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Ion-exchange behavior of carboxylate groups in fibrous cellulose oxidized by the TEMPO-mediated system

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Abstract

When native cellulose is treated by catalytic oxidation with 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)/NaBr/NaClO under aqueous conditions, significant amounts of carboxylate and aldehyde groups can be introduced on surfaces of cellulose I crystallites and into disordered regions without any changes in crystallinity of cellulose I or in the original fibrous morphology. In this study, behavior of ion exchange of carboxylate groups in the TEMPO-oxidized fibrous cellulose prepared from cotton linters was compared with that of fibrous carboxymethyl cellulose (F-CMC) with almost the same carboxylate content as that of the TEMPO-oxidized cellulose. These fibrous celluloses were soaked in various metal salt solutions, and metal ion contents in the celluloses were determined by X-ray fluorescence analysis after washing with water and drying of the celluloses. In all metal salts examined in the ion-exchange experiments, the TEMPO-oxidized cellulose had metal ion contents higher than those of F-CMC. Especially, lead, calcium and silver ions were greatly introduced into the TEMPO-oxidized cellulose with the metal ion/carboxylate molar ratio of about 1:1. The adsorption selectivity of metal ions on the TEMPO-oxidized cellulose was also studied using aqueous solutions containing multiple metal salts for soaking, and the following selectivity order was obtained:

$$Pb^{2+} > La^{3+} > Al^{3+} > Cu^{2+} > Ba^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+},\ Sr^{2+},\ Mn^{2+},\ Ca^{2+} > Mg^{2+}$$

Moreover, swelling ability of the TEMPO-oxidized celluloses having various metal carboxylate groups in water and wet tensile strength of handsheets prepared thereof were studied in terms of kinds of metal ion introduced. Degree of dissociation of the metal carboxylate groups in these celluloses is likely to affect the results of the above characteristics of the TEMPO-oxidized celluloses.

Keywords: TEMPO; Cellulose; Oxidation; Ion exchange; CMC; Metal adsorption

1. Introduction

The removal and recovery of toxic metal ions from wastewater have become important research areas in terms of environmental issues, and widely been studied from various aspects in recent years. A number of approaches such as ion exchange, adsorption, chemical precipitation, reverse osmosis and electrodialysis techniques have been developed for this purpose. Synthetic resins having functionalities to form chelate structures are also candidate compounds for the removal and recovery of toxic metal ions in wastewater. However, in the case of petroleum-based synthetic polymers, suitable post treatments of the used resins containing metal ions are required, and it may cause secondary pollution during the post treatments. Moreover, most petroleum-based synthetic polymers are neither renewable nor biodegradable.

On the other hand, cellulose is the most abundant and renewable biopolymers, and is one of the promising raw materials available in terms of cost for the preparation of various functional materials. However, because native cellulosic fibers generally have quite low carboxyl and other functional groups, they have no or nearly no metal-anchoring capability per se. Hence, many attempts have been made to utilize cellulose as a metal scavenger through some derivatizations. Native polysaccharides having ionic functional groups such as alginic acid, chitosan, pectin and

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other polyuronic acids have been also studied in terms of ion-exchange behavior in water containing various metal ions (Deans & Dixon, 1991; Guibal, 2004; Haug & Smidsrød, 1965; Hebeish & El-Hilw, 1997). The most typical method to introduce carboxyl groups into cellulose is carboxymethylation with monochloroacetic acid under alkaline conditions generally containing i-propanol, and large amounts of carboxymethyl cellulose (CMC) have been produced at industrial level. Water-solubility of CMC is controllable by controlling the degree of substitution (DS) of the CM group, and fibrous CMC can be prepared, when the DS values are lower than about 0.1.

Recently, another efficient chemical method to introduce carboxylate groups into cellulose has been developed: catalytic oxidation of cellulose using 2,2,6,6-tetramethylpyperidine-1-oxy radical (TEMPO), sodium bromide and sodium hypochlorite under aqueous conditions (Bragd, van Bekkum, & Besemer, 2004). Although cellulose is insoluble but just suspended in water at the initial stage, water-soluble β-1,4-linked polyglucuronic acid sodium salt (i.e. cellouronic acid) having a homogeneous chemical structure can be obtained quantitatively by the TEMPO-mediated oxidation at pH 10.5 and room temperature within 30 min, when regenerated and mercerized celluloses are used as the starting materials (Isogai & Kato, 1998; Tahiri & Vignon, 2000). On the other hand, when native celluloses are used, the initial fibrous morphology is mostly maintained even after the TEMPO-mediated oxidation under harsh conditions, and only small amounts of water-soluble fractions (generally 0–5% mass recoveries, depending on the oxidation conditions) can be obtained. In the previous paper, detailed analytical results such as carboxylate and aldehyde contents and yields of water-insoluble fibrous fractions of the TEMPO-oxidized native cellulose prepared under various conditions were reported. Because crystallinity index and crystal size of cellulose I in native cellulose are nearly unchanged even after the TEMPO-mediated oxidation, carboxylate and aldehyde groups must be present on crystal surfaces and in disordered regions with high density. Thus, the TEMPO-mediated oxidation can be regarded as one of the most efficient surface modification methods for native celluloses under aqueous conditions, and significant amounts of carboxylate and aldehyde groups can be introduced selectively on crystal surfaces and in disordered regions without any introduction of the functional groups into inside cellulose I crystallites (Isogai & Kato, 1998; Kitaoka, Isogai, & Onabe, 1999; Saito & Isogai, 2004; Saito et al., 2005b; Saito, Yanagisawa, & Isogai, 2005a). The TEMPO-oxidized fibrous cellulose prepared from native cellulose may, therefore, be one of the suitable materials for metal ion adsorption in water.

