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Carbohydrate Polymers 49 (2002) 23–31

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

# Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp

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Received 2 March 2001; revised 11 June 2001; accepted 1 July 2001

## Abstract

The abilities of native and modified sugar beet pulps to remove Ni(II) and Cu(II) ions from aqueous solutions were compared. Their preparation by chemical treatments (saponification, hot 0.05 M HCl and cold 0.05 M NaOH extractions) is described. The sugar composition, which was strongly affected during these modifications, is discussed in terms of metal sorption efficiencies. The influence of these modifications was also evaluated by comparing the content of the functional groups determined by potentiometric titration, and the rate and extent of Cu(II) and Ni(II) uptakes onto the raw and modified materials. Nickel and copper sorptions were fast and complete within 30 min and the kinetic parameters were calculated using a second order model. The equilibrium data fitted well with the Langmuir model and showed the affinity order of the materials for the metal ions. The base-extracted pulp and saponified pulp exhibited the highest Ni(II) and Cu(II) ion uptakes among the materials tested.

*Keywords*: Sorbents; Polysaccharides; Metal ions; Adsorption; Modelling

## 1. Introduction

Pollution by heavy metals is an important environmental problem due to their toxic effects and accumulation throughout the food chain. Processes for metal removal like biosorption have been suggested as being cheaper and more effective than chemical (precipitation) or physical (ion exchange and membrane technology) technologies. Biosorption involves the use of biological materials that form complexes with metal ions using their ligands or functional groups. The use of micro-organisms such as bacteria (Texier, Andrès & Le Cloirec, 1999), fungi and algae (Kratochvil & Volesky, 2000; Schiewer & Wong, 1999;Yang & Volesky, 1999) in treating waste effluents containing toxic metal ions is today an attractive technique but is not yet suitable for applications on a large scale.

Numerous by-products of agro-industrial production have been studied for potential use as inexpensive biosorbents (Laszlo & Dintzis, 1994; Marshall, Wartelle, Boler & Toles, 2000). One of these low-cost sorbents particularly suited to biosorption is sugar beet pulp, which exhibits a large capacity to bind metals (Dronnet, Renard, Axelos & Thibault, 1997; Gerente, Couespel du Mesnil, Andrès & Le Cloirec, 2000). About $14 \times 10^6$ tonnes of sugar beet pulp are produced every year in Western Europe, where it is mainly used as animal feed (Micard, Renard, Colquhoun & Thibault, 1997). The pectic substances, which account for more than 40% of the dry matter, are complex heteropolysaccharides containing galacturonic acid, arabinose, galactose and rhamnose as the major sugar constituents (Dronnet et al., 1997). Due to the carboxyl functions of galacturonic acid, pectic substances are known to strongly bind metal cations in aqueous solution (Kartel, Kupchik & Veisov, 1999). Chemical modification has led to improvements in the cation exchange capacity of agricultural by-products (Laszlo & Dintzis, 1994; Marshall et al., 2000; Wartelle & Marshall, 2000). The metal-binding capacity of the native or modified sugar beet pulp has been demonstrated in previous studies (Dronnet, Axelos, Renard & Thibault, 1998) but little attention has been paid to the identification of the active binding sites involved in the metal uptake.

The aim of this study is to investigate the impact of different chemical treatments of native sugar beet pulp on the recovery of Ni(II) and Cu(II) ions. These metals are

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0144-8617/02/$ - see front matter
PII: S0144-8617(01)00301-0

found extensively in effluents from the microelectronics and electroplating industries (Ho & McKay, 1999). The preparation and composition of the modified materials are described and the extent of copper and nickel sorptions is discussed, with the aim of achieving a better knowledge of the metal sorption parameters. The differences in copper and nickel recoveries, among the sugar beet pulps tested, are discussed as a function of structural changes during their preparation.

## 2. Materials and methods

### 2.1. Materials

Sugar beet pulp was obtained from Lyven (Cagny, France). It was ground using a hammer mill then sieved. The samples of particle size smaller than 250 μm were discarded as they probably contain soil and sand particles (Michel, Thibault, Barry & De Baynast, 1988). Only material with a particle size between 250 and 500 μm was used for the subsequent extractions. This fraction was washed with deionised water (20 g $l^{-1}$) for 12 h, filtered and air-dried at 40°C. This pulp was called native pulp (NP).

### 2.2. Native pulp modifications

Saponified pulp (SP) was obtained by adjusting the pH of a suspension of NP (25 g $l^{-1}$) to 12 with 1 M NaOH at 4°C. The suspension was kept at pH 12 and stirred for 2 h. After neutralisation to pH 5.5 with 1 M HCl, the pulp was then filtered off and washed three times with 2 l deionised water. It was then washed with 70% ethanol, dried by solvent exchange (95% ethanol and acetone) and air-dried at 40°C.

Acid-extracted pulp (AEP) and base-extracted pulp (BEP) were prepared according to the procedure proposed by Bertin, Rouau and Thibault (1988). NP (50 g) was extracted three times with 2 l 0.05 M HCl for 30 min at 85°C. After neutralisation at pH 5.5, the mixture was filtered and thoroughly washed with deionised water. Acid-extracted pulp (AEP) was air-dried after solvent exchange and weighed. Base-extracted pulp (BEP) was obtained by stirring 50 g of AEP three times with 0.05 M NaOH for 30 min, at 4°C, using a total volume of 2 l. After neutralisation and filtration, the material was washed with deionised water, dried as above and weighed.

