# Chitosan N-Benzyl Sulfonate Derivatives as Sorbents for Removal of Metal Ions in an Acidic Medium

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## SYNOPSIS

We synthesized chitosan-based sorbents for the uptake of metal cations in acidic solutions. Chitosan was reacted with 2-formylbenzene sodium sulfonate and 4-formyl-1,3-benzene sodium disulfonate in the presence of $NaCNBH_3$ to yield N-benzyl mono- and disulfonate derivatives of chitosan. IR and NMR spectra confirmed the presence of benzyl sulfonate groups. The degrees of substitution of the monosulfonate chitosan derivatives were in the range of 80%, while those of disulfonate derivatives were about 50%. These sulfonate derivatives of chitosan were tested on the sorption of heavy metals $Cd^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Fe^{3+}$, and $Cr^{3+}$. The sorption capacities for disulfonate compounds were better than for monosulfonate compounds. This phenomenon was attributed to the amphoteric character of the monosulfonate derivatives. To improve the capacity of adsorption of monosulfonate compounds, the amino groups of these compounds were protected by the benzyloxycarbonyl groups. The protection of amino groups of disulfonate derivatives by benzyloxycarbonyl also improved their sorption capacity. The resulting protected polymers were tested for sorption of heavy metals. Both protected polymers were more efficient than are the parent nonprotected polymers. The synthesized sulfonate derivatives of chitosan are especially adapted to the sorption of heavy metals from the acidic industrial effluents. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Heavy metal ions are pollutant species that have to be removed from effluents. The current methods[1] for the elimination of heavy metals are filtration, chemical precipitation, ion exchange, sorption, electrodeposition, electrodeionization, and membrane techniques. The main limitation of these technologies is their low efficiency in the removal of trace levels of metal ions. The sorption on biopolymers is reported to be the best method for the elimination of metal in a low concentration (ppm or ppb level). Both the efficiency and the selectivity of this method are attributed to the chelation and ion-exchange mechanisms. Chitosan, a poly(D-glucosamine), is obtained by deacetylation of chitin, a natural polymer extracted from crustacea shells. It

and its derivatives have abundantly been reported to be efficient transition-metal sorbents.[2-6] The waste waters containing metal ions present commonly an acidic pH. Chelatant amino polymers like chitosan[7] or synthetic polyvinylamine-based resins[8-10] have a low efficiency in metal uptake in this pH range (protonation of the amino groups). Moreover, the amino polymers, like chitosan, are soluble in acidic media and therefore cannot be used as sorbents in these conditions. Muzzarelli[11] reported a sulfuric acid–ammonium sulfate pretreated chitosan with a good capacity for some transition metal in solution at pH 3. In the case of carboxymethyl[12] and carboxybutyl[13] derivatives of chitosan, both amino and carboxylic groups are involved in the metal chelation. However, their activity is depressed by lowering the pH. Our aim was to synthesize chitosan derivatives with strong cation-exchange properties. Membranes and resins carrying benzene sulfonic groups are classified among strong cation exchangers and have good performances in acidic media. We

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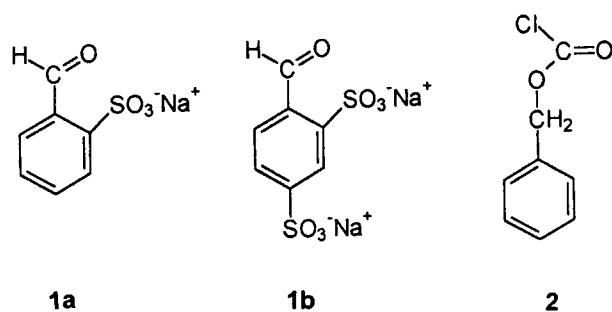
**Structure 1** Formyl benzene sulfonate derivatives used for the functionalization of chitosan and the amino protecting group.

synthesized $N$-benzyl sulfonic derivatives of chitosan. This article reports the chemical modification of chitosan by grafting benzyl sulfonic groups to obtain strong cation-exchanger derivatives of chitosan.