In this paper, therefore, the TEMPO-oxidized fibrous cellulose having sodium carboxylate groups was subjected to soaking in various aqueous metal salt solutions, and its ion-exchange behavior and adsorption selectivity of metal ions were studied in comparison with those of fibrous carboxymethyl cellulose (F-CMC) with almost the same carboxylate content as that of the TEMPO-oxidized cellulose. Moreover, swelling ability of the TEMPO-oxidized celluloses having various metal carboxylate groups in water and wet tensile strength of handsheets prepared thereof were studied in terms of kinds of metal ion introduced.

2. Materials and methods

2.1. Materials

Cotton linters cellulose (Ash-less filter pulp, Advantec Toyo Co., Ltd., Japan) was used as a native cellulose sample subjected to the TEMPO-mediated oxidation. Fibrous carboxymethyl cellulose (F-CMC) (CM1, Whatman Biochemicals Ltd., England) was used as a reference sample, and its sodium carboxylate content was 0.47 mmol/g. TEMPO, sodium bromide, 9 mass % sodium hypochlorite solution and other chemicals were of laboratory grades (Wako Pure Chemicals, Co., Japan), and used without further purification.

2.2. TEMPO-mediated oxidation of cellulose

Cellulose (10 g) was suspended in water (750 mL) containing TEMPO (0.025 g) and sodium bromide (0.25 g), and the TEMPO-mediated oxidation of the cellulose slurry was started by adding NaClO (2.42 mmol/g cellulose) at room temperature and pH 10.5. After stirring the cellulose slurry for 2 h, the oxidation was quenched by adding aqueous ethanol. The fibrous TEMPO-oxidized product was washed thoroughly with water by filtration, and dried by lyophilization followed by vacuum drying at 30 °C for 48 h. The recovered mass ratio of the fibrous TEMPO-oxidized cellulose was 90.6%. Content of sodium carboxylate groups in the fibrous TEMPO-oxidized cellulose was 0.48 mmol/g. TEMPO-oxidized celluloses prepared under conditions different from the above ones and having carboxylate contents of 0.11 and 0.60 mmol/g were also prepared and used for some experiments (Saito & Isogai, 2004).

2.3. Ion-exchange treatment of carboxylate groups in TEMPO-oxidized cellulose

The fibrous TEMPO-oxidized cellulose (0.3 g) having sodium carboxylate groups was suspended in an aqueous metal salt solution (40 mL). The mole of metal salt dissolved in the aqueous cellulose slurry was set to be about 60 times as much as those of sodium carboxylate groups of the TEMPO-oxidized cellulose present in the slurry. After stirring the cellulose slurry at room temperature for 6 h, the fibrous cellulose fraction was washed thoroughly with water (320 mL) by filtration. These TEMPO-oxidized celluloses having various metal carboxylate groups were dried by lyophilization followed by vacuum drying at 30 °C for 48 h. These metal salt-treated celluloses were subjected to X-ray fluorescence analysis for determining metal ion contents. The following metal salts were used for the ion-exchange treatments; magnesium chloride, aluminum chloride, calcium chloride, cobalt chloride, nickel chloride, copper (II) chloride, strontium chloride, cadmium chloride, barium chloride, lanthanum chloride, silver nitrate and lead (II) acetate. In the case of adsorption selectivity experiments, where solutions containing multiple metal salts were used, aluminum nitrate, lanthanum nitrate, copper acetate and barium acetate were adopted at pH 3.0, 4.5 or 6.0 in place of the chlorides for preventing precipitation of lead-related compounds in the cellulose slurries containing chloride ions.

2.4. Stability test of metal carboxylate structures in TEMPO-oxidized cellulose

TEMPO-oxidized celluloses having lead, lanthanum, silver, nickel and calcium carboxylate groups were prepared beforehand by the ion-exchange treatments as described in the above section. These TEMPO-oxidized celluloses with various metal carboxylate groups (0.3 g each) were dispersed in either water (pH 5.5), 0.25 M $NaNO_3$ at about pH 7 or aqueous HNO_3 at pH 1.7 (40 mL each), and these cellulose slurries were stirred at room temperature for 6 h, and then the cellulose fraction was washed with water (320 mL) by filtration. After lyophilization and vacuum drying, these celluloses were subjected to determination of metal ion contents.