### 2.3. Analytical methods

Galacturonic acid content was quantified colorimetrically by the automated *m*-hydroxybiphenyl method (Ahmed & Labavitch, 1977). Neutral sugars were reduced, acetylated and quantified with a GLC system (Perkin–Elmer), using an OV-225 column. Inositol was used as internal standard. Micronized samples were pre-hydrolysed by $H_2SO_4$ 72% for 30 min at 25°C, diluted to 1 M and heated at 100°C for 2 and 6 h (Micard, Renard & Thibault, 1996).

The degrees of methylation (DM, moles of methanol per 100 galacturonides) and acetylation (DAc, moles of acetic acid per 100 galacturonides) were analysed by an HPLC system (Waters 590-1), using a C18 Superspher Merk column. Elution was carried out with dilute sulphuric acid (pH 3.8) at a flow rate of 0.7 ml $min^{-1}$ after saponification of the samples (1 M NaOH in 50% (v/v) aqueous propan-2-ol, for 1 and 2 h). All these analyses were performed in duplicate and good agreement was found with standard errors lower than 5%.

### 2.4. Functional group evaluation by potentiometric titration (Boehm, 1966)

Potentiometric titrations were performed according to Boehm's method (1966) by adding 0.1 M base solutions of increasing strength ($NaHCO_3$, $Na_2CO_3$, NaOH and $NaOC_2H_5$) to the protonated sugar beet pulps. The acidity constants of carboxyl groups, lactones and phenols differ over several orders of magnitude and this method consists of differentiating these various types of groups by their neutralisation behaviour. The most convenient way to determine the concentration of strong carboxyl groups is to perform a neutralisation experiment with a dilute solution of $NaHCO_3$. $Na_2CO_3$ solution is suitable for the determination of weak acidity as found in lactones. Very weak acidity, as in phenolic groups, can react with strong alkali, like NaOH. Lastly, the carbonyl groups react only with sodium ethoxide ($NaOC_2H_5$) and not with the other titrants. In this work, $NaOC_2H_5$ neutralisation was not taken into account since this strong base entailed saponification of the methoxylated carboxyl groups and acetyl groups in the pectins, resulting in an overestimation of the neutralisation equivalents.

Base solutions were freshly prepared and maintained under a nitrogen atmosphere. The equipment used consisted of a titrimeter (Radiometer Copenhagen) with an automatic burette. Titrations were carried out in an enclosed glass cell at 21.0 ± 0.5°C under nitrogen in order to avoid dissolution of carbon dioxide in the solution. First, the sugar beet pulp was protonated with 0.01 M HCl for 1.5 h according to the methodology described previously by Bertin et al. (1988) and dried at 40°C. Then, 1 g of protonated pulp was suspended in 100 ml of a 0.1 M $NaNO_3$ solution, to maintain the same ionic strength during the titration, and stirred for 1.5 h under nitrogen prior to titration. Successive increments of base were added. Between each titrant addition, equilibrium was considered reached when the drift readings were less than 0.1 mV for 10 s. Lastly, a titration was performed by addition of NaOH 0.1 M to a control, i.e. $NaNO_3$ without pulp. Each titration experiment was carried out in duplicate.

The experimental cation exchange capacity (CEC) deduced from potentiometric titration was compared with the theoretical one ($CEC_{th}$) calculated from the degree of methylation and the galacturonic acid content, with the assumption that only the free carboxylic groups were

Table 1
Yield and sugar composition of NP, SP, AEP and BEP sorbents

| Sorbent | Yield[a] | Sugar composition[b] | | | | | | | | DM[c] | DAc[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Rha | Fuc | Ara | Xyl | Man | Gal | Glc | GalA | | |
| NP | 100.0 | 24 | 02 | 196 | 14 | 13 | 55 | 215 | 206 | 52 | 59 |
| SP | 89.0 | 23 | 02 | 206 | 15 | 14 | 56 | 245 | 208 | 05 | 24 |
| AEP | 66.6 | 26 | 02 | 117 | 19 | 18 | 60 | 350 | 190 | 34 | 45 |
| BEP | 52.7 | 23 | 02 | 100 | 21 | 21 | 57 | 389 | 160 | < 01 | 07 |

[a] Expressed as percentage dry weight calculated from NP material.

[b] Expressed as mg $g^{-1}$ dry weight of the material.

[c] Degree of methylation (DM) and acetylation (DAc) expressed as moles of methanol or acetic acid for 100 galacturonides.

responsible for cation binding capacity:

$$\mathrm{CEC_{th}} = \frac{[\mathrm{GalA}]\left(1 - \frac{\mathrm{DM}}{100}\right)}{176.16}, \tag{1}$$

where $\mathrm{CEC_{th}}$ is expressed as mmol $g^{-1}$ of dry weight. DM is the degree of methylation of the sample, [GalA] the galacturonic acid content of the material (mg $g^{-1}$) and 176.16 g $mol^{-1}$ the molecular weight of the anhydrogalacturonic acid.