## EXPERIMENTAL

### Materials

Chitosan supplied by Protan contained 70% of deacetylated amino groups. The sodium cyanoborohydride, 2-formylbenzenesulfonic acid, sodium salt dihydrate (**1a**), 4-formyl-1,3-benzenedisulfonic acid, disodium salt hydrate (**1b**), and benzylchloroformate (**2**) were Aldrich chemicals (Structure 1). Metallic solutions for sorption tests were prepared from the Aldrich standard solutions.

### Synthesis of the Monosulfonate Derivatives A1 and A2 (Table I and Schemes 1 and 2)

The method consists of the preparation of $N$-aryl derivatives by a reductive alkylation,[14] a technique

discovered by Borch et al.[15] and applied to chitosan by Hall and Yalpani.[16]

Five grams of chitosan was dissolved in 500 mL of 0.5% aqueous solution of acetic acid. Methanol, 450 mL, was added to the chitosan solution. Ten grams of sodium cyanoborohydride was dissolved under vigourous stirring, and 3 min later, aldehyde **1a**, dissolved in 150 mL of methanol, was added. In the next 3 min, the viscosity of the solution decreased and a white precipitate appeared. Stirring was maintained during the desired time at ambient temperature. The mixture was then filtered and the precipitate was washed successively with 3 L of distilled water and 1 L of acetone. The product was dried overnight at 40°C. A light brown powder was obtained after crushing.

### Synthesis of the Disulfonate Derivatives B1 and B2 (Table I, Scheme 1, and Structure 2)

The method was similar to that applied to the monosulfonate derivative except that aldehyde **1b** was dissolved in 150 mL of distilled water. The amount of methanol in the initial solution was 650 mL. The modified polymer was washed with water and acetone by the centrifugation method.

### Synthesis of the Protected Benzyloxyformate Derivatives: Synthesis of A1Z and B2Z (Table II and Structure 2)

Mono-(**A1**) or disulfonate (**B2**) derivatives (2 g) were dissolved in 250 mL of 0.1$M$ NaOH; the solution was cooled and kept between 5 and 10°C. A solution of benzylchloroformate (**2**) in toluene (50% w/w) was added with vigorous stirring. NaOH was added to keep the mixture alkaline during the addition of **2**. After 1 h, the ice-water bath was removed

**Table I  Mono and Disulfonate Derivatives Synthesis: Parameters and $SO_3^-$ Content**

| Compound | Chitosan | Aldehyde 1a or 1b | Molar Ratio CHO/NH$_2$ | Reaction Time | $SO_3^-$ Content meq/g[a] | meq/g[b] | DS[c] (%) |
|---|---|---|---|---|---|---|---|
| A1 | 5 | 26.3 | 4 | 2.5 | 2.98 | 2.15 | 85 |
| A2 | 3 | 15.0 | 4 | 22.0 | 2.58 | 2.13 | 83 |
| B1 | 5 | 20.5 | 3 | 17.0 | 2.61 | 2.63 | 50 |
| B2 | 5 | 26.0 | 4 | 14.0 | 3.10 | 2.87 | 55 |

The weight of NaBH$_3$CN used was twice that of chitosan.
[a] Potentiometric method.
[b] Elemental analysis.
[c] Calculated from elemental analysis data.
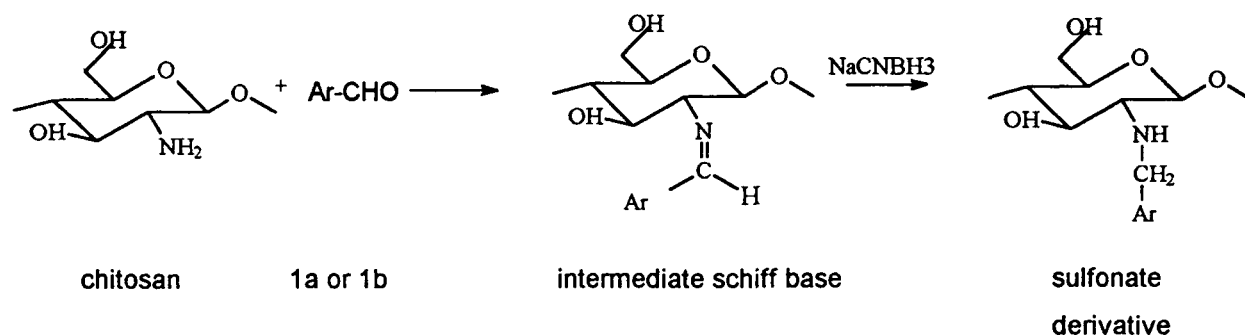
**Scheme 1** Reductive alkylation of chitosan with formylbenzene sulfonate groups.