2.5. Preparation of handsheets

The TEMPO-oxidized cellulose fibers having sodium carboxylate groups without any beating treatments were subjected to handsheet making with a basis weight of 60 g/m^2 according to TAPPI Test Method T205 om-88 (2001a). No additives were used in the handsheet making. After being pressed, the wet webs were dried at 23 °C and 50% relative humidity for more than 1 day. Wet tensile index of specimen strips with 15 mm width of the handsheets were measured on the basis of TAPPI Test Method T456 om-87 (2001b). Alternatively, the aqueous solution for soaking of the specimen strips in the wet-tensile test changed from water to the above metal salt solutions. Soaking time of the specimen strips in the aqueous solution was set to be 30 min. Then, the excess solution was removed by pressing with blotting papers in a similar manner for each specimen strip, and then the strips were immediately subjected to the tensile test.

2.6. Analyses

Carboxylate content in the fibrous TEMPO-oxidized cellulose was determined by the electric conductivity titration method (Saito & Isogai, 2004; Saito, Yanagisawa, & Isogai, 2005a). The dried cellulose fibers (0.30 g) having various metal carboxylate groups were converted to pellets using a KBr disk apparatus, and subjected to X-ray fluorescence analysis by means of a MESA-500 (Horiba, Co., Japan). The amounts of metal ions present in the cellulose samples as the counter ions of carboxylate groups were determined at least three times for each sample by using calibration curves prepared, and deviations of the obtained values were about ±5%. The pellet samples were also subjected to X-ray diffraction measurement by the reflection method using a Rigaku RINT 2000 with monochromatic Cu Kα radiation at 40 kV and 40 mA. The ion-exchanged cellulose samples soaked in water at room temperature for 6 h were centrifuged at 1500 gravity and 20 °C for 15 min, and water retention values (WRVs) were calculated from the following equation:

$$\mathrm{WRV}(\%) = 100 \times (W_w - W_d)/W_d$$

where W_w is the mass of the wet sample after centrifugation, and W_d is that after drying of the wet sample at 105 °C for 3 h.

3. Results and discussion

3.1. Ion exchange behavior of the TEMPO-oxidized cellulose

In this study, ion-exchange behavior from sodium carboxylate to others for the TEMPO-oxidized cellulose with carboxylate content of 0.48 mmol/g was compared with those for the original cotton linters and fibrous carboxymethyl cellulose (F-CMC), which had sodium carboxylate groups of 0.02 and 0.47 mmol/g, respectively. Fig. 1 shows metal ion contents in the three cellulose

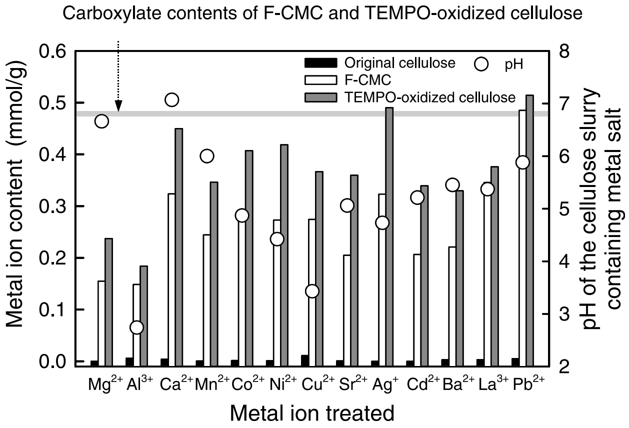

Fig. 1. Metal ion contents in the original cellulose, TEMPO-oxidized cellulose and fibrous carboxymethyl cellulose (F-CMC) after the ion-exchange treatment with metal salt solutions. Carboxylate contents of these celluloses were 0.02, 0.48 and 0.47 mmol/g, respectively. The pH values of cellulose slurries containing each metal salt are also plotted.

samples after the soaking treatment in various metal salt solutions. The original cotton linters contained nearly no or quite low metal ions, i.e. 0.000–0.011 mmol/g, even after the soaking treatments because of the quite low carboxyl content. On the other hand, the TEMPO-oxidized cellulose and F-CMC had clear ion-exchange behavior from sodium carboxylate groups to other metal carboxylates. The metal ion contents in the TEMPO-oxidized cellulose and F-CMC varied, depending on the metal salt used in the ion-exchange treatment. Lead, silver and calcium ions were preferably introduced into the celluloses as counter ions of carboxyl groups by ion exchange, while the degree of ion exchange from sodium to aluminum or magnesium ion was relatively low. In all cases examined, the TEMPO-oxidized cellulose had clearly higher metal ion contents than those of F-CMC. Moreover, it is noticeable that most of carboxyl groups in the TEMPO-oxidized cellulose form the lead or calcium carboxylate salts with the molar ratio of 1:1 like the structure of Cellulose-COOCaCl; nearly no structures like (Cellulose-COO)$_2$Ca or (Cellulose-COO)$_2$Pb are formed.

