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A metal sorbent with an unbound complexing agent: polyethylenimine – bead cellulose

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Summary

A sorbent was prepared with branched polyethylenimine fixed on bead cellulose without chemical reaction. The "jack-in-the-box" effect was used by means of which a part of the originally adsorbed PEI remains, after treatment with strong acid, almost irreversibly fixed to cellulose. The sorbent contains 1.4 - 3.0 mmol N/g of dry matter and is able to bind some double-charged cations from acid solutions, both from buffered media (pH 2-4) and from hydrochloric acid (1-4M).

Introduction

A great number of chelating sorbents are known and many of them are used in practice. All of them are obtained by immobilizing an appropriate low-molecular chelating agent (grouping) on an insoluble polymer matrix. Common methods of immobilizing a low-molecular substance are its attachment by a chemical bond to a polymer matrix, its anchoring in the pores of a porous carrier and its entrapment in a polymer skeleton. Characteristic feature of the first and third method is firm attachment, but also a labour-consuming preparation of the sorbent and difficult accessibility of the active component, manifested in the low chelation rate. On the contrary, the second method is characterized by a simple preparation of the sorbent and by a good accessibility of the active component, but also by its considerable losses due to washing out of the low-molecular substance.

A method of immobilization on the polymer skeleton which guarantees both the durability of attachment of the low-molecular component and its good accessibility would be highly desirable. The problem seems to be difficult to solve in general. A specific solution to the problem, however, can be found for some soluble polymeric chelating agents as shown in the present communication.

Experimental

Bead cellulose (Secheza Lovosice) (1), in the water-swollen state contained c. 5 g H_2O/g dry matter; bead size 0.1-0.8 mm, porosity 90%, pore size 20-1000 nm, exclusion limit (GPC) $10^4 - 10^6$. Polymin P (BASF Ludwigshafen), aqueous solution of branched polyethylenimine contained 53.2% H_2O (by K. Fischer titration) and 16.0% of total nitrogen (by Kjeldahl method).

From that amount, 20.7, 44.4 and 34.9% N were primary, secondary and tertiary nitrogen, respectively. (The content of primary and tertiary nitrogen was determined according to (2), the content of secondary nitrogen was calculated by difference.)

Bead cellulose - PEI sorbent. 8 g of water-swollen bead cellulose was shaken with aqueous PEI (9g/l) at pH c. 11.0 for 4 hours and PEI-cellulose, after being removed by suction, was shaken (4 hours) with 250 ml of 0.01M-HNO_3. The cellulose was separated by filtration with a sintered-glass filter and used in the sorption without washing. The sorbent thus prepared contained 1.4 mmol N/g dry matter.

A modified method of Perrine and Landise (3,4) was used in the determination of small concentrations of PEI in aqueous solutions; its determination limit (5) is 15 mg/l. The metal ion content in solutions after sorption was determined by differential pulse polarography, mostly after the mineralization of PEI.

Sorption of metal ions. To 0.8 g of the moist cellulose - PEI sorbent an aqueous solution of 1.5 or 0.002 mmol of metal ion and acetate buffer of pH 5.00 were added, pH was adjusted with 1M HNO_3 or 0.1M NaOH and the volume of the mixture was filled up to 10 ml. In the similarly performed sorption from hydrochloric acid media the concentration of metal ions in the resulting solution was 0.0008 or 0.0002 mol/l, the HCl concentration varied from 1 to 4 mol/l.

Results and Discussion

Polyethylenimine contains very active complexing groupings $\supset NCH_2CH_2N \subset$ in its macromolecules, and hence is known as a water-soluble strong chelating agent (6,7). Chelating sorbents based on PEI obtained either by the attachement of PEI to a polymeric carrier (8) or by the crosslinking of PEI (9) have been mentioned in the literature. However, the preparation of these sorbents is labour-consuming and their chelating properties are throughout poorer than those of PEI. In this article a very simple way of immobilization of PEI on bead cellulose is described.*

The existence of a certain affinity of branched polyethylenimine towards cellulose was observed previously. Since that time the phenomenon has been utilized to anchor small amounts of PEI to paper for paper chromatography (10), to powder cellulose for thin layer chromatography (11), or in the sorption of metal ions from aqueous solutions on cellulosic materials.