and the solution was stirred overnight at room temperature. The polymer was then precipitated by acidification of the reaction medium and washed with water and acetone by the centrifugation method.

## Characterization of the Chitosan Derivatives

The confirmation of the structure of the modified polymers was carried out by IR, NMR spectroscopy, titration, and elemental analysis. Sulfonate group determination by *potentiometric titration* was as follows: The chitosan derivatives, 75 mg, was dissolved in 50 mL of $0.01 M$ NaOH and KCl $0.2 M$; the pH was plotted against the volume of HCl $0.02 N$ added.

The *elemental analysis* was carried out and the degree of substitution (DS) was determined using a theoretical curve plotting the weight percentage of sulfur against the DS. Both methods, titration and elemental analysis, gave results in the same range value, but the latter method appeared to be more confident and reproducible than was the titrimetric method and it was used as the reference method.
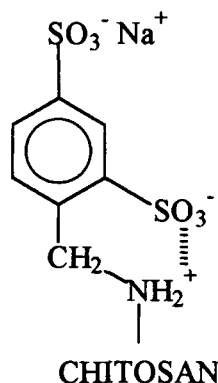


**Scheme 2** Intramolecular interaction between amino and sulfonate groups.

## Metal-sorption Experiments

The sorption capacities of the products were evaluated by the batch method. Polymer, 100 mg, was added to 50 mL of solution containing 5 ppm of the metal ion. The solution was prepared from a standard 1000 ppm solution diluted with a $0.05 M$ HCl–KCl buffer (pH 2). The solution was stirred on a rotative shaker for 90 mn for the sufficient time necessary to raise the equilibrium. The sorbent was then removed by centrifugation and the concentration in metal ions of the solution was measured by atomic absorption spectrometry (Perkin-Elmer 1100 B AAS spectrometer). The results (Table III) are reported in terms of weight percentage of uptake of the metal. Preliminary kinetic experiments showed that a 90 mn contact time is sufficient to reach the equilibrium.

## Sorption Isotherms Experiments

The **A1, B2Z,** and derivatives were evaluated by the plotting of Freundlich equilibrium isotherms which are expressed by the following equation:

$$\log X/M = \log K + 1/n \log C_e$$

$X/M$ is the amount of $Cr^{3+}$ sorbed per unit weight of sorbent (mg/g) and $C_e$ is the final concentration. $K$ and $1/n$ are the Freundlich isotherm constants. $K$ represents the sorption capacity, and $1/n$, the sorption intensity. These constants are reported in Table IV. The adsorbant, 50 mg, was put in the presence of 25 mL of the metal solution of respective concentrations of 2, 5, 10, 20, and 40 ppm; the mixture was left on a rotative shaker for 90 mn and the final concentration $C_e$ was measured.