### 2.5. Sorption experimental procedures

Analytical grade reagents were used in all cases. Stock solutions of Cu(II) and Ni(II) at 20 and 10 g $l^{-1}$, respectively, were prepared in deionised water using copper and nickel chloride. All working solutions were prepared by diluting the stock solutions with deionised water.

#### 2.5.1. Sorption kinetics

Kinetic experiments were performed in 1000 ml batch reactors at 21.0 ± 0.5°C. First, 2 g of beet pulp were introduced in 800 ml of deionised water. Prior to the introduction of the metal ions, the flasks were vigorously stirred for 1.5 h to hydrate the beet pulp and the initial pH was adjusted to 5.5 with 0.1 M HCl. The suspension of NP was not adjusted since it buffered naturally at pH 5.5. The initial concentrations of Ni(II) and Cu(II) ions were both $8 \times 10^{-4}$ M for all tests. After the introduction of the metal, samples were collected at suitable time intervals, filtered through a 0.45 μm cellulose acetate membrane filter and then analysed with an atomic absorption spectrophotometer (Perkin–Elmer 2280).

The kinetics of sorption of Ni(II) and Cu(II) ions were modelled using a pseudo-second order rate equation developed by Ho and McKay (2000). The kinetic rate equation is:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \tag{2}$$

where $k$ (g $mmol^{-1}$ $min^{-1}$) is the rate constant of sorption, $q_e$ (mmol $g^{-1}$ of dry weight) the amount of divalent metal ion sorbed at equilibrium, $q_t$ (mmol $g^{-1}$ of dry weight) is the amount of divalent metal ion on the surface of the sorbent at any time $t$ (min). Taking into account the initial sorption rate $v_0$ (mmol $g^{-1}$ $min^{-1}$):

$$v_0 = kq_e^2. \tag{3}$$

Eq. (2) can be rearranged to obtain:

$$\frac{t}{q_t} = \frac{1}{v_0} + \frac{1}{q_e}t. \tag{4}$$

The values of $v_0$ and $q_e$ can be determined experimentally by plotting $t/q_t$ versus $t$ (Ho & McKay, 2000).

#### 2.5.2. Sorption isotherms

The sorption experiments were carried out in 500 ml bottle flasks at 21.0 ± 0.5°C. 1 g of beet pulp was thoroughly mixed with 400 ml deionised water for 1.5 h to hydrate the material. The initial pH was adjusted to 5.5 with 0.1 M HCl. The initial concentrations for Cu(II) and Ni(II) ranged from 0.2 to 2.5 mmol $l^{-1}$ for each sample. Equilibrium times were deduced from the kinetic experiments and fixed at 1 h. The final pH was measured and the reaction mixtures were filtered through a 0.45 μm cellulose acetate membrane. The filtrate was analysed for the concentration of Cu(II) and Ni(II). The quantity of metal sorbed at equilibrium, $q_e$ (mmol $g^{-1}$ of dry weight), was deduced from the mass balance between initial concentration and concentration at time $t$ in solution.

The equilibrium data were analysed in accordance with the Langmuir sorption isotherm as:

$$q_e = \frac{q_m b C_e}{1 + bC_e}, \tag{5}$$

where $q_m$ (mmol $g^{-1}$) is the maximum sorption capacity corresponding to complete monolayer coverage, $q_e$ (mmol $g^{-1}$) the sorption capacity at the equilibrium solute concentration $C_e$ (mmol $l^{-1}$), and $b$ is the equilibrium constant related to the energy of sorption (l $mmol^{-1}$). The Langmuir isotherm theory assumes that the adsorbed layer is one molecule in thickness, i.e. a monolayer adsorption.

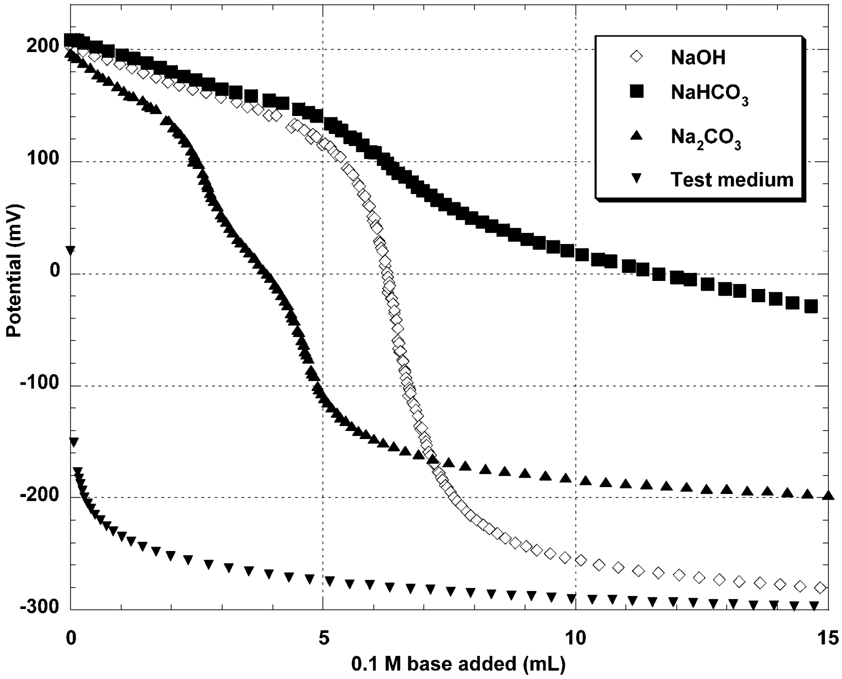


Fig. 1. Potentiometric titrations of the protonated BEP by the addition of base solution (0.1 M) of increasing strength.