The pH values of the cellulose slurries containing each metal salt are also plotted in Fig. 1, and were various, depending on the salt used. No direct relationship seems to be observed between the pH of the cellulose slurry and the metal ion content. Because no sodium ions remained at all in either the TEMPO-oxidized cellulose or F-CMC after the ion-exchange treatment, all sodium carboxylate groups in these celluloses might have had some chances to contact with the added metal ions or H^+ during the soaking treatments. Thus, the metal ion contents lower than the carboxylate content of each cellulose, i.e. 0.47 or 0.48 mmol/g, can be explained in terms of partial formation of free carboxylic acid (i.e. cellulose-COOH) and/or partial formation of salt structures between one metal ion and either two or three carboxylate groups (e.g. cellulose-COO-MOOC-cellulose). A part of free carboxyl groups in, for example, the F-CMC sample treated with silver nitrate may have been formed also during washing process with de-ionized water at pH 5.5, which is due to partial dissolution of carbon dioxide in air into the de-ionized water.

The effect of pH of cellulose slurries on the metal ion content for the TEMPO-oxidized cellulose and F-CMC was investigated for three metal salts, and the results are plotted in Fig. 2. These pH values were adjusted by adding a diluted HCl solution into the cellulose slurries containing metal salts. Barium, nickel and calcium contents in the celluloses clearly decreased by decreasing the pH from 4.0–4.1 to 2.5–2.7, because changes from these metal carboxylate salts to free carboxylic acids occurred to some extents at the low pH values of 2.5–2.7. The differences in the metal ion contents between the celluloses treated at pH 4.0–4.2 and pH 5.5–5.9 were not so remarkable. In all pH values examined, the metal ion contents in the TEMPO-oxidized cellulose were clearly higher than those of F-CMC.

A series of ion-exchange experiments was carried out at different metal salt concentrations in cellulose slurries; the amounts of metal salts in the cellulose slurries varied at 60 moles, 6 moles and 1 mole per one sodium carboxylate group in the TEMPO-oxidized cellulose or F-CMC in the slurry. However, the metal contents determined were nearly unchanged between the celluloses treated at the different metal salt concentrations. Thus, the metal salt concentration in the cellulose slurries had little influence on the ion-exchange behavior for both the two celluloses in the range of metal concentrations examined so far.

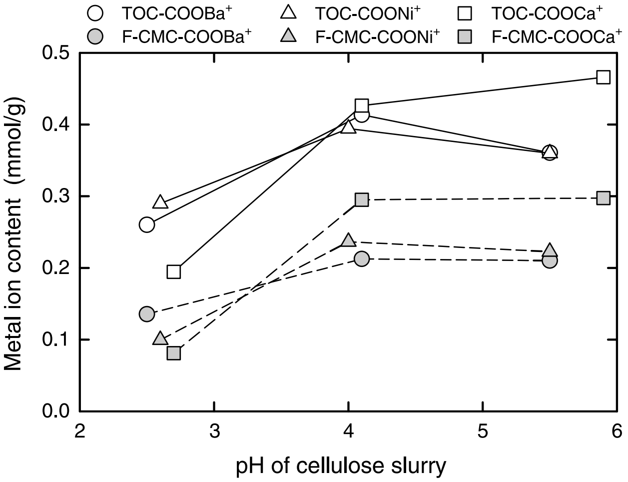

Fig. 2. Changes in metal ion content in TEMPO-oxidized cellulose (TOC) and fibrous carboxymethyl cellulose (F-CMC) after the ion-exchange treatment at different pH values.

The difference in the ion-exchange behavior between the TEMPO-oxidized cellulose and F-CMC observed in Figs. 1 and 2 may be due to that in the chemical structure of carboxylate groups, i.e. anhydroglucuronic acid sodium salt and sodium carboxymethyl substituents for the former and the latter, respectively. Because any sodium ions did not remain at all in the metal salt-treated celluloses, the metal carboxylate groups once formed in either the TEMPO-oxidized cellulose or F-CMC by ion exchange may be partly converted to free carboxylic acids during the washing process with water at pH 5.5. Fig. 3 shows X-ray diffraction patterns of the two celluloses. The TEMPO-oxidized cellulose clearly had the crystal structure of cellulose I, whose crystallinity index and crystal size of [100] direction were almost equal to those of the original cotton linters; sodium carboxylate groups introduced by the TEMPO-mediated oxidation are located only on the crystal surfaces and in disordered regions with high density in the TEMPO-oxidized cellulose (Saito et al., 2005b). On the other hand, F-CMC had the crystal structure of cellulose II, because a concentrated NaOH treatment is required even for partial carboxymethylation of cellulose for activation of hydroxyl groups; mercerization occurs during the fibrous carboxymethylation process. Thus, differences in not only the chemical structures but also crystal structures