## RESULTS AND DISCUSSION

The results presented in Table I show that the reaction time and the variation of the excess of the
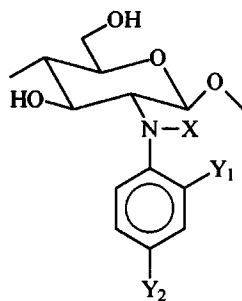
| Compound | X | Y1 | Y2 |
|---|---|---|---|
| **A1** and **A2** | -H | $-SO_3^-Na^+$ | -H |
| **B1** and **B2** | -H | $-SO_3^-Na^+$ | $-SO_3^-Na^+$ |
| **A1Z** | $-CO-O-CH_2-Ph$ | $-SO_3^-Na^+$ | -H |
| **B2Z** | $-CO-O-CH_2-Ph$ | $-SO_3^-Na^+$ | $-SO_3^-Na^+$ |

**Structure 2** Chitosan $N$-benzyl sulfonate derivatives.

sulfonated benzaldehyde do not have any important influence on the DS. Potentiometric titrations of the derivatives result in a curve with two distinct pH jumps as designed in Figure 1. The first inflection point ($V_0$) corresponds to the neutralization of the excess of NaOH and also to the protonated amino groups (primary and secondary). The second inflexion point ($V_1$) corresponds to the protonation of the sulfonate groups. The amount of the sulfonate groups (meq/g) of the polymer was obtained from the difference between the $V_1$ and $V_0$ values. The results are reported in Table I. The successive neutralization of the $NH_2$ and $SO_3^-$ entities was reported by Nud'ga et al.[17] in their study of sulfoethyl chitosan. The same principle was applied for the determination of the $SO_3^-$ content in the study of sulfated N-carboxymethyl chitosans by Muzzarelli et al.[18]

Elemental analysis (Table I) reports a greater $SO_3^-$ content (meq/g) for the disulfonated derivatives. The DS is more important with aldehyde **1a** than with **1b**: Eighty percent of $NH_2$ groups are

substituted in the case of monosulfonated derivatives, and 50%, by the disulfonated derivatives. The decrease of the $SO_3^-$ content (Table II) in the protected derivatives **A1Z** and **B2Z** is in correlation with the fact that the grafting of the benzyloxyformate group increases the molecular weight of the polymer.

IR spectra of **A1** and **B2** (Fig. 2) show a broad band at 3420 $cm^{-1}$, relative to the hydroxyl and amino groups. Sulfonic acid hydrates absorption bands are detected at 2400–2000 and 1231–1235 $cm^{-1}$. The band at 1655 $cm^{-1}$ corresponds to the stretching frequency of the acetyl groups of chitosan. The *ortho*-disubstituted benzene ring of **A1** was confirmed by the peaks at 1446, 1016, and 768 $cm^{-1}$. The strong peak observed at 838 $cm^{-1}$ is relative to the 1,2,4-substituted benzene ring of the **B2** compound. The analysis of the IR spectra of disulfonated polymers and their corresponding protected derivatives are not conclusive. The only difference observed was the weak band at 1420 $cm^{-1}$ and the broadening of the band at 1653 $cm^{-1}$ (carbonyl or

**Table II    Protection of Mono and Disulfonate Derivatives: Synthesis Parameters and $SO_3^-$ Content**

| Compound | **A1** or **B2** (g) | **2 or 3** (g) (Molar Excess) | Solvent | Reaction Time | meq $SO_3^-/g^a$ | meq $SO_3^-/g^b$ |
|---|---|---|---|---|---|---|
| **A1Z** | 3.3 | 2.1–(2.0)$^c$ | NaOH 0.1$N$ | 16 | 2.27 | 2.02 |
| **B2Z** | 2.0 | 4.6–(5.3)$^c$ | NaOH 1$N$ | 17 | 2.39 | 2.77 |

$^a$ Potentiometric method.
$^b$ Elemental analysis.
$^c$ Molar ratio aldehydic compound/free $NH_2$ groups.