## 3. Results and discussion

### 3.1. Chemical composition of the sorbents

The sugar composition and content of methanol (DM) and acetic acid (DAc) of NP, SP, AEP and BEP samples are given in Table 1.

Polysaccharides in NP accounted for 72.5% of the dry matter. The rest constitutes proteins, lignin, ferulic acid and some mineral materials (Bertin et al., 1988). NP contained three major components i.e. glucose (215 mg g$^{-1}$), arabinose (196 mg g$^{-1}$) and galacturonic acid (206 mg g$^{-1}$). The other sugars, except galactose (55 mg g$^{-1}$), occurred in very small amounts (<24 mg g$^{-1}$). With DM and DAc values of 52 and 59%, this composition was in good agreement with previously published values (Dronnet et al., 1998; Micard et al., 1997).

Saponification removed about 11% of the NP weight and did not significantly affect the final sugar composition. This reaction led to an important decrease in the degree of methylation (DM) from 52 to 5%. The loss of acetyl substituents was less efficient, probably because acetic acid was not only bound to hydroxyl groups of galacturonic units but also to other structural polymers (Rombouts & Thibault, 1986) thus leading to a difference in reactivity with the base. However, the efficient loss of methanol from the carboxylic groups increased the cation exchange capacity of SP.

Sequential extractions with hot 0.05 M acid and cold 0.05 M alkali, well known for removing different fractions of pectins, were applied to NP (Bertin et al., 1988). The overall yields in AEP and BEP were 66.6 and 52.7% of the initial NP weight, respectively. The structure and composition of the samples were affected by the extraction processes, which may also have affected their functional properties. Carbohydrates constituted the main part of AEP and BEP fractions, 78.2 and 77.3% of dry weight, respectively.

The main components of AEP were neutral sugars, especially glucose (350 mg g$^{-1}$) from cellulose. Arabinose was strongly affected by the acid treatment since 60.2% was removed, probably because the arabinofuranosyl linkages in arabinans are more labile than the other glycosidic linkages between neutral sugar residues (Voragen, Pilnik, Thibault, Axelos & Renard, 1995). This treatment led to the solubilisation of 38.6% of the initial galacturonic acid content. Since the galacturonic acid content was still 190 mg g$^{-1}$ in AEP with a DM value of 34%, the pectic backbone was not totally extracted during the acid treatment.

BEP was especially rich in cellulose with 389 mg g$^{-1}$ as glucose. The alkali treatment led to an efficient decrease in the initial galacturonic acid content (59%) and in the degrees of esterification. It suggests a significant loss of pectic substances. Arabinose, galactose and rhamnose were the major non-cellulosic neutral sugars. Small amounts of xylose and mannose (21 mg g$^{-1}$) were also present. The significant extraction of pectic polysaccharides during the alkali treatment could be due to saponification of ester bonds between pectins and hemicellulose (Sun & Hughes, 1999). However, BEP was not devoid of pectins and a strongly bound pectic material was evidenced (160 mg g$^{-1}$ as galacturonic acid).

More generally, the relative glucose content greatly increased during the acid and alkali treatments. It is

Table 2
Estimation of acidic functional groups on the sorbents

| | NP | SP | AEP | BEP |
|---|---|---|---|---|
| Strong carboxyl groups (μeq $g^{-1}$) | 246 ± 3 | 471 ± 2 | 241 ± 3 | 272 ± 4 |
| p$K_a$ | 3.7 | 3.7 | 3.7 | 4.6 |
| Weak carboxyl groups (μeq $g^{-1}$) | 220 ± 5 | 340 ± 6 | 308 ± 4 | 257 ± 4 |
| p$K_a$ | 4.8 | 4.3 | 4.8 | 6.1 |
| Very weak acidic groups (μeq $g^{-1}$) | 109 ± 5 | 169 ± 16 | 173 ± 3 | 235 ± 3 |
| Estimation of the cation exchange capacity CEC (μeq $g^{-1}$) | 575 ± 13 | 980 ± 24 | 722 ± 10 | 764 ± 11 |
| Theoretical cation exchange capacity $CEC_{th}$ (μeq $g^{-1}$) | 562 | 1 122 | 710 | 904 |

interesting to note that close amounts of galactose, rhamnose and galacturonic acid were extracted after acid (27.3, 27.9, 38.5%, respectively) and alkali (45.4, 49.5, 59%, respectively) treatments, which suggests that they are part of the same pectic polymers.

### *3.2. Functional group analysis*

The analysis of the functional groups is essential to the selection of biosorbents that can be used in the treatment of metal-contaminated effluents (Texier, Andrès, Illemassene & Le Cloirec, 2000).