We established that the sorption of PEI by bead cellulose is of physical nature and obeys the Langmuir isotherm

$$w = 0.125\ \rho/(0.770+\rho) \qquad \text{(at 20 °C)}$$

where w is the weight fraction of PEI in the sorbent and ρ is

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*In this communication we are concerned only with purposefully unfunctionalized, i.e. underivatized cellulose. If strongly acid groups (SO_3H, $OPO(OH)_2$) are introduced into cellulose the bond of PEI to it is of chemical (ionic) nature (e.g., in the product PEI-cellulose SERVACEL).

the equilibrium weight concentration of PEI in solution (3). This conclusion and the type of sorption isotherm are in accordance with the published results (12,13). The sorption depends on pH of the solution from which it takes place; the maximum sorption is achieved at pH c. 11 (Fig. 1). Desorption of PEI is also pH-dependent (Fig. 2, curve A), and its maximum is attained at pH c. 1. In more acid solutions the desorption decreases considerably and at pH < 1 the so-called "jack-in-the-box" effect described previously (14-16) manifests itself markedly. In the protonization of PEI in an acid medium the volume of PEI macromolecule increases as a consequence of repelling forces between adjacent ammonium groups bearing like charges. Thus, it can happen that a PEI macromolecule, having penetrated in an unprotonized (or little protonized) form into

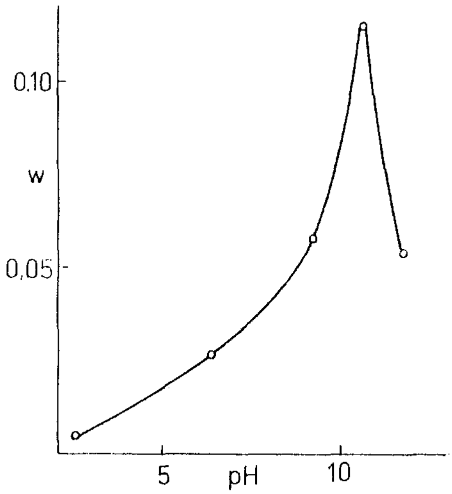

Fig. 1. The dependence of the weight fraction (w) of sorbed PEI on pH in the static sorption on bead cellulose. (Bead cellulose containing 0.12 g of dry matter was shaken with 25 ml of the aqueous solution of PEI (9.7 g/l) at the given pH at 20°C.)

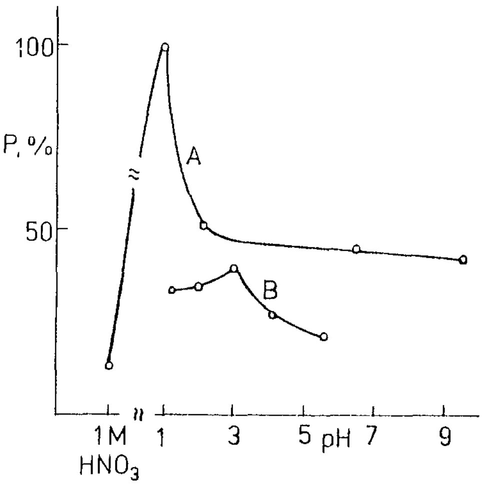

Fig. 2. The fraction of desorbed PEI depending on pH. A The sorbent was prepared as in Fig. 1 using PEI concentration 12.0 g/l, pH 11. Static desorption with 25 ml of the solution of the given pH. B the sorbent was prepared as in Fig. 1 using PEI concentration 9.0 g/l, pH 11 and PEI fixed by 1M-HNO$_3$. The sorbent filled into a 150×9 mm column was eluted with 0.1-0.0004M HNO$_3$ (ionic strength 0.1) or 0.1M-NaNO$_3$ at a flow rate 1 ml/min.

micropores of cellulose, is not able, after protonization and hence increase of its volume, to escape.