**Table III   % of Metal Uptake by the Sorbents at pH 2**

| Sorbent | $Cd^{2+}$ [a] | $Zn^{2+}$ [a] | $Ni^{2+}$ [b] | $Pb^{2+}$ [c] | $Cu^{2+}$ [c] | $Fe^{3+}$ [c] | $Cr^{3+}$ [c] |
|---------|------|------|------|------|------|------|------|
| A1  | 0 | 0 | 0  | 0  | —  | 0  | 7  |
| A2  | — | — | —  | 0  | —  | 0  | 4  |
| B1  | — | — | 3  | 4  | 3  | 19 | 23 |
| B2  | — | — | 8  | 8  | 8  | 25 | 26 |
| A1Z | 5 | 7 | 9  | 12 | 8  | 37 | 43 |
| B2Z | — | — | 10 | 11 | 10 | 37 | 45 |

Initial concentration: [a] 1 ppm; [b] 2.5 ppm; [c] 5 ppm.

carbamate group). The carbamate group of **A1Z** is detected by the broadening of 40 cm$^{-1}$ of the band at 1653 cm$^{-1}$. A weak band at 1420 cm$^{-1}$ relative to the monosubstituted benzene of the benzyloxycarbonyl group can be observed.

The $^1$H-NMR characterization of **A1** and **A1Z** is reported in Figure 3. The presence of peaks in the aromatic region confirms the grafting of the sulfonic groups on the chitosan chain. The protection step of the amino groups was confirmed by the increase of a peak corresponding to aromatic protons and by the appearance of a new singlet at 4.5 ppm corresponding to the benzylic protons.

Table III reports the results obtained for the uptake of divalent and trivalent metallic ions by the modified chitosans using the batch method. Unsuccessful results were obtained in the experiments with the divalent cations $Cd^{2+}$, $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ when **A1** was used as the sorbent. In the case of the trivalent cations, only $Cr^{3+}$ was slightly adsorbed by monosulfonated derivatives. Better results are reported for the disulfonate derivatives: Some decrease in the concentration of $Ni^{2+}$, $Pb^{2+}$, and $Cu^{2+}$ is detectable for **B1** and in a greater extent for **B2** (probably due to the more important DS of **B2**). Sorption is more evident with the $Fe^{3+}$ and $Cr^{3+}$ solutions whose concentrations decrease from 5 ppm to 4.05 and 3.84 ppm, respectively. That sharp difference, measured for the sorption of divalent and trivalent cations, confirms the importance of the cation charge and the ionic mechanism of the sorption. The difference in the uptake of the metals, measured between the mono- and the disulfonated

**Table IV   Freundlich Isotherm Constants**

| Sorbent | pH | $1/n$ | $K \times 10^{-4}$ |
|---------|----|-------|----------|
| A1Z | 2 | 0.621 | 4.44 |
| B2Z | 2 | 0.803 | 3.29 |
| B2Z | 4 | 0.323 | 51.3 |

sorbents cannot be explained only by the fact that the former have a greater amount of sulfonate equivalent per gram of polymer. The **B2** compound has 1.33 times more sulfonate groups than does **A1**, but its uptake for $Cr^{3+}$ is 3.8 times greater. This phenomenon can be explained by the global charge of the polymer. At pH 2, the primary and secondary amino groups of both chitosan derivatives are undoubtedly protonated. This involves repulsive interactions with the positively charged ions.

Furthermore, another attractive electrostatic interaction can probably occur between those positive sites and the sulfonate groups. As a consequence, the negative character of sulfonic groups is weaker and the absorption properties of the derivatives are weakened. Such a type of interaction has already been reported by Naggi et al.,[19] who showed the possible occurrence of an intramolecular zwiterionic interaction in chitosan 6-sulfate that increased the rigidity of the chain segments at low pH values. The better results obtained for disulfonated derivatives can be attributed to the second sulfonate group in the para-position. The $SO_3^-$ group, in the para-position of the disulfonated derivatives, has good accessibility for the metal ions in solution and cannot interact with the neighboring positively charged amino groups. Therefore, the global charge of the polymer, in the conditions of the experiments, is neutral for monosulfonated derivatives and negative for disulfonated derivatives.

