SORPTION OF LEAD AND CADMIUM ON OSTSORB P AND OSTSORB SA-5 CELLULOSE SORBENTS

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The effect of pH and ionic strength on the exchange capacity of sorbents based on modified bead cellulose was examined for the sorption of Pb^{2+} and Cd^{2+} ions. Ion exchange of these cations in aqueous solutions is nonselective on Ostsorb SA-5, which is cellulose containing functional groups based on H-acid. The medium acidic Ostsorb P cation exchanger with functional groups formed by the phosphoric acid fragment, on the other hand, sorbs lead, and to a lesser extent also cadmium, also at high ionic strengths of the medium even at low pH values.

The ion exchanger properties of cellulose and its derivatives have been known since the 1930s, when they also were employed for analytical applications[1]; nevertheless, they have been more frequently used in fields other than the separation of inorganic substances. However, as in the case of synthetic resins, the cellulose matrix can be modified with various ion exchanger functional groups, and this offers additional opportunities for the application of cellulose ion exchangers, in the conventional way or by complexation. Under favourable conditions, many of the ion exchangers from the two groups can be used for selective sorption of some ions, which is often a prerequisite for a successful solution of specific separation or enrichment problems. Among substances that have found application are, e.g., C-cellulose with functional carboxy groups[2], a medium acidic derivative of P-cellulose with phosphoric acid functional groups[2 – 4], carboxymethylcellulose referred to as CM-cellulose[5], DEAE-cellulose[5,6], and DEAHP-cellulose[5]; chelating cellulose sorbents include, e.g., ion exchangers with functional groups based on diethylenetriamine[5,7,8], 8-hydroxyquinoline[5,7], salicylic acid[5], diethylenetriaminetetraacetic acid[5,7,9], chromotropic acid[10], 4-(pyridylazo)-resorcinol[11], and diethyldithiocarbamates[12].

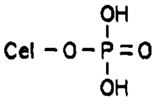
The present work is a contribution to the investigation of the sorption of lead and cadmium ions on cellulose ion exchangers based on a medium acidic cation exchanger, Ostsorb P (P-cellulose), and an ion exchanger whose matrix is modified with a functional group the active part of which is 1-hydroxy-8-amino-3,6-disulfonic acid, Ostsorb SA-5.

EXPERIMENTAL

Chemicals and Apparatus

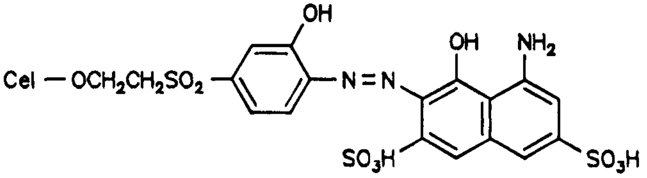
Lead and cadmium in solutions were determined with an Atomspek-H 1550 single-beam atomic absorption spectrophotometer (Hilger and Watts, U.K.), the solution pH was measured with an OP-205/1 instrument fitted with an OP 8083 glass electrode (Radelkis, Hungary). Additional equipment included an LT-1 shaking machine (Kavalier, Czechoslovakia), a glass column 22 mm i.d. with a sintered glass bed and a ground-in valve at the outlet, and conventional laboratory glassware.