Fig. 1 shows the potentiometric titration curves of the protonated BEP sample. Similar curves were obtained for the three other sorbents but with different equivalence volumes. It is obvious that different moieties with distinct acidities were present according to the shapes of the titration curves. From the pH values deduced at the two-half equivalence points of the curves, it was possible to determine the global acidity (p$K_a$) of each functional group. The quantitative and qualitative estimations of the functional groups are given in Table 2 for all the materials tested. These results reflect the changes induced by the overall chemical treatments.

The titration curves obtained by the addition of $Na_2CO_3$ solution have always presented two distinct waves showing the presence of strong and weaker acidic groups, probably of carboxylic type according to their respective p$K_a$, 3.7 and 4.8. The same p$K_a$ values were found for NP and AEP samples. These two acidities predominated in NP and represented 81% of the total acidity (466 ± 8 μeq $g^{-1}$ of dry matter) whereas the very weak acidity, probably of phenolic type from lignin, ferulic acid and some charged groups from proteins, was less abundant (109 ± 5 μeq $g^{-1}$). Each of these moieties is a potential ligand for metal ions. The numerous carboxylic groups in the pectic backbone induce high values of strong acidity in the native material.

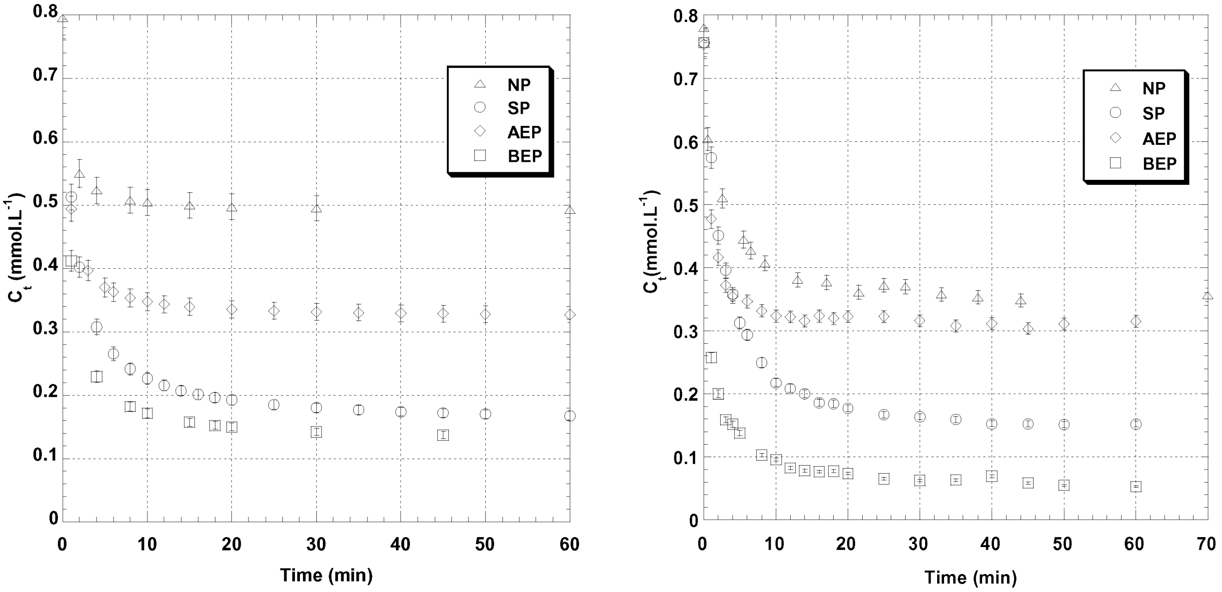
The significant difference between the acidity constants 3.7 and 4.8 (Table 2) of the carboxyl groups could be explained by the heterogeneity of the chemical neighbourhood along the pectic backbone. It could also be suggested that the intermolecular distribution of the carboxyl groups along the pectic chains is not regular. These results are very important since this difference in acidity of the carboxyl groups will certainly induce a difference in metal ion reactivity.

The saponification reaction led to an increase in the CEC from 575 ± 13 to 980 ± 24 μeq $g^{-1}$ due to the decrease in DM from 52 to 5. However, this experimental CEC is slightly lower than the theoretical one ($CEC_{th} = 1122\ \mu eq\ g^{-1}$). Only the second acidity constant of the carboxyl functions was affected by the saponification reaction, from 4.8 to 4.3. As the methanol was released, the acidic behaviour of the pectic backbone was probably reinforced with new free carboxyl groups, which led the second acidity constant 4.8 to approach 3.7.

The acid treatment led to an increase in the CEC from 575 ± 13 to 722 ± 10 μeq $g^{-1}$, which is in good accordance with the theoretical value of 710 μeq $g^{-1}$. This improvement could easily be explained by the fact that some demethylation may also take place during this acid extraction process (Voragen et al., 1995). It could be also suggested that the released pectins were highly methylated. Thus the remaining pectins, with a lower DM, contained more free carboxylic groups. This effect was also observed when preparing the BEP material. Despite the efficient loss of pectic materials, the CEC was found to be 764 ± 11 μeq $g^{-1}$, which was in good agreement with the theoretical one. This high value was attributed to the fact that, although galacturonic acid content was low, all of them carried free carboxylic groups whereas they were partially methylated in AEP. It is also possible that the alkali extraction resulted in uncontrolled hydrolysis of ester links, thus leading to the appearance of new binding sites in BEP. This alkali treatment induced extensive modifications of the polysaccharides, since the acidity constants of the carboxyl groups both increased from 3.7 to 4.6 and from 4.8 to 6.1, respectively. This is consistent with the loss of a part of the acid pectic materials.