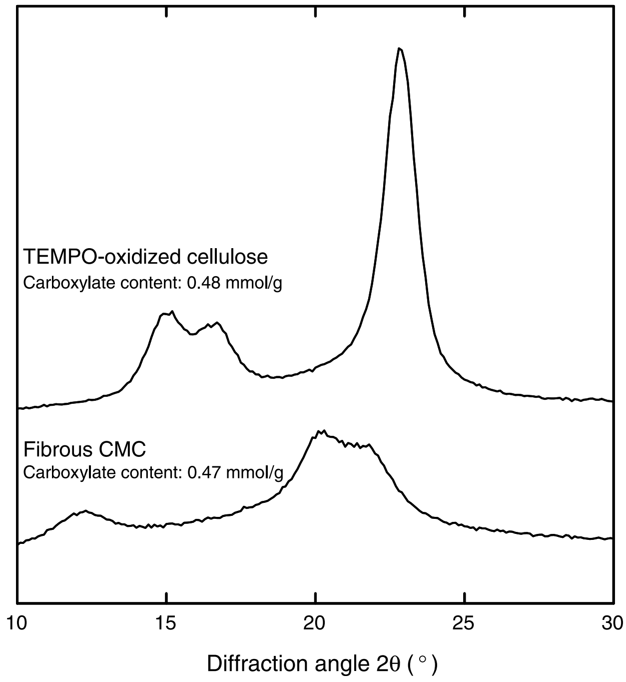

Fig. 3. X-ray diffraction patterns of TEMPO-oxidized cellulose and fibrous carboxymethyl cellulose (F-CMC).

and/or distribution of carboxylate groups between the TEMPO-oxidized cellulose and F-CMC may have brought about the different ion-exchange behavior in Fig. 1.

3.2. Adsorption selectivity of metal ions on the TEMPO-oxidized cellulose

In this section, adsorption selectivity of metal ions on the TEMPO-oxidized cellulose was compared with that for F-CMC. Fig. 4 illustrates contents and molar ratios of metal ions adsorbed on the TEMPO-oxidized cellulose by each ion-exchange treatment using a mixture of multiple metal ions. In order to evaluate the metal adsorption selectivity under similar conditions, the pH values of the cellulose slurries were adjusted to 3.0, 4.5 or 6.0 with a diluted HNO_3 solution. There was a trend that total metal ion contents became lower at pH 3.0, because free carboxylic acids are partly formed in the TEMPO-oxidized cellulose under these conditions. The metal ion contents and their ratios in each bar in Fig. 4 lead to the following adsorption selectivity of metal ions on the TEMPO-oxidized cellulose:

$Pb^{2+} > La^{3+} > Al^{3+} > Cu^{2+} > Ba^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}, Sr^{2+}, Mn^{2+}, Ca^{2+} > Mg^{2+}$

In particular, the adsorption selectivity of Pb^{2+}, La^{3+}, Al^{3+} and Cu^{2+} was remarkably high, while clear adsorption selectivity was not observed for the metal ions below Ba^{2+}.

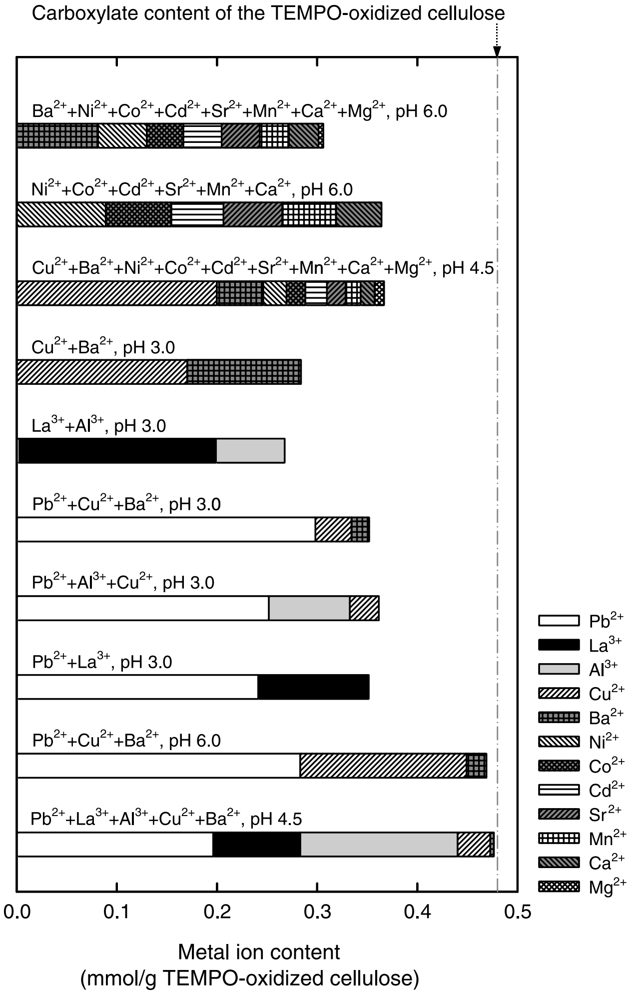

Fig. 4. Contents of metal ions and their ratios in TEMPO-oxidized cellulose after the ion-exchange treatment with aqueous solutions containing multiple metal salts. The pH values of the cellulose slurries were adjusted by addition a diluted HNO_3 solution.