All chemicals were of reagent grade purity, supplied by Lachema, Brno; these included hydrochloric acid, nitric acid, sodium hydroxide, lead nitrate and cadmium sulfate. Sodium perchlorate was obtained from Reakhim, C.I.S. Deionized water was prepared. The cellulose ion exchangers Ostsorb P and Ostsorb SA-5 are products of Spolchemie in Ústí nad Labem. They consist of bead cellulose modified in the side chain with a functional group. Ostsorb P is a medium acidic cation exchanger with the phosphoric acid fragment (*I*) bonded to the cellulose by the ester bond. The analytical mass exchange capacity Q_a as given by the manufacturer is 0.2 mmol Cu/g, the water content is 73 – 83%, i.e., 2.7 – 4.8 g H_2O/g. The dissociation constants are given by $pK_1 \approx 3$ and $pK_2 \approx 7$ (ref.[13]). Ostsorb SA-5 is an ion exchanger based on spherical cellulose containing functional groups derived from 4-(1′-hydroxy-8′-amino-3′,6′-disulfonaphthyl-2′-azo)-3-hydroxyphenylethylsulfone (*II*). The theoretical mass exchange capacity is Q_0 = 0.2 mmol/g. The ion exchanger is manufactured to customer's order[14]. The ion exchangers were invariably used in the H^+ form, into which they were converted by column elution with a roughly seven-fold volume of hydrochloric acid (0.1 mol l^{-1}) and subsequently with water to a negative reaction. They were stored in deionized water. Prior to use, the swelled exchanger was sucked on a Büchner funnel using a water jet pump, and weighed in with a precision of 0.01 g. The water contents of Ostsorb P and Ostsorb SA-5 were 87% and 84%, respectively. The observed exchange capacities were conventionally related to 1 g of dry ion exchanger.



$$\text{Cel}-O-\overset{\overset{\large OH}{|}}{\underset{\underset{\large OH}{|}}{P}}=O$$

I



II

Determination of Lead and Cadmium by AAS

Calibration solutions of lead and cadmium at mass concentrations of the metals of ρ = 1 – 5 mg l^{-1} were prepared by diluting stock solutions of 1 000 mg l^{-1} concentration. Weighed amounts of lead nitrate or cadmium sulfate octahydrate were dissolved in deionized water, and the solutions were made acidic with nitric acid to pH 4 – 5; the latter also applied to the calibration solutions. The absorbances of the solutions were measured in an acetylene–air flame at 217.5 and 229.0 nm for Pb and Cd, respectively. The correlation coefficients of regression curves in the absorbance vs metal concentration plots were higher than 0.99, the relative standard deviation for ten replicate measurements on the instrument for a metal concentration ρ = 2 mg l^{-1} was lower than 3% in either case.

Measurement of the Course of Lead Sorption by the Ion Exchangers Ostsorb P and Ostsorb SA-5

Suspensions containing 100 ml of a lead solution at a concentration of $\rho = 5$ mg l^{-1} and 0.5 g of the swelled ion exchanger in 250 ml beakers were stirred with an electromagnetic stirrer for 1, 2, 3 and 4 h. The pH of the suspensions was measured continuously with the pH-meter and held at pH 5 by adding NaOH (10^{-3} mol l^{-1}). After the preselected time the solutions were filtered through a dry S1 sintered glass filter, and the lead concentration was determined by AAS.

Measurement of the Dependence of the Ion Exchanger Capacity on pH

Suspensions of 100 ml of the lead or cadmium solution at $\rho = 5$ mg l^{-1} and 0.5 g of the swelled ion exchangers at pH 3 – 9 (Ostsorb P) or pH 1 – 10 (Ostsorb SA-5) were stirred for 2 h in 250 ml beakers. The pH was monitored and held at the preselected value by adding HCl or NaOH (10^{-3} mol l^{-1}). Thereafter the solutions were filtered through an S1 sintered glass filter, made acidic with HNO_3 (1 mol l^{-1}) where necessary, and the metals were determined by AAS.

Testing the Reproducibility of the Ion Exchanger Capacity Measurement

Suspensions of 100 ml of lead or cadmium solutions at $\rho = 5$ mg l^{-1} and 0.5 g of the ion exchangers Ostsorb P or Ostsorb SA-5 in six closed 150 ml ground-in flasks were shaken on a shaking machine for 2 h. The pH was adjusted with NaOH (10^{-3} mol l^{-1}) so that after the experiment its value was pH 6 and pH 5 for Ostsorb P and Ostsorb SA-5, respectively. The resulting pH was verified pH-metrically.

