970	0.917	36.90	0.0316	1.5946	1.14
Cd	0.962	0.781	58.47	0.0219	1.4584	1.12
Zn	0.962	0.874	39.37	0.0318	1.5962	1.13

between heavy metal ions and the adsorbent, and K , which is related to bond strength [Shukla and Pai, 2005b]. Natural kapok fiber is hydrophobic and does not become wet in water. Therefore, some difficulty was inherent to the formulation of the regular data of the adsorption-desorption experiment with regard to the unmodified kapok fibers. Therefore, this study was conducted in order to determine the pattern of absorption-desorption in the kapok fiber with the data obtained from the second treatment sample to which carboxyl groups had been introduced. The Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites, and the empirical Freundlich equation predicated on sorption onto a heterogeneous surface. All of these values, along with those of the determination coefficient, R^2 , for the Langmuir and Freundlich isotherms for adsorption of the Pb, Cu, Cd, and Zn on the chemically oxidized kapok fibers, are shown in Table 4. The R^2 values for the adsorption of all four of the heavy metal ions were nearly 0.97 in the case of the chemically oxidized kapok fibers. This result indicates the favorable applicability of the Langmuir model to these adsorptions. However, the Freundlich isotherm indicated a poorer fit with the experimental data when compared with the Langmuir isotherm. This result is considered to indicate that the adsorption of the heavy metal ions and the kapok fibers is the result of the chemical adsorption mechanism, not the physical adsorption phenomenon. Among the four heavy metal ions used in this experiment, the Q_0 value of Cd was highest at 58.47, whereas Pb, Cu, and Zn evidenced similar values, ranging between 36.90 and 39.37. However, the b value was lowest for Cd at 0.0219, while the values for Pb, Cu, and Zn were quite similar, in a range between 0.0316 and 0.0318. This result is suggested the similarity of the adsorption pattern of heavy metal ions for the chemically oxidized kapok fibers. According to Shukla and Pai (2005), in the results of their study regarding the absorption patterns of Cu, Ni and Zn using oxidized jute fibers, the Q_0 value ranged between 3.37 and 8.40, with a b value ranging between 0.007 and 0.099. However, in the present experiment, both the Q_0 and b values were high, and this was attributed to the

**Fig. 6.** Freundlich plot for the adsorption of heavy metal ions on chemically oxidized kapok fiber.

index of the outstanding adsorption capacity of the chemically oxidized kapok fiber, as compared to the jute fiber oxidized by hydrogen peroxide. Fig. 6 shows that the adsorption of heavy metal ions on chemically oxidized kapok fiber is consistent with the Freundlich isotherm model and the k and n constants were determined as 1.12-1.18 and 1.4584-1.6013, respectively. The values of n indicate the favorable adsorption of heavy metal ions onto the chemically oxidized kapok fiber. The enhanced adsorption of heavy metal ions onto the chemically oxidized kapok fibers can be attributed to the generation of $-COOH$ groups.

Repeated adsorption-desorption studies. The results of the determined adsorption rates for the evaluation of the possibility of re-use of the chemically oxidized kapok fiber are provided in Fig. 7. In addition, the results obtained for the desorption experiment with 0.20 N HCl on the heavy metal ions adsorbed on the kapok fiber are also shown in Fig. 7. The adsorption ratios of the heavy metal ions were 89.75-93.55%, and desorption ratios were 93.66-95.47%, respectively. The adsorption capacity of the chemically oxidized kapok fiber for re-use was outstanding. Desorption was nearly complete for the chemically oxidized kapok fibers. However, the absorption-desorption rates for each of the heavy metal ions were not particularly different. This indicates that the chemically