Similar results were obtained also for F-CMC (Fig. 5), and gave the following order of adsorption selectivity:

$Pb^{2+} > La^{3+} > Al^{3+} > Cu^{2+} > Ba^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Sr^{2+}, Mn^{2+}, Ca^{2+} > Mg^{2+}$

As shown in Figs. 4 and 5, adsorption selectivity of metal ions on the cellulose samples behaved in similar manner at pH 3.0, 4.5 and 6.0 except for Al^{3+}. Adsorption selectivity between La^{3+} and Al^{3+} became reversed at pH 3.0 and 4.5 for both the two celluloses (see the 5th and last bars from the top in Figs. 4 and 5). It is well known that Al^{3+} ions form polyaluminum cations and other complicated compounds in the pH range of 4–6 though oxolation and olation in water (Arnson, 1982). This specific behavior of aluminum ions probably has led to the anomalous results in Figs. 4 and 5. The adsorption selectivity of metal ions observed for the two celluloses is mostly explainable by the degree of electronegativity of each metal ion. In addition, the adsorption

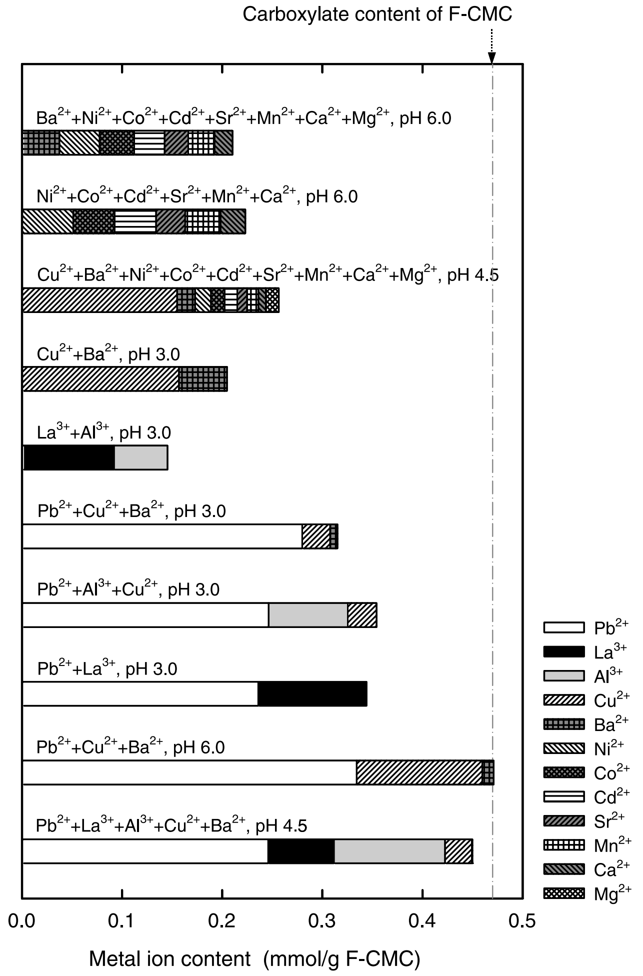

Fig. 5. Contents of metal ions and their ratios in fibrous carboxymethyl cellulose (F-CMC) after the ion-exchange treatment with aqueous solutions containing multiple metal salts. The pH values of the F-CMC slurries were adjusted by addition a diluted HNO_3 solution.

selectivity of metal ions obtained in this study is quite similar to that reported for alginates (Haug & Smidsrød, 1965). Thus, the primary factor influencing the adsorption selectivity is the electronegativity of each metal ion.

3.3. Stability of metal carboxylate structures in the TEMPO-oxidized cellulose

Fig. 6 shows metal ion contents in the TEMPO-oxidized cellulose having various metal carboxylate groups after some soaking treatments for evaluation of the stability of each metal carboxylate structure. The starting cellulose samples were prepared beforehand by the soaking treatment of the TEMPO-oxidized cellulose in salt solutions and then drying. It is natural that the metal ion contents were nearly unchanged after the treatment in water. When the celluloses were treated in an aqueous HNO_3 solution at pH 1.7, significant amounts of metal ions originally present in the cellulose samples decreased by ion exchange from metal carboxylates to free carboxylic acids. However, lead and lanthanum carboxylate groups had some resistance to removal from the celluloses even by the acid treatment, and more than 20% of the original metal ions remained in there.