### *3.3. Kinetic studies results*

Fig. 2(a) and (b) shows the concentration-decay curves for Ni(II) and Cu(II) ions obtained by batch contact time studies on the different sorbents. For all materials, it is shown that the Cu(II) and Ni(II) sorptions were very fast. The majority of nickel ions were removed within the first 15 min of contact for all beet pulps tested. For copper, the major uptake occurred in the first 20 min. However, the equilibrium times were slightly different between the



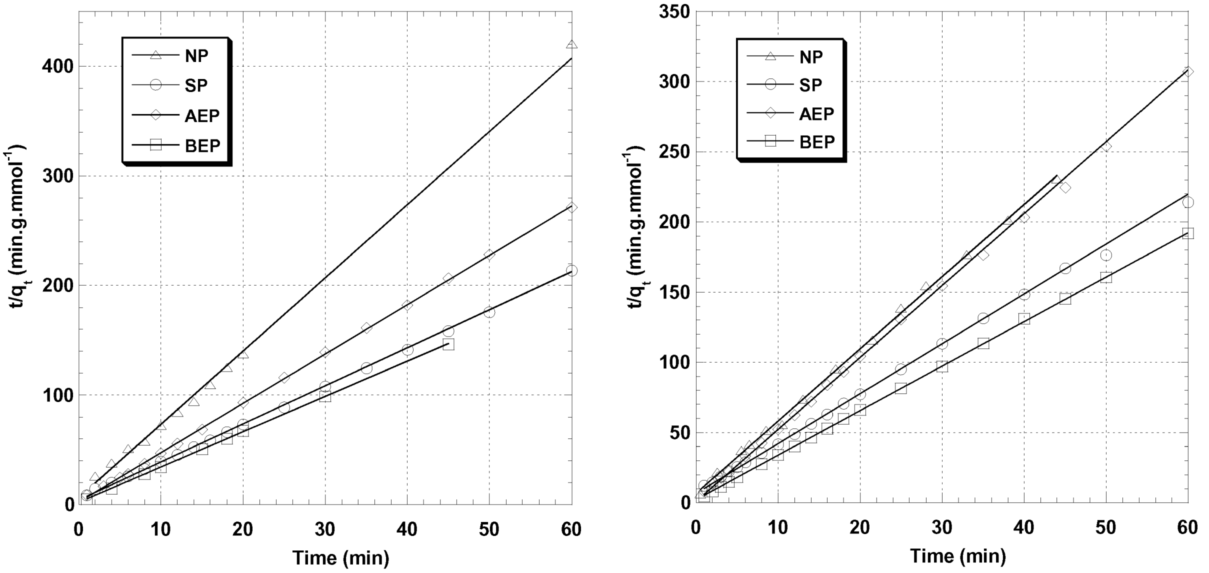
(a) (b)

Fig. 2. Ni(II) (a) and Cu(II) (b) sorption kinetics on NP, SP, AEP and BEP samples at $pH_i$ 5.5, for an initial metal concentration of 0.8 mM and beet pulp dose of 2.5 g $l^{-1}$.

materials. For nickel ions, the equilibrium states were reached after 15 min contact time on NP and AEP materials and 30 min on SP and BEP samples. The copper sorption was achieved after 20 min contact time on NP and AEP and 30 min on SP and BEP. From Fig. 2(a) and (b), large differences between the kinetic rates of sorption and the metal recoveries are suggested.

In order to evaluate these differences, the kinetics of sorption of Ni(II) and Cu(II) ions were described with a pseudo-second order model (Ho & McKay, 2000). Fig. 3(a) and (b) shows nickel and copper data plotted ($t/q_t$ versus $t$) so that the $v_0$ and $q_e$ values in Eq. (4) can be determined. These values are given in Table 3 for nickel and copper series. As shown in Table 3, the regression coefficients for the linear plots are very good (0.999 for all the kinetics). The initial sorption rate ($v_0$) values ranged from 0.232 to 0.450 mmol $g^{-1}$ $min^{-1}$ for nickel removal, and from 0.149 to 0.994 mmol $g^{-1}$ $min^{-1}$ for copper.

First, the initial rate of sorption ($v_0$) of Ni(II) onto NP was higher than that of Cu(II) even though nickel was less



(a) (b)

Fig. 3. Plots of $t/q_t$ versus time ($t$) for the sorption kinetics of Ni(II) (a) and Cu(II) (b) ions onto NP, SP, AEP and BEP sorbents ($[M^{2+}]_0 = 0.8$ mM and beet pulp dose of 2.5 g $l^{-1}$). The straight lines represent the second order model.