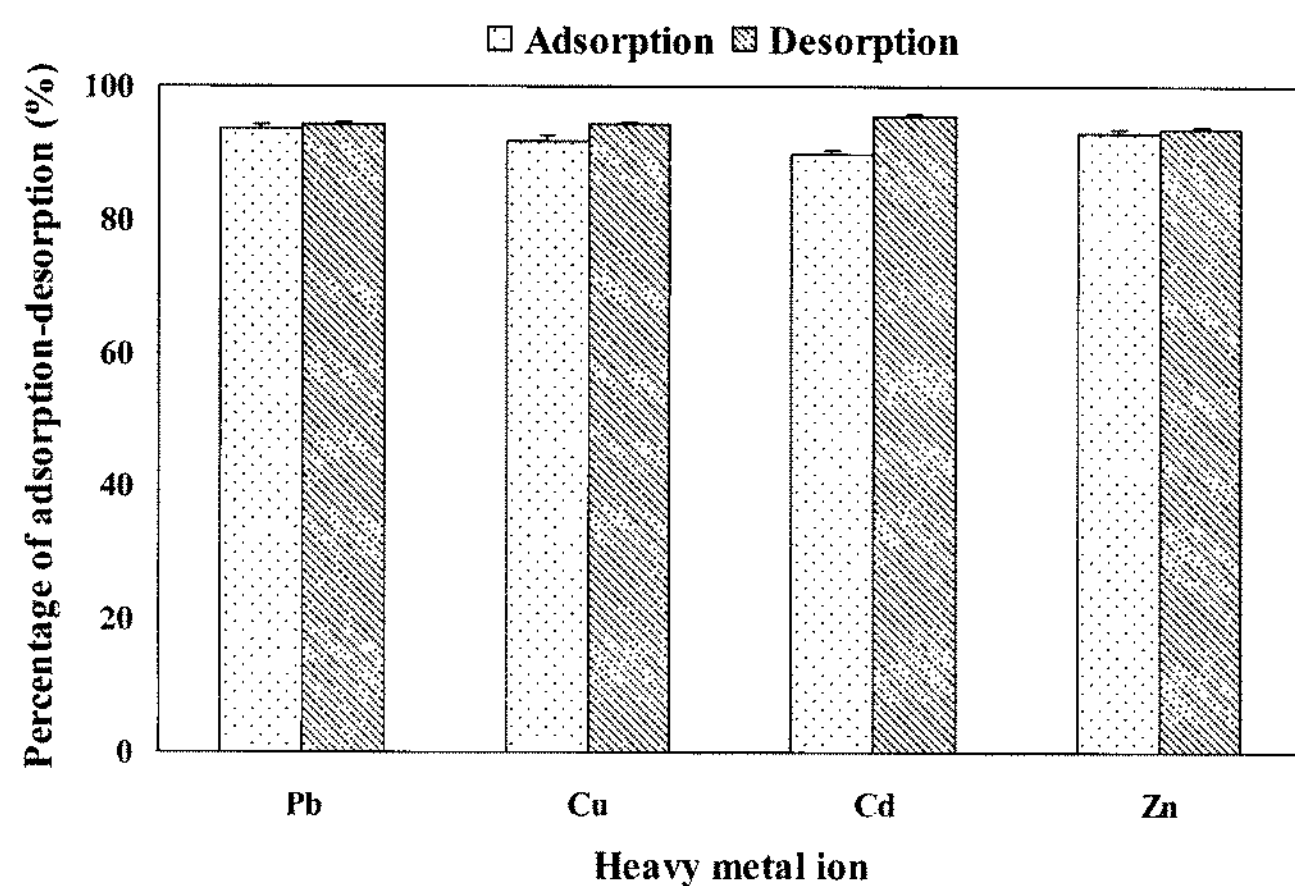


Fig. 7. Adsorption and desorption of heavy metal ions on chemically oxidized kapok fiber.

