

SORPTION OF CADMIUM AND LEAD BY CHELATING ION EXCHANGERS OSTSORB DITHIZON AND OSTSORB SALICYL

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The pH and I (ionic strength) dependences of exchange capacity of chelating ion exchangers Ostsorb based on spherical cellulose modified with functional groups of dithizone and salicylic acid have been studied in the sorption of Pb(II) and Cd(II) ions. The cellulosic selective sorbents Ostsorb DITHIZON and Ostsorb SALICYL can be used for sorption of Pb(II) and Cd(II) ions from aqueous solutions of $I = 0 - 1 \text{ mol l}^{-1}$ (Pb) and $I = 0 - 5 \text{ mol l}^{-1}$ (Cd); the dithizone ion exchanger retains both metals most effectively at pH 7 - 8, the salicyl ion exchanger at pH 5.5 - 6.5 (Pb) or pH 4 - 9 (Cd). Because of the formation of precipitates of hydrolytic products of the two metals in neutral and alkaline media, it is suitable to carry out the sorption in media of mild acidity if possible, particularly so at the metal concentrations above 1 mg l^{-1} . Increasing ionic strength affects the exchange capacity for both metals in a negative way.

Salicylic acid and dithizone are well-known complex-forming reagents finding wide application in analytical chemistry^{1,2}. Dithizone is used for qualitative and quantitative determination and extraction of lead, mercury, copper, silver, nickel and other metals; salicylic acid is a suitable reagent for spectrophotometric determination of iron, copper, titanium, uranium, lanthanum, and for masking a number of cations.

Therefore it is clear that these compounds are utilized also for preparation of selective sorbents serving for extractions, concentrations, and separations in liquid-solid systems³. Particularly, the supports modified with dithizone functional groups have found wide applications. These groups are coated on the surface of solid phase by simple wetting it with a dithizone solution in a suitable solvent, e.g. acetone^{4,5}, 1,2-dichlorobenzene⁶, carbon tetrachloride⁷; instead of dithizone also used was the more stable zinc dithizonate dissolved in chlorobenzene⁸. Another way of modification is the ion exchange reaction between the sulfonated dithizone and anion exchanger Amberlite IRA 400 (ref.⁹). The supports used include e.g. polyurethane⁴, diatomite sorbent Chromosorb W-HP (ref.⁶), cellulose acetate⁷, polystyrene^{5,8}; an efficient sorption of Ag(I), Cu(II), and Mg(II