In an alkaline and weakly acid medium (pH c. 1.5-11), the most probable phenomenon is formation of hydrogen bonds between hydroxy groups of cellulose and unprotonized nitrogen atoms, or possibly electrostatic interactions of carboxylate groups and protonized nitrogen atoms (as a rule, bead cellulose contains up to 0.02 mmol COOH/g). In strongly acid solutions (up to pH 1.5) the "jack-in-the-box" effect predominates. An alternative explanation for PEI fixation on cellulose in strongly acid medium, viz. a ionic bond between PEI and COOH is not plausible for two reasons: the amount of COOH in cellulose is too low to be able to bind relatively large amounts of PEI and - in a strongly acid medium - it is not possible to assume the presence of carboxylate ions.

The "jack-in-the-box" effect can be used in the preparation of a cellulose-based sorbent in which PEI is sufficiently firmly retained for practical application in the separation of some metal ions from aqueous solutions. If PEI is fixed by treating the sorbent with, e.g., 1M HNO_3 then, in the subsequent dynamic desorption at a definite pH, less PEI is eluted than from the sorbent in which no fixation has been performed (Fig. 2, curve B). For practical purposes, it is more advantageous to use 0.01M HNO_3 for fixation even if it is fixed by 50 % less PEI than in the former case. The latter sorbent, however, can be used in the sorption of metal ions in the pH range 2-4.6 without formation of any turbidity in the aqueous phase.

The sorption (but also fixation, see Fig. 2) of PEI on cellulose can also be performed in dynamic conditions, i.e. in a column. After sorption, the unsorbed PEI can be practically completely washed out with two column volumes. Thus, a content of c. 5 % N in the sorbent can be reached, compared with 0.1 mmol N/g, i.e. 0.14 % N, using fibre or powder cellulose. In the fixation of sorbed PEI on bead cellulose with 1M HNO_3 a N content of c. 3 mmol/g, i.e. c. 4 % N can be easily achieved.

It is possible to assume that the cations capable of forming ammine complexes are bound by the cellulose - PEI sorbent. This is why the sorption of Zn, Cd, Cu(II), Co(II) and Ni(II) from aqueous solutions was investigated, at two metal ion concentration levels and from buffered or acid media. The dependence of distribution coefficients of the metals, D_g, on pH in the sorption from acetate buffered solutions is given in Fig. 3. At low concentrations of metal ions in starting solutions (0.0002 mol/l) the D_g values are considerably higher and their increase at pH > 5 is more pronounced than in the case of higher concentrations (0.15 mol/l). In the buffered medium, however, no marked selectivity necessary for the separation of the studied ions was observed.

The sorption of the same metal ions from hydrochloric acid media was also studied. The dependence of D_g on HCl concentration at two metal ion concentrations (0.0008 and 0.0002 mol/l) is shown in Fig. 4. The D_g values for Cu, Zn, Cd and Co do not differ much, either among themselves or in their dependence on the initial metal ion concentration. However, a pronounced difference in the D_g values can be observed for Ni at its lower initial concentration, where D_g = 150 ml/g is reached, independently of HCl concentration.

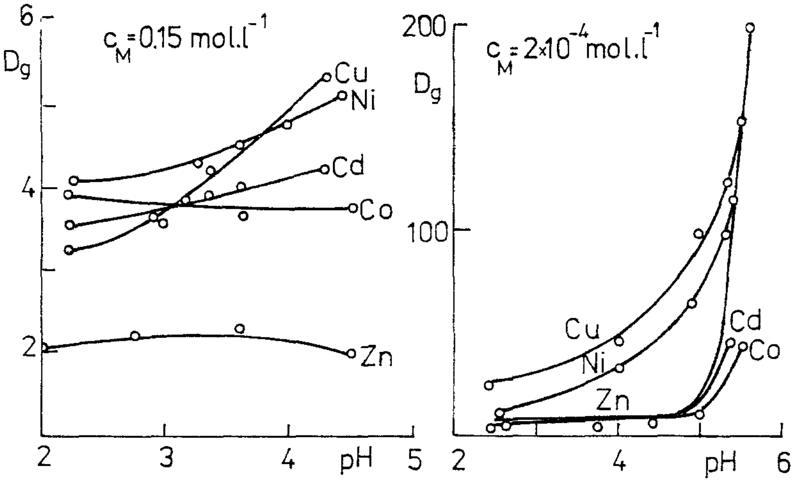

Fig. 3. The dependence of metal distribution coefficients (D_g, ml/g dry matter) on pH in the sorption from an acetate medium (c_M initial metal ion concentration).