This conclusion has led us to synthesize the **A1Z** and **B2Z** derivatives with a protected amino group. The protection of the amino groups prevents the interaction between the amino and the sulfonic groups. The protected polymers **A1Z** and **B2Z** give better results than do unprotected systems in the sorption experiments, especially for $Fe^{3+}$ and $Cr^{3+}$ (Table III). The protection of amino groups increases especially the performance of the monosulfonated derivative. The difference is less marked in the case of the disulfonated derivatives.
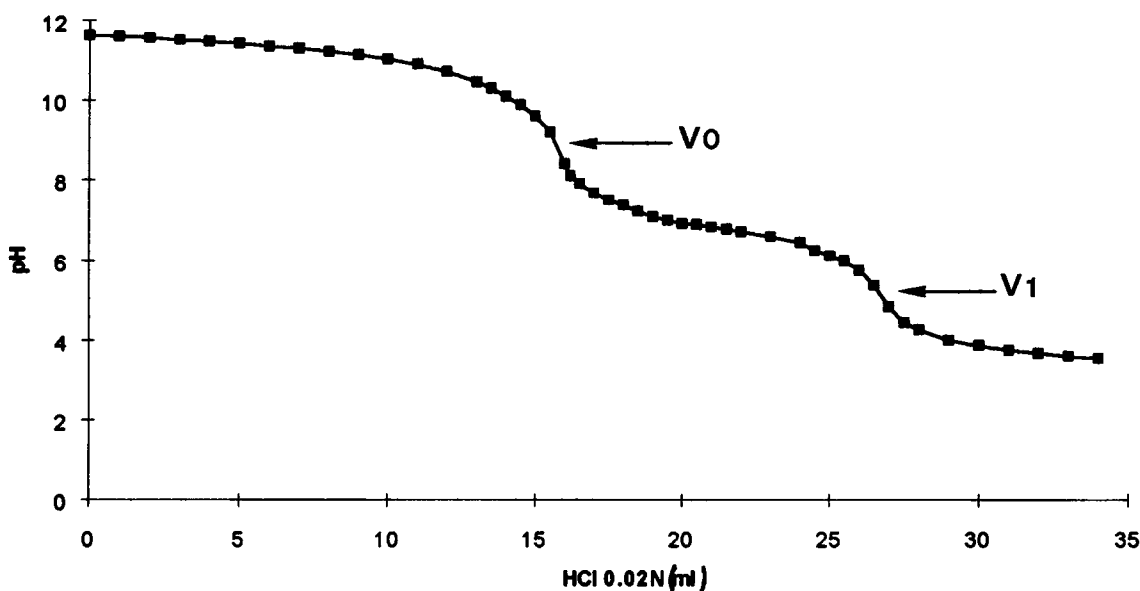
**Figure 1**   Potentiometric titration of compound **A1**.

The effect of the grafting of the benzylchlorofor-
mate group is more observable in the case of the
sorption of $Fe^{3+}$ and $Cr^{3+}$. In the case of $Fe^{3+}$, the
sorption capacity increase is 38% for monosulfon-
ated derivatives and 17% for disulfonated deriva-
tives. In the case of $Cr^{3+}$, the respective data are 36
and 18%. Undoubtedly, the protection of the amino
groups by the benzylchlorobenzyloxycarbonyl group
gives the expected increase in the sorption capacity
of the polymers and confirms our theory presented

in Scheme 2. The increase in sorption capacity, more
evident for the mono- than for the disulfonated de-
rivatives, can be explained by the fact that the first
ones have a DS 30% over that of the second ones.
Moreover, the two sulfonate groups of **B2** and **B2Z**
probably do not interact with two metal cations for
steric hindrance reasons.

