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Sorption of Some Metal Cations by a Modified Biopolymer Based on the Mycelium of *Penicillium chrysogenum*

Rudolf Jílek, Josef Novosad, Jaromír Jandl, Karel Pospíšilík and Jana Hofírková

Veterinary Research Institute, Hudcova 70, CS-621 32 Brno, Czechoslovakia

Summary

Three types of a modified biopolymer based on the mycelium of Penicillium chrysogenum were evaluated as to their sorption characteristics for Hg^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+}. Their useful and total sorption capacities were calculated from their respective breakthrough curves. The highest sorption capacity was recorded for Hg^{2+}. Evidence is presented that the retained metals can be easily eluted with diluted mineral acids.

Introduction

The starting material for preparation of the modified polymer is the mycelium of Penicillium chrysogenum, a complicated mixture of substance groups a number of which are potentially capable to retain cations of heavy metals in particular. The main components of the mycelium (JANICKI and SKUPIN 1958) are proteins and neutral and nitrogenous polysaccharides. Added to this are free amino acids, lipids and inorganic substances. Of particular value is the presence of chitin. This substance or its deacetylated form, chitosan, is also essential to the biopolymer function.

Since the good sorption characteristics of the mycelium do not correspond to its mechanical properties, the mycelial mass must be reinforced with urea-form-aldehyde resin. Even so, the mycelium remains the main component in spite of its partial degradation or possibly transformation by reactions with the reinforcing agents (JÍLEK et al. 1976). The modified biopolymer thus prepared represents a number of sorbents based on the mycelium of Penicillium chrysogenum that are protected by the registered trademark Ostsorb. Sorption activity of the modified biopolymer is due mainly to the major components of the mycelium (see above).

The capability of the modified polymer to retain selected cations (Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}) known as major pollutants was investigated using the following three types of Ostsorb, namely Ostsorb-Z, the basic Ostsorb type as described above; Ostsorb-CM where the number of carboxyl groups was increased (POSPÍŠILÍK et al., in press); and Ostsorb-Ti developed by activation of the basic sorbent with titanium compounds

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(NOVOSAD et al. 1977). It should be noted that sorption is influenced, among other things, by the pH of the influent. In the experiments described below the pH of cation solutions was chosen so as to correspond to the optimum region for sorption of the given cation as found in previous studies (see e.g. JÍLEK et al. 1979). In view of practical application it is essential to assess not only the sorption capacity, but also the possibility of eluting the retained metal. Therefore we studied also the possibility of elution with diluted mineral acids.

Experimental

Determination of breakthrough curves

To determine the breakthrough curves for the three Ostsorb types, a 130 mm glass column (13 mm id) with sintered glass (S 1) was packed quantitatively with swollen biosorbent the mass of which in the dry state was 5.0 g and the particle size ranged from 0.2 to 0.8 mm. The volume of swollen sorbent in the column was 13.2 ccm. Flow of the influent having a concentration of 1.10^4 mg $Me.l^{-1}$ was maintained by a peristaltic pump; the specific flow rate was equal to 3 volumes of solution per one volume of biosorbent per hour. The pH of the influents was as follows: Hg = 1.93; Pb = 3.92; Cu = 3.83 and Cd = 5.12.

Determination of useful and total sorption capacity

Useful capacity, which refers to the breakthrough point, depends in general on the sensitivity of the method used to determine the moment at which ions have passed through the sorbent in the column. In the present study the term "useful capacity" (C_n) denotes the amount of cations retained by the sorbent till $C/C_o = 0.01$ where C and C_o are cation concentrations of the effluent and influent, respectively. In this case sorption in the last fraction has reached 99 % and the C/C_o in the preceding fractions is 0.01. Total sorption capacity (C_t) is determined from the breakthrough curves. It equals the amount of cations retained by the sorbent till $C/C_o = 0.5$ (SAMUELSON 1966).

Determination of elution curves

After dynamic sorption was completed, the modified biopolymer was washed with 200 ml distilled water and the retained cations were eluted with 1 M HNO_3 (Pb^{2+}, Cd^{2+} and Cu^{2+}) or 1 M HCl (Hg^{2+}) using the same apparatus and conditions as were used for the sorption. Metal concentrations in the individual fractions were determined by the atomic absorption method in a Perkin-Elmer spectrophotometer, model 300.

Results and Discussion

Breakthrough curves of Hg^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+} for the modified biopolymers Ostsorb-Z, -Ti and -CM are shown in Fig. 1-3. The useful and total sorption capacities calculated for the polymers under study are presented in Table 1.

TABLE 1

Sorption Capacities of the Modified Biopolymers for Hg^{2+}, Pb^{2+}, Cu^{2+} and Cd^{2+}

Type of the modified biopolymer	Sorption capacity $\mu mol.g_s^{-1}$	Hg^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}
Ostsorb-Z	c_u	300	164	282	226
	c_t	780	310	557	316
Ostsorb-Ti	c_u	410	261	244	235
	c_t	910	345	428	364
Ostsorb-CM	c_u	380	267	337	245
	c_t	950	429	637	443