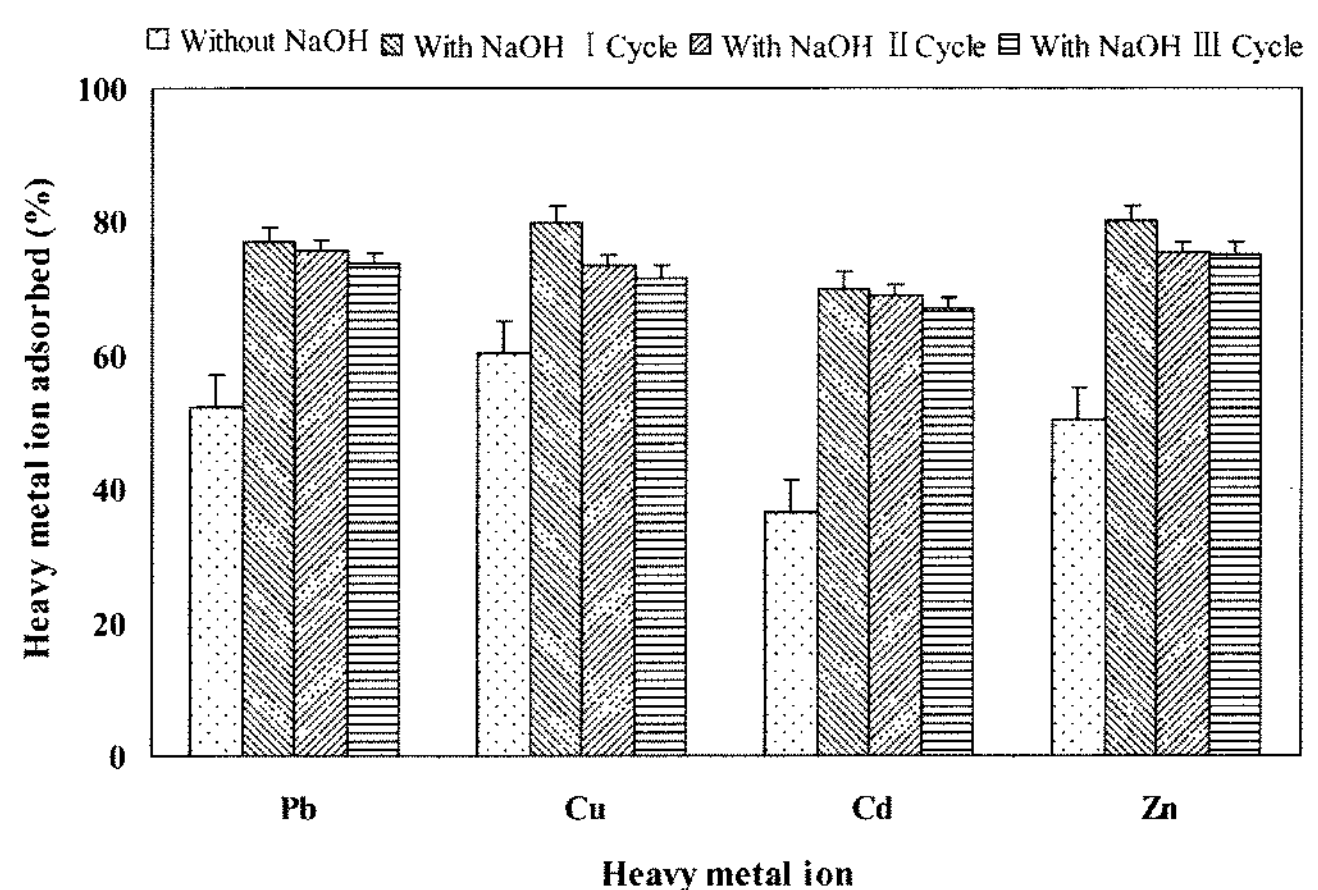


Fig. 8. Adsorption of heavy metal ions on regenerated kapok fiber.

oxidized kapok fibers are an outstanding natural adsorption material, with a very high efficiency due to the carboxyl or carbonyl groups. Three cycles of adsorption-desorption were conducted with in-between regeneration steps. It can be clearly observed, in Fig. 8, that the adsorption efficiency was retained only in cases of treatment with 0.5 g/L sodium hydroxide solution after desorption. When the desorbed fibers were reused without the intermediate treatment with NaOH, the reduction in the adsorptive capacity was noted for all the materials [Shukla and Pai, 2005]. Thus, Pb, Cu, Cd and Zn ions showed adsorption rates of 93.55, 91.83, 89.75, and 92.85% on the chemically oxidized kapok fibers, and these values decreased to 52.14, 60.19, 36.54, and 50.19% when the fibers were only washed after desorption, rather than regenerated using NaOH. However, when such regeneration treatments were applied, the re-adsorption values were found to be 76.95, 79.95, 69.95, and 79.98% for I cycle with NaOH, 75.55, 73.45, 69.00, and 75.48% for II cycle with NaOH, and 73.58, 71.55, 66.87, and 75.00% for III cycle with NaOH, after each desorption-adsorption cycle. This shows that the modified fibers evidenced adsorption characteristics almost identical to those of the original adsorbent. According to Shukla and Pai (2005), during desorption (washing by 0.2 N HCl), the heavy metal ions are replaced by H^+ ions from the eluting acid. We also noted a substantial lowering of pH after adsorption, when the desorbed materials without NaOH treatment were subjected to a second round of adsorption. This difference was attributed to the replacement of H^+ ions for heavy metal ions from the materials, resulting in a reduction in the pH of the starting bath. In the case of the desorbed materials regenerated with sodium hydroxide, Na^+ is released into the solution during adsorption. Hence, Na^+