Measurement of the Dependence of the Ion Exchanger Capacity on the Solution Ionic Strength

Suspensions containing 100 ml of lead or cadmium solutions at $\rho = 5$ mg l^{-1} and ionic strength $I = 0$ to 1 (adjusted with sodium perchlorate, 1 mol l^{-1}) and 0.5 g of the ion exchanger, accommodated in closed 150 ml ground-in flasks, were shaken on a longitudinal shaking machine for 4 h. To the solutions was added NaOH (10^{-3} mol l^{-1}) in volumes determined beforehand so that after the experiment the pH was 6 and 7 for Ostsorb P and Ostsorb SA-5, respectively. The ion exchanger was filtered off, the filtrate was made acidic with a drop of HNO_3 (1 mol l^{-1}), and the metals were determined by AAS.

DISCUSSION

Rate of Lead Sorption by the Ion Exchangers

At pH 5 in sodium perchlorate-free solution, the exchange capacity for lead ions in 1, 2, 3 and 4 h was 0.27, 0.30, 0.31 and 0.31 mmol g^{-1}, respectively, for Ostsorb P, and 0.16, 0.17, 0.18 and 0.18 mmol g^{-1}, respectively, for Ostsorb SA-5. Hence, the exchange equilibrium establishes roughly in three hours, while in two hours the level attained is approximately 95%. A similar sorption course can be expected for cadmium ions. Based on this finding, a time of 2 h was chosen for the contact between the ion exchangers and the metal solutions in the subsequent experiments.

Dependence of the Exchange Capacity on pH

The results are given in Table I, which demonstrates that the exchange capacity of Ostsorb P for lead and cadmium ions increases with increasing pH; the increase, however, is not very pronounced, and physical sorption of the hydrolysis products of the metals at pH > 8 may be involved. The two cations are retained rather strongly even from acid solutions, of which use can be made in practical applications. Repeated experiments revealed the occurrence of a minimum in the Q_a vs pH curves at pH 4, and for cadmium also at pH 6. Similar shapes of the Q_a vs pH curves have been observed by Chaluš[2] for the sorption of various cations on P-cellulose manufactured by Serva, Heidelberg, in solutions buffered with acetate buffer. In contrast to Ostsorb P, Ostsorb SA-5 retains virtually no ions at pH 1 – 2; the exchange capacity increases over the pH 3 – 10 range to attain values of 0.33 and 0.66 mmol g^{-1} for Pb^{2+} and Cd^{2+} ions, respectively. Thus, while the maximum exchange capacity of Ostsorb SA-5 is nearly the same as that of Ostsorb P, in the acid region the exchange capacity of the former ion exchanger is lower than that of the latter. For the sorption of lead on Ostsorb SA-5, the Q_a vs pH curve has a minimum, as in the case of Ostsorb P, it lies, however, at pH 8. Its nature was not studied in detail.

In order to assess the precision with which the exchange capacities of the two ion exchangers can be measured, five replicate experiments were performed for each ion exchanger and cation. The results of a simple statistical evaluation are summarized in Table II. The reproducibility of the results, expressed by the relative standard deviation s_r, was satisfactory ($s_r < 5\%$), particularly for Ostsorb P ($s_r < 2\%$). The exchange capacity was determined with a precision of approximately 0.01 mmol g^{-1}. The pH after the experiment differed from the required value by ±0.05 pH units.