In the sorption from an acetate medium it is possible to assume the formation of complexes in which nitrogen atoms of the fixed PEI act as donor atoms. In the sorption from HCl media the metal ions are bound as chloro complexes, most probably by an electrostatic interaction between the complex anion and the protonized form of the fixed PEI. Interestingly

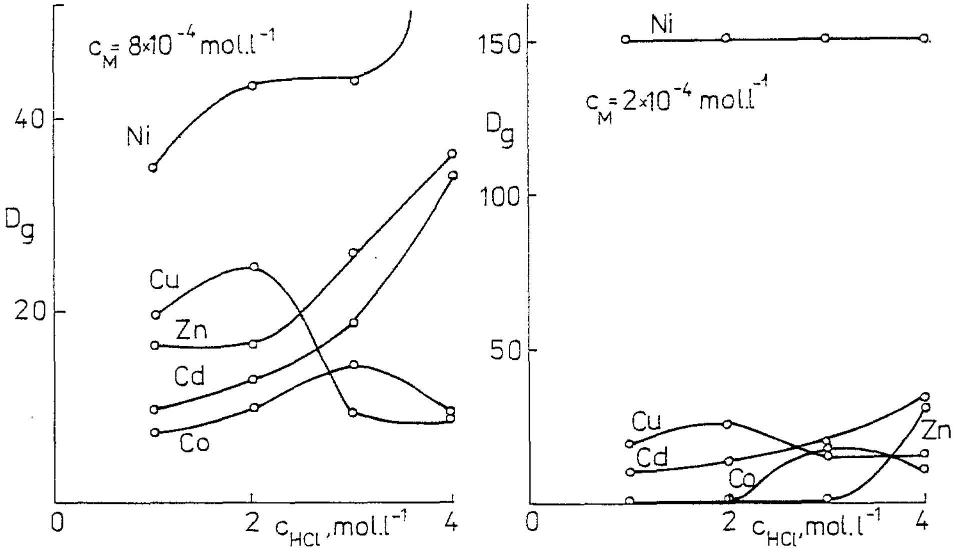

Fig. 4. The dependence of metal distribution coefficients (D_g, ml/g dry matter) on initial HCl concentration.

enough, the observed dependence of D_g on HCl concentration does not correlate with regions of the predominating existence of individual metal chloro complexes of the type $[MCl_3]^-$.

References

1. Štamberg, J., Peška, J., React. Polym., Ion Exch. Sorbents 1, 145 (1983)
2. Emelin, E.A., Kitukhina, G.S., Zharkov, V.V., Zh. Anal. Khim. 28, 1599 (1973)
3. Horáková, H., Thesis, Prague Inst. Chem. Technol., 1987
4. Perrine, T.D., Landis, W.Z., J. Polym. Sci. 5, 1993 (1967)
5. Currie, L.A., Anal. Chem. 40, 586 (1968)
6. Gembitskii, P.A., Zhuk, D.S., Kargin, V.A., Polyethylenimine (in Russian), Nauka, Moscow, 88 (1971)
7. Kobayashi, S., Hiroishi, K., Tokunoh, M., Saegusa, T., Macromolecules 20, 1496 (1987)
8. Kahovec, J., Matějka, Z., unpublished results
9. Rivas, B.L., Maturana, H.A., Perich, I.M., Angne, U., Polym. Bull. 14, 239 (1985)
10. Randerath, K., Angew. Chem. 74, 780 (1962)
11. Boyer, R.F., Redmond, M.A., Biotechnol. Bioeng. 25, 1311 (1983)
12. Kindler, W.A., Swanson, J.W., J. Polym. Sci., Part A-2 9, 853 (1971)
13. Nedelcheva, M.P., Stoilkov, G.V., J. Appl. Polym. Sci. 20, 2131 (1976)
14. Allan, G.G., Akagane, K., Neogi, A.N., Reiff, W.M., Mattila, T., Nature 225, 175 (1970)
15. Akagane, K., Allan, G.G., Shikizai Kyokaishi 46, 233 (1973); Chem. Abstr. 79, 70536 (1973)
16. Akagane, K., Allan, G.G., Shikizai Kyokaishi 44, 515 (1971); Chem. Abstr. 76, 142564 (1972)

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