loading is required after desorption and washing, in order to recover the material's original adsorption capacity. Using the oxidized jute fiber, repeated adsorption-desorption studies were conducted on the heavy metals, Cu, Ni, and Zn. As a result of the three regeneration experiments with NaOH, the absorption rates of the heavy metals such as Cu, Ni, and Zn were found to be 53.14, 56.43, and 45.57%, respectively [Shukla and Pai, 2005b]. However, the adsorption rates of Pb, Cu, Zn, and Cd in the present study were high, at 73.58, 71.55, 75.00, and 66.87%, respectively. It appears, then, that the chemically oxidized kapok fiber has a higher adsorption and regeneration capability than the hydrogen peroxide-oxidized jute fiber.

Chemically oxidized kapok fibers are effective adsorbent for the removal of metal ions. Our results indicate that chemically oxidized kapok fibers can be used as excellent adsorbents of heavy metals polluting industrial wastewaters. The enhanced adsorption of heavy metal ions onto chemically oxidized kapok fibers can be attributed to the generation of -COOH groups.

References

- Aksu Z and Kutsal T (1990) A comparative study for bio-adsorption characteristics of heavy metal ions with *C. vulgaris*. *Environ Technol* **11**, 979-987.
- Changgeng Z (1991) Studies on heavy metal removal from industrial water by insoluble straw xanthate. *Water Treat* **6**, 211-218.
- Chen CL (1992) Nitrobenzene and cupric oxide oxidation. *In Method in lignin chemistry*, Lin SY, Dence CW (eds.) pp. 301-321, Springer-Verlag, Berlin.
- Chung BY, Iiyama K, and Han KW (2003) Compositional characterization of cacao (*Theobroma cacao* L.) hull. *Agric Chem Biotechnol* **46**, 12-16.