TABLE I
Dependence of the exchange capacity Q_a (mmol g^{-1}) of Ostsorb P and Ostsorb SA-5 in the sorption of Pb^{2+} and Cd^{2+} ions on pH (sodium perchlorate-free solution) ($I = 0$)

Ion	pH									
	1	2	3	4	5	6	7	8	9	10
					Ostsorb P					
Pb^{2+}			0.28	0.16	0.30	0.33	0.33	0.33	0.37	
Cd^{2+}			0.56	0.48	0.56	0.44	0.62	0.63	0.64	
					Ostsorb SA-5					
Pb^{2+}	0.00	0.01	0.11	0.14	0.17	0.19	0.22	0.14	0.31	0.33
Cd^{2+}	0.01	0.02	0.11	0.15	0.16	0.18	0.23	0.32	0.66	0.66

The Effect of Ionic Strength on the Sorption

The effect of the presence of other ions on the sorption of lead and cadmium was established by measuring the exchange capacities for the two cations at a preselected pH and various ionic strengths adjusted with sodium perchlorate. Table III demonstrates that in the case of Ostsorb SA-5, the presence of sodium ions has an unfavourable

TABLE II

Statistical evaluation of reproducibility of exchange capacity measurements[a] for Ostsorb P and Ostsorb SA-5 ion exchangers and the sorption of Pb^{2+} and Cd^{2+} ions (sodium perchlorate-free solution)

Ion	$\bar{Q}_a$ mmol g^{-1}	s	s_r %	$L_{1,2}$	l %
			Ostsorb P		
Pb^{2+}	0.327	0.0017	0.52	0.327 ± 0.002	1.22
Cd^{2+}	0.442	0.0069	1.56	0.442 ± 0.008	3.88
			Ostsorb SA-5		
Pb^{2+}	0.172	0.0058	3.37	0.172 ± 0.012	13.95
Cd^{2+}	0.159	0.0073	4.59	0.159 ± 0.009	11.32

[a] $\bar{Q}_a$ mean analytical mass exchange capacity from five experiments, s standard deviation of measurement of Q_a, s_r relative standard deviation, $L_{1,2}$ 95% confidence interval of measurement of Q_a, l relative width of the 95% confidence interval.

TABLE III

Dependence of exchange capacity Q_a (mmol g^{-1}) on ionic strength I (concentration of sodium perchlorate) of solution in the sorption of Pb^{2+} and Cd^{2+} ions

Ion	pH					
	0	0.001	0.01	0.1	0.5	1
			Ostsorb P			
Pb^{2+}	0.33	0.32	0.30	0.25	0.10	0.01
Cd^{2+}	0.62	0.53	0.28	0.01	0.00	0.00
			Ostsorb SA-5			
Pb^{2+}	0.19	0.08	0.04	0.01	0.00	0.00
Cd^{2+}	0.18	0.04	0.01	0.01	0.01	0.00

effect at ionic strengths as low as $I = 0.001$, corresponding to a mass concentration of sodium in the solution of $\rho = 23$ mg l^{-1} (the starting lead or cadmium concentration was $\rho = 5$ mg l^{-1}). The exchange capacity of the ion exchanger for lead and cadmium decreases to approximately one-half and one-quarter, respectively, as compared to the sodium-free solutions. If the sodium ion concentration is additionally tenfold increased, cadmium ions virtually cease to be retained by the ion exchangers, while lead ions are retained but slightly. Hence, in such conditions the Ostsorb SA-5 ion exchanger is inapplicable to the selective sorption of the ions concerned.

With Ostsorb P the presence of sodium ions has a less marked effect on the sorption of cadmium and, in particular, lead ions. Cadmium is retained by the ion exchanger to a large extent even at $I = 0.01$ (ρ(Na) = 230 mg l^{-1}). The exchange capacity for lead decreased from the value of 0.33 mmol g^{-1} at $I = 0$ to 0.1 mmol l^{-1} at $I = 0.5$ (ρ(Na) = 11 500 mg l^{-1}). (All the experiments pertain to the initial concentration of the metals $\rho = 5$ mg l^{-1}, so that the sodium-to-lead molar ratio at $I = 0.5$ is 20 700.) Thus, Ostsorb P can be used for selective sorption of lead ions from solutions containing sodium ions, and perhaps also other ions, in a high excess.

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