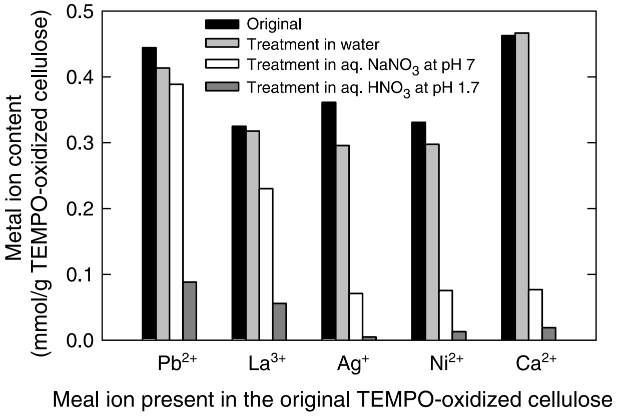

Fig. 6. Changes in metal ion content of TEMPO-oxidized celluloses having various metal carboxylate groups after the treatments in water, aqueous $NaNO_3$ solution at pH 7 and aqueous HNO_3 solution at pH 1.7.

When the celluloses were treated in 0.25 M $NaNO_3$ at pH 7, they had different metal ion contents or showed different detachment behavior of metal ions from the celluloses. More than 78% of silver, nickel and calcium ions originally present in the TEMPO-oxidized celluloses were removed by this treatment, while lead and lanthanum ions had clear resistance to removal. It was reported that gel formation behavior of alginates was governed by the kinds of divalent metal ions present in the alginate solutions. When the metal ion/carboxylate bonds are strong or degree of dissociation of the metal carboxylates is low, alginates or water-soluble CMC form stable gel structures (Haug & Smidsrød, 1965; Heinze, Helbig, & Klemm 1993). In contrast, degree of dissociation of the metal carboxylates is sufficiently high like sodium alginate, aqueous alginate solutions keep their solution states without forming any gels. Thus, the different stability of metal carboxylates to the 0.25 M $NaNO_3$ treatment in Fig. 6 may have been reflected by strength of the metal ion/carboxylate bonds or degree of dissociation of the metal carboxylates.

3.4. Water retention values of the TEMPO-oxidized celluloses having various metal carboxylate groups

Fig. 7 depicts water retention values (WRVs) of the TEMPO-oxidized celluloses having various metal carboxylate groups. Generally, WRVs of cellulosic pulps reflect their swelling abilities in water, if the shapes of the pulps are similar to each other. The WRV remarkably increased from 60% to 260% by the introduction of hydrophilic and highly dissociated sodium carboxylate groups into the original cotton linters through the TEMPO-mediated oxidation. Introduction of calcium carboxylate groups into cellulose also resulted in an increase in WRV. On the other hand,

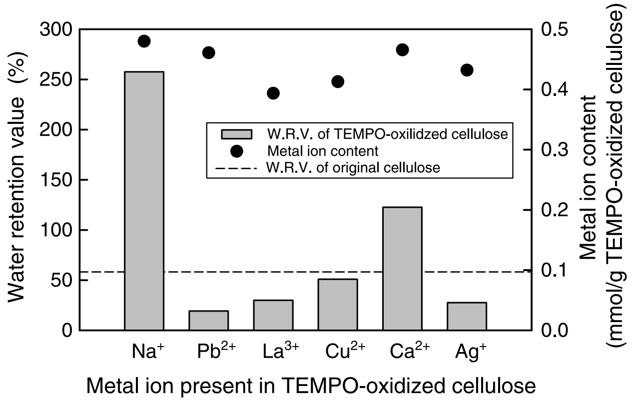

Fig. 7. Water retention value of TEMPO-oxidized celluloses having various metal carboxylate groups.

the TEMPO-oxidized celluloses having lead, lanthanum, copper and silver carboxylate groups decreased the swelling abilities, and the WRVs became lower than that of the original cotton linters. Especially, the cellulose having lead carboxylate groups gave the lowest WRV in the samples examined. Similar results in changes of swelling abilities were also reported for gels of CMC metal salts (Heinze et al., 1993). Thus, the WRVs or swelling abilities of the TEMPO-oxidized celluloses having various metal ions must be influenced by the degree of dissociation of the metal carboxylate groups in water. These results of WRVs in Fig. 7 are well consistent with those of stability of the metal ion/carboxylate bonds in Fig. 6 except for the case of silver ion, and the discrepancy of the results for the silver carboxylate groups between Figs. 6 and 7 are unknown at this moment.

3.5. Handsheet properties prepared of the TEMPO-oxidized cellulose

It was reported that wet tensile strength of handsheets was remarkably improved when bleached hardwood kraft pulp for papermaking was partially treated with the TEMPO/NaBr/NaClO system (Kitaoka et al., 1999; Saito & Isogai, 2005). Probably some aldehyde groups at the C6 position of cellulose formed by the TEMPO-mediated oxidation as the intermediate structure and located at the pulp fiber surfaces contribute to the wet strength improvement of the handsheets by the formation of inter-fiber hemiacetals linkages during the handsheet-making process (Saito et al., 2005a). Because the kraft pulp contained about 15% hemicellulose, wet strength of handsheets prepared of cotton linters having high α-cellulose content and high crystallinity index was measured in terms of the carboxylate content of the TEMPO-oxidized celluloses. Moreover, the effect of the structures of metal carboxylate groups in the TEMPO-oxidized celluloses on wet tensile strength of the handsheets prepared thereof was investigated using divalent and trivalent metal salt solutions as soaking solvents in the wet strength test.