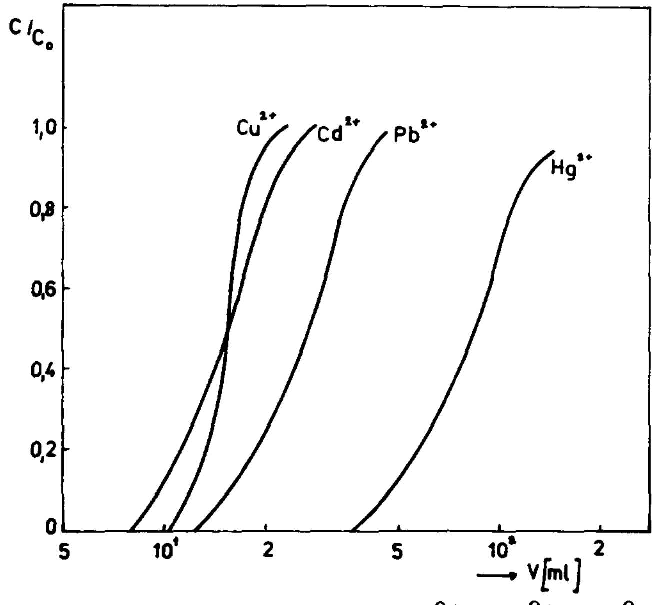

Fig. 1. Breakthrough curves of Cd^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+} for Ostsorb-Z, a modified biopolymer

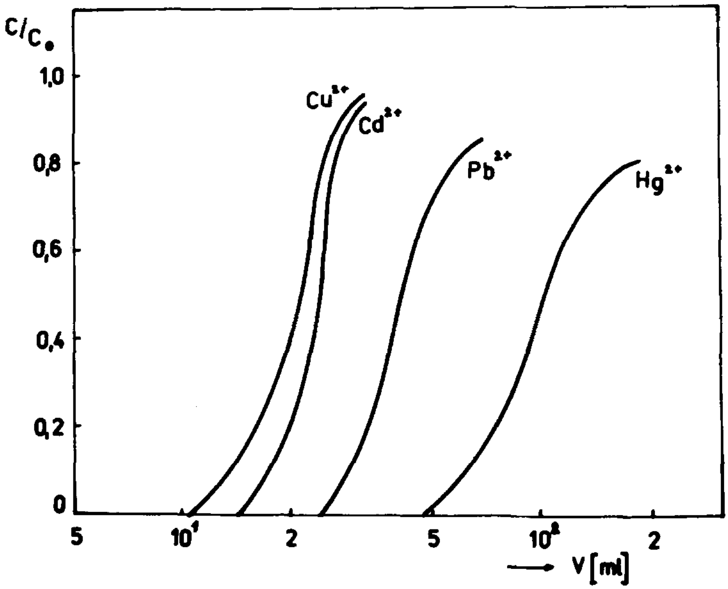

Fig. 2. Breakthrough curves of Cd^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+} for Ostsorb-Ti, a modified biopolymer activated with titanium compounds

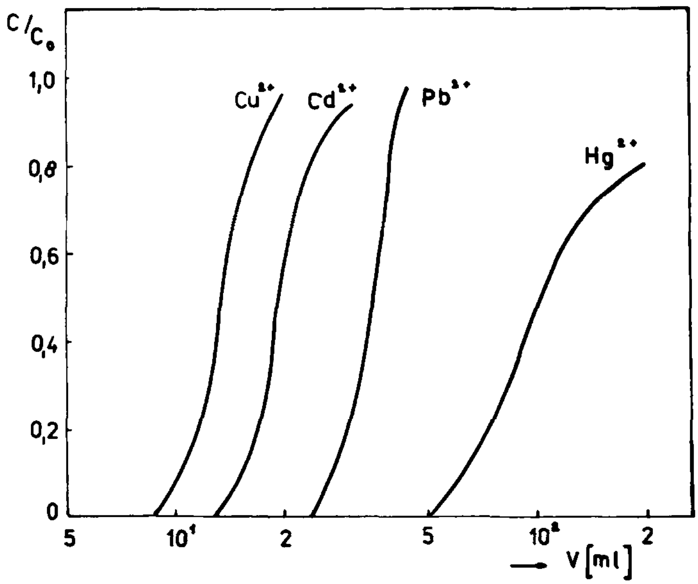

Fig. 3. Breakthrough curves of Cd^{2+}, Cu^{2+}, Pb^{2+} and Hg^{2+} for Ostsorb-CM, a modified biopolymer with an increased concentration of carboxyl groups

Elution curves of the four cations for the three modified biopolymers are shown in Fig.4.

The results suggest that the modified biopolymers have good sorption characteristics for Cu^{2+}, Cd^{2+} and particularly for Pb^{2+} and Hg^{2+}. Since Ostsorb-CM showed the highest sorption capacity in practically all the cases, it can be concluded that the increased concentration of carboxyl groups in the modified biopolymer promotes its sorption capacity. As can be seen from Fig.4, heavy metal cations retained by the modified biopolymers based on the mycelium of Penicillium chrysogenum can be easily eluted with diluted mineral acids and the biopolymers can be prepared for further use.

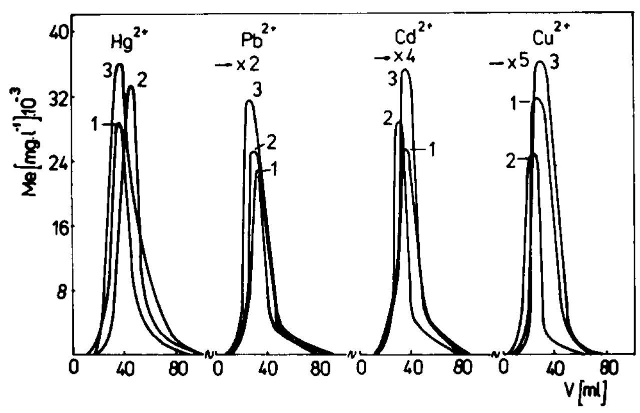

Fig.4. Differential elution curves of Hg^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+} for the modified biopolymers Ostsorb-Z (curves No.1), Ostsorb-Ti (curves No.2) and Ostsorb-CM (curves No.3)

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