Table 3
Nickel and copper sorption data derived from the second order kinetic model ($[M^{2+}]_0 = 8 \times 10^{-4}$ M, $pH_i = 5.5$, and beet pulp dose 2.5 g $l^{-1}$)

| $M^{2+}$ | Sorbent | $q_e$ (mmol $g^{-1}$) | $v_0$ (mmol $g^{-1}$ $min^{-1}$) | $r^2$ |
|---|---|---|---|---|
| Ni | NP | 0.135 | 0.275 | 0.999 |
| | SP | 0.287 | 0.232 | 0.999 |
| | AEP | 0.221 | 0.424 | 0.999 |
| | BEP | 0.31 | 0.45 | 0.999 |
| Cu | NP | 0.192 | 0.162 | 0.999 |
| | SP | 0.281 | 0.149 | 0.999 |
| | AEP | 0.194 | 0.994 | 0.999 |
| | BEP | 0.315 | 0.472 | 0.999 |

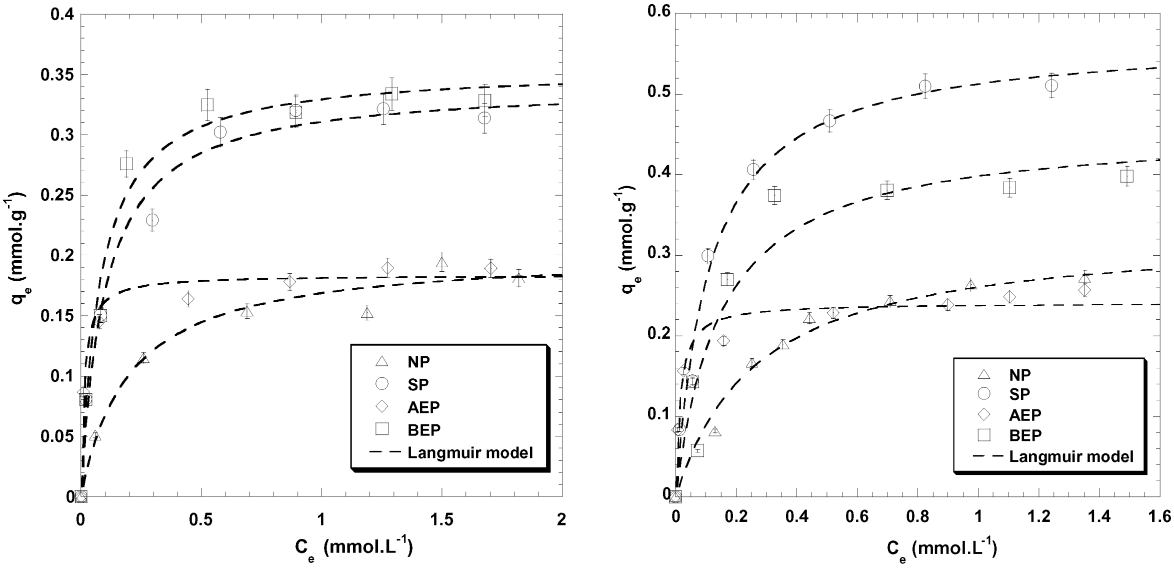
Table 4
Langmuir parameters applied to the different metal-polysaccharide sorption isotherms

| $M^{2+}$ | Sorbent | $q_m$ (mmol $g^{-1}$) | $b$ (l $mmol^{-1}$) | $r^2$ |
|---|---|---|---|---|
| Ni | NP | 0.202 | 4.96 | 0.978 |
| | SP | 0.341 | 10 | 0.985 |
| | AEP | 0.183 | 73.6 | 0.982 |
| | BEP | 0.355 | 12.57 | 0.982 |
| Cu | NP | 0.33 | 3.73 | 0.984 |
| | SP | 0.57 | 8.95 | 0.989 |
| | AEP | 0.241 | 71.3 | 0.978 |
| | BEP | 0.457 | 6.72 | 0.925 |

removed than copper at the equilibrium state. For both Ni(II) and Cu(II) ions, a slight reduction of the initial sorption rates on SP material was observed, when compared with NP. It appears that the saponification of the native sugar beet pulp resulted in a reduction of the initial sorption rates but, simultaneously, in an enhancement of the quantities of Ni(II) and Cu(II) sorbed at equilibrium. The initial nickel sorption rate was increased on AEP and more markedly on BEP sorbent. On the contrary, the initial copper sorption rate was higher on AEP (0.994 mmol $g^{-1}$ $min^{-1}$) than on BEP (0.472 mmol $g^{-1}$ $min^{-1}$). More generally, it seems that the more extracted the pectins, the faster the initial sorption rates. This was probably due to the enhanced availability and accessibility of the residual chemical moieties induced by the loss of pectic material. Among the pulps tested, BEP exhibited the highest nickel and copper uptakes at equilibrium (0.310 and 0.315 mmol $g^{-1}$, respectively) although SP contained more functional groups. On BEP, the change in acidity of the carboxyl groups possibly resulted in a better affinity for the metal ions. The same affinity order was found for Ni(II) and Cu(II) ions i.e. BEP > SP > AEP > NP. The very fast sorption kinetics, observed for all sorbents, represent an advantageous aspect when designing water treatment systems.