Isotherm results confirm the sorption measure-
ments (Fig. 4). At pH 2, **A1Z** and **B2Z** have similar
sorption capacities (close values of $K$) and the slope
of the curves shows that the mechanism of sorption
is mainly ionic with a part of physical sorption. A
sorption isotherm measurement carried out at pH
4 indicates a strong increase of the sorption capacity
of **B2Z**, probably due to the decrease of the com-
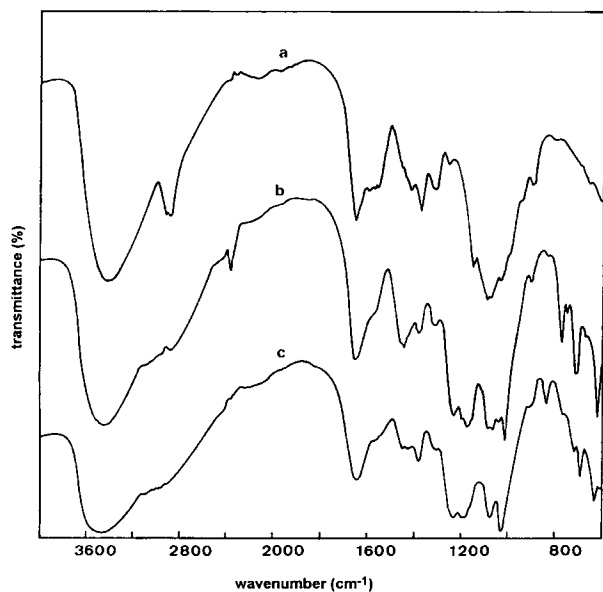petition between the $H^+$ and the metal cation for
the $SO_3^-$ group.

## CONCLUSION

This work is one of the first attempts to use chitosan
derivatives as sorbents in acidic media. The results
obtained for the sulfonate derivatives of chitosan
were better than those obtained for the parent poly-
mer in the acidic region. The amphoteric character
of the derivatives was unfavorable for the sorption
results. This was especially true for the monosul-
fonate derivatives. This problem has been resolved
by the introduction of a protective group that pre-
vents the protonation of the amino groups. In this
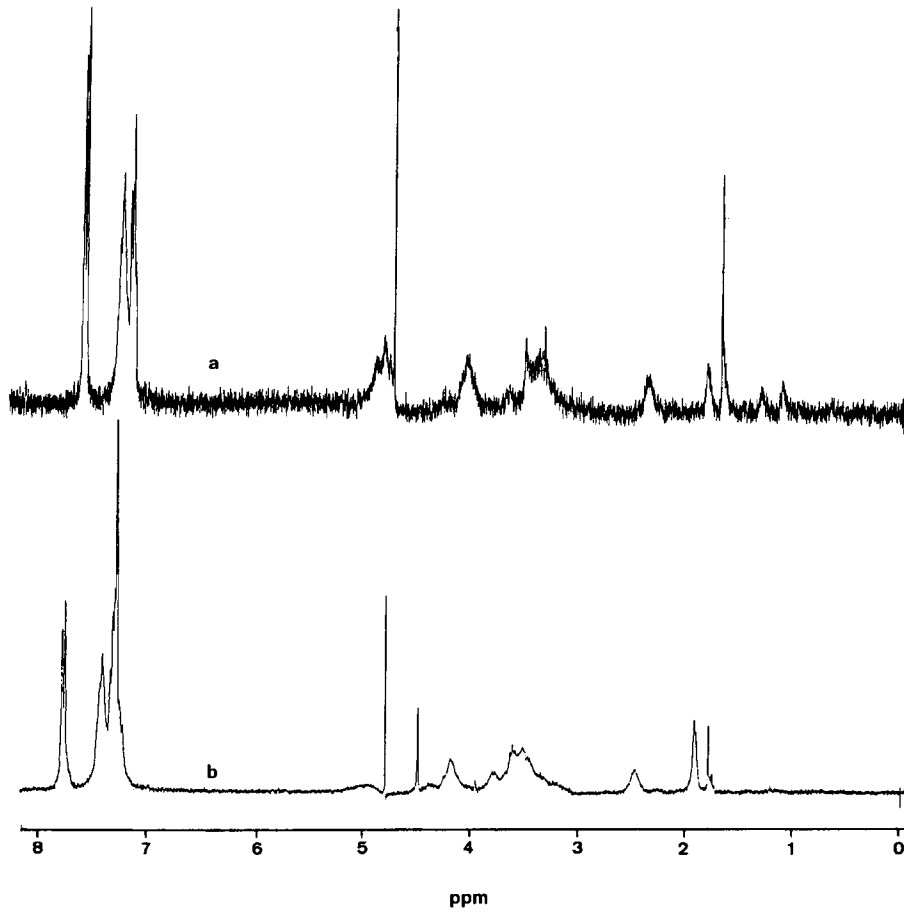work, two main sorbents have shown good perfor-