- Dönmez GC, Aksu Z, Öztürk A, and Kutsal T (1999) A comparative study on heavy metal biosorption characteristics of some algae. *Process Biochem* **34**, 885-892.
- Faix O (1992) Fourier transform infrared spectroscopy. In *Method in lignin chemistry*, Lin SY, Dence CW (eds.) pp. 83-109, Springer-Verlag, Berlin.
- Fukagawa N, Meshitsuka G, and Ishizu A (1992) 2D NMR study of residual lignin in beech kraft pulp combined with selective cleavage with pivaloyl iodide. *J Wood Chem Technol* **12**, 425-445.
- Hori K, Flavier ME, Kuga S, Lam TBT, and Iiyama K (2000) Excellent oil absorbent kapok [*Ceiba pentandra* (L.) Gaertn.] fiber: fiber structure, chemical characteristics, and application. *J Wood Sci* **46**, 401-404.
- Iiyama K and Lam TBT (1990) Lignin in wheat internodes Part 1: The reactivities of lignin units during alkaline nitrobenzene oxidation. *J Sci Food Agric* **51**, 481-491.
- Jin Z, Akiyama T, Chung BY, Matsumoto Y, Iiyama K, and Watanabe S (2003) Changes in lignin content of leaf litters during mulching. *Phytochemistry* **64**, 1023-1031.
- Kandah M (2001) Zinc adsorption from aqueous solutions using disposal sheep manure waste (SMW). *Chem Eng J* **84**, 543-549.
- Kim UJ and Kuga S (2001) Ion-exchange chromatography by dicarboxyl cellulose gel. *J Chromatogr A* **919**, 29-37.
- Kim UJ, Wada M, and Kuga S (2004) Solubilization of dialdehyde cellulose by hot water. *Carbohydr Polymers* **56**, 7-10.
- Kumar A, Rao NN, and Kaul SN (2000) Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal-preparation, characterization and application. *Biores Technol* **71**, 133-142.
- Marani D, Mezzana M, Passino R, and Tiravanti G (1980) Starch xanthate and polycations in heavy metal removal from wastewaters. *Environ Technol Lett* **1**, 141-150.
- Marani D, Mezzana M, Passino R, and Tiravanti G (1981) Treatment of industrial effluent for heavy metal removal using the water soluble starch xanthate process. Proceedings of the International Conference on Heavy Metals in the Environment. 92-95, Amsterdam.
- Matheickal JT, Yu Q, and Woodburn GM (1999) Biosorption of cadmium(II) from aqueous solutions by pretreated biomass of marine alga *Durvillaea potatorum*. *Water Res* **33**, 335-342.
- McKay G, Ho YS, and Ng JCY (1999) Biosorption of copper from waste waters: A review. *Separ Purif Methods* **28**, 87-125.
- Park SJ and Kim YM (2005) Adsorption behaviors of heavy metal ions onto electrochemically oxidized activated carbon fibers. *Mat Sci Eng* **391**, 121-123.
- Pino GH, Mesquita LMS, Torem ML, and Pinto GAS (2006) Biosorption of cadmium by green coconut shell powder. *Miner Eng* **19**, 380-387.
- Rayford WE, Wing RE, and Doane WM (1979) Carboxy-containing starch graft polymer: Preparation and use in heavy metal removal. *J Appl Polymer Sci* **24**, 105-113.
- Roggo Y, Duponchel L, and Huvenne JP (2004) Quality evaluation of sugar beet (*Beta vulgaris*) by near-infrared spectroscopy. *J Agric Food Chem* **52**, 1055-1061.
- Sharma DC and Forster CF (1993) Removal of hexavalent chromium using Sphagnum moss peat. *Water Res* **27**, 1201-1208.
- Shukla SR and Pai RS (2005a) Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust. *Separ Purif Methods* **43**, 1-8.
- Shukla SR and Pai RS (2005b) Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. *Biores Technol* **96**, 1430-1438.
- Srivastava HCP, Mathru RP, and Mehrotra I (1986) Removal of chromium from industrial effluent by adsorption on sawdust. *Environ Technol Lett* **7**, 55-63.
- Tan WT, Ooi ST, and Lee CK (1993) Removal of chromium (VI) from solution by coconut husk and palm pressed fibers. *Environ Technol* **14**, 270-282.
- Veglio F and Beolchini F (1997) Removal of metals by biosorption: a review. *Hydrometallurgy* **44**, 301-316.
- Wei JF, Wang ZP, Zhang J, Wu YY, Zhang ZP, and Xiong CH (2005) The preparation and the application of grafted polytetrafluoroethylene fiber as a cation exchanger for adsorption of heavy metals. *React Funct Polym* **65**, 127-134.
- Wende G and Fry S (1997) O-Feruloylated, O-acetylated oligosaccharides as side-chains of grass xylans. *Phytochemistry* **44**, 1011-1018.
- Wing RE and Doane WM (1981) Wastewater treatment of acid cadmium rinses. *Plat Sur Finish* **68**, 50-53.
- Wing RE, Rayford WE, Doane WM, and Russell CR (1978) Preparation of insoluble cationic starches and their uses in heavy metal anion removal. *J Appl Polymer Sci* **22**, 1405-1415.
- Wing RE, Swanson CL, Doane WM, and Russell CR (1974) Heavy metal removal with starch xanthate cationic polymer complex. *J Wat Pollut Conf Fed* **46**, 2043-2047.
- Yu M, Tian W, Sun DW, Shen WB, Wang GP, and Xu N (2001) Systematic studies on adsorption of 11 trace heavy metals on thiol cotton fiber. *Anal Chim Acta* **428**, 209-218.