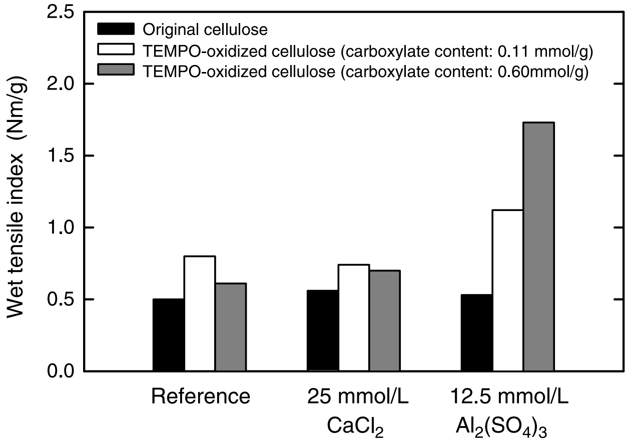

Fig. 8. Wet tensile index of handsheets prepared from the original cellulose and TEMPO-oxidized celluloses having carboxylate groups of 0.11 and 0.60 mmol/g. Water, 0.025 M $CaCl_2$ and 0.0125 M $Al_2(SO_4)_3$ solutions were used as the soaking solvents in the wet strength test.

Fig. 8 shows wet tensile strength of the handsheets prepared from the original cotton linters and TEMPO-oxidized celluloses. Because cotton linters having a swelling ability lower than those of wood kraft pulps in water give inter-fiber bond areas smaller than those for kraft pulps in handsheets, the absolute wet tensile index of the handsheets prepared from the original cotton linters was quite low. However, the improvement of wet tensile strength was detected for the TEMPO-oxidized cellulose having carboxylate groups of 0.11 mmol/g. The TEMPO-oxidized cellulose with carboxylate content of 0.60 mmol/g prepared by further oxidation rather decreased the wet tensile strength of the handsheets prepared thereof, and similar patterns were observed also for the kraft pulp handsheets (Kitaoka et al., 1999; Saito & Isogai, 2005). When the soaking solvent in the wet strength test was replaced from water to a 0.025 M calcium chloride solution, the pattern of wet tensile index of the handsheets was roughly unchanged for the three celluloses, indicating the formation of calcium carboxylate groups in place of sodium carboxylate groups in the TEMPO-oxidized cellulose has little influence on the wet tensile strength of the handsheets prepared thereof. In contrast, when a 0.0125 M aluminum sulfate solution was used as the soaking solvent in place of water, wet tensile index of the handsheets clearly increased with increasing the carboxylate content in the TEMPO-oxidized celluloses. Because the degree of dissociation of aluminum carboxylate is quite low, some inter-fiber cross linkages like the structure of Cellulose-COOAl(OH)OOC-Cellulose are formed in the handsheets prepared of the TEMPO-oxidized celluloses during the soaking treatment of the specimen strips in the aluminum sulfate solution (Lindgren, Persson, & Öhman, 2001), thus resulting in further improvement of wet tensile strength by the formation of additional inter-fiber cross linkages through the formation of aluminum carboxylate structures.

4. Conclusion

Metal ion contents in the TEMPO-oxidized celluloses after the ion-exchange treatments using various metal salt solutions varied, depending on the metal salt used for soaking. Especially, lead, calcium and silver ions were preferably introduced into the TEMPO-oxidized cellulose as counter ions of the carboxylate groups with the metal ion/carboxylate molar ratio of about 1:1. The TEMPO-oxidized cellulose had metal ion contents higher than those of F-CMC in all ion-exchange treatments examined. Metal ions once adsorbed on the TEMPO-oxidized cellulose were mostly or partly removed by the soaking treatments in aqueous HNO_3 at pH 1.7 or aqueous $NaNO_3$ at pH 7, depending on the degree of dissociation of the metal carboxylate groups in the TEMPO-oxidized celluloses in water. The following order of adsorption selectivity of metal ions on the TEMPO-oxidized cellulose was obtained:

$$Pb^{2+} > La^{3+} > Al^{3+} > Cu^{2+} > Ba^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}, Sr^{2+}, Mn^{2+}, Ca^{2+} > Mg^{2+}$$

The primary factor affecting the above adsorption selectivity of metal ions is the electronegativity of each metal ion. The degree of dissociation of the metal carboxylate groups influences swelling abilities in water or water retention values of the TEMPO-oxidized celluloses having various metal carboxylate groups. Because degree of dissociation of aluminum carboxylate groups is quite low, wet tensile strength of handsheets prepared from the TEMPO-oxidized celluloses increased with increasing the carboxylate content in the celluloses, when an aluminum sulfate solution was used as the soaking solution in the wet strength test.

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