### 3.4. Sorption isotherm results

Equilibrium sorption studies were performed to provide the maximal capacities for all sorbents tested. Fig. 4(a) and (b) represents the respective sorption isotherms of Ni(II) and Cu(II) onto the native and modified materials. The Langmuir parameters $q_m$ and $b$, with the respective correlation coefficients $r^2$, are presented in Table 4. For copper and nickel ions, the experimental data correlate well with the Langmuir equation as shown in Fig. 4(a) and (b). Whatever their composition, it seems that all materials removed more Cu(II) ions than Ni(II) ions, confirming the tendency noticed with the kinetic experiments.



(a) (b)

Fig. 4. Sorption isotherms of Ni(II) (a) and Cu(II) (b) ions onto the native (NP) and modified (SP, AEP and BEP) pulps at $pH_i$ 5.5 and for 2.5 g $l^{-1}$ beet pulp dose (the lines represent Langmuir plots).

The copper sorption capacities obtained from the Langmuir isotherm (Table 4) were in quite good agreement with the experimental CEC values (Table 2), which confirmed a direct link between these two parameters. With a CEC value of 575 μeq g$^{-1}$, NP material was able to remove 0.330 mmol g$^{-1}$, i.e. 660 μeq g$^{-1}$ of Cu(II) ions. The latter value was slightly higher than the CEC. It is possible that not only the ionic moieties are involved in the copper binding but also some neutral functions like hydroxyl or carbonyl groups from neutral sugars (Rendleman, 1978). The affinity order was $\mathrm{BEP} > \mathrm{SP} > \mathrm{AEP} \approx \mathrm{NP}$ for Ni(II) and $\mathrm{SP} > \mathrm{BEP} > \mathrm{AEP} \approx \mathrm{NP}$ for Cu(II) ions. Despite its high functional group content, AEP did not efficiently remove Ni(II) and Cu(II) ions, when compared with NP. As a result of the acid treatment, it seemed that the binding sites on AEP were not available for the metallic cations as they were for protons during the titration experiments.

For all the sorbents, the maximal nickel sorption capacities were always lower than the respective CEC. It is possible that nickel ions react only with some groups of the same acidity and not with all moieties in the sugar beet pulp. It could also be suggested that the ligands developed a lower affinity for Ni(II) than for Cu(II) ions. However, this assumption was not really confirmed by the equilibrium constant values *b* determined with the Langmuir model. In Table 4, the greater the stability of the metal-polysaccharide complexes, the higher the *b* values. For NP, SP and AEP, the equilibrium constants were not really different between copper and nickel ions. On BEP material, a significant difference between the b values was noticed. BEP seemed to form more stable complexes with Ni(II) ions than with Cu(II) ions. Thus, despite a lower content of functional groups, BEP removed more Ni(II) ions than SP. For metal ions, the stability of the complexes is determined largely by the basicity of the donor group (i.e. the availability of the electron). The greater the basicity, the greater the stability of the complex (Rendleman, 1978). The high affinity of the BEP material for Ni(II) ions can possibly be explained by the increase in basicity of the donor groups that was observed previously ($\mathrm{p}K_\mathrm{a}$ improved from 3.7 to 4.6 and from 4.8 to 6.1; see Table 2). This effect was not really observed for Cu(II) ions since its uptake was more efficient on SP than on BEP material. Copper ions seemed to be less affected by the $\mathrm{p}K_\mathrm{a}$ changes, probably because they are known to form complexes with very high stability despite a poor basicity of the donor group (Rendleman, 1978).

All these parameters have to be taken into account to better understand the metal-binding process onto the polysaccharides. These results make sugar beet pulp a promising substrate to remove metal ions from polluted effluents.

## 4. Conclusion

In this study, the waste pulp of sugar beet remaining from extraction of sugar, saponification, and extraction of pectins has been considered as metal sorbent. The chemical modifications applied to the native material resulted in an improvement of the cation exchange capacities. All polysaccharides removed better Cu(II) than Ni(II) ions. Due to the loss of all methoxyl groups from the carboxylic moieties, the saponification of the NP improved significantly its ability to fix Cu(II) and Ni(II) ions. The acid and base extractions resulted in an efficient loss of the pectins. As expected, once removed and so partly degraded, the pectic material had an influence on the metal binding kinetics and capacities. The affinity order was $\mathrm{BEP} > \mathrm{SP} > \mathrm{AEP} \approx \mathrm{NP}$ for Ni(II) and $\mathrm{SP} > \mathrm{BEP} > \mathrm{AEP} \approx \mathrm{NP}$ for Cu(II) ions. Despite the loss of the pectic polymers, the cellulose rich BEP sorbent was also able to sorb efficiently the two metal ions. From potentiometric titrations, we were also able to draw conclusion about the nature and quantity of the functional groups onto each sorbent. It was confirmed that the native sugar beet pulp is dominated by negatively charged sites that are largely carboxylate groups with some weaker acidic groups.

This type of structural investigation enables an accurate prediction of the metal binding properties of the materials. This requires understanding the fundamental chemistry of the metal binding process, including the identity of the functional groups responsible for the metal ion binding.

## Acknowledgement

The authors wish to acknowledge S. Levigne for his help in sugar analysis and for valuable discussions.

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