**Figure 2**   IR spectra of (a) chitosan, (b) **A1**, and (c) **B2**.

**Figure 3**    $^1$H-NMR spectra of (a) **A1** and (b) **A1Z**.
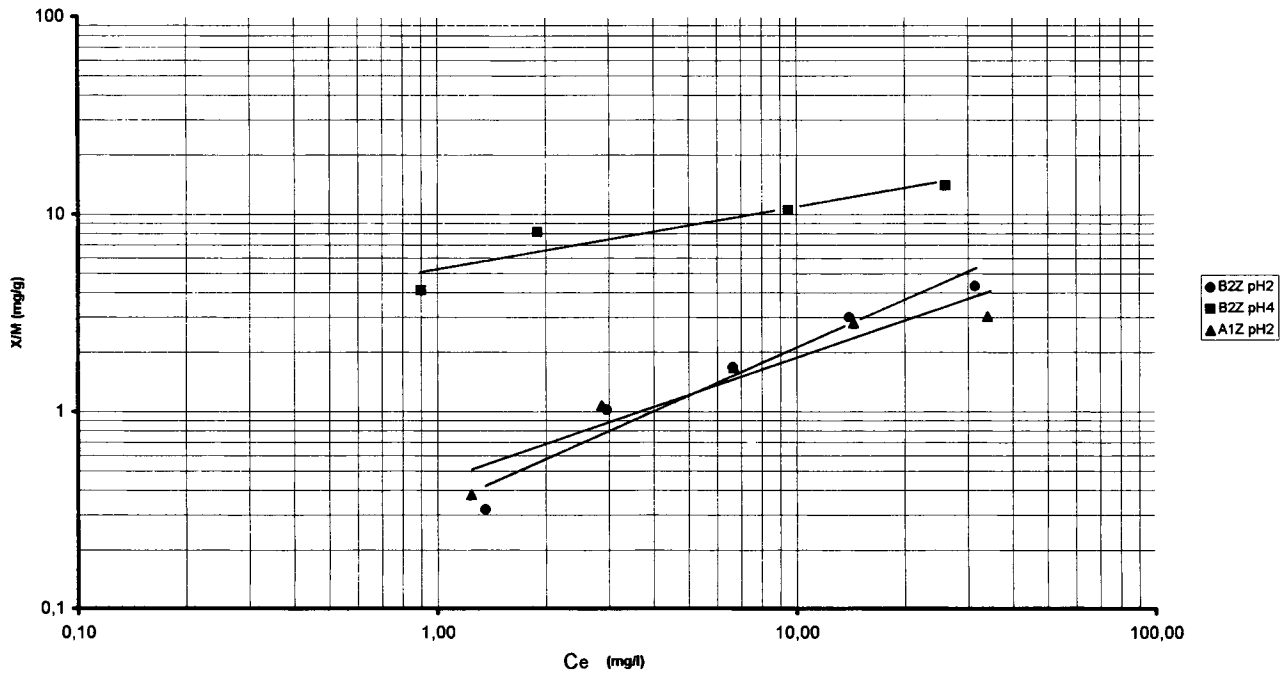


**Figure 4**    Freundlich isotherms plots: (●) **B2Z**, pH 2; (■) **B2Z**, pH 4; (▲) **A1Z**, pH 2.

mance: the disulfonated derivative and the protected monosulfonated derivative. A one-step synthesis reaction is the advantage of the first and a low cost of the aldehydic monosulfonate reactive is the advantage of the second. The chemical modification presented in this article has been applied on chitosan deposited on a textile support. The results obtained in filtration experiments of acidic solutions containing chromium and lead will be published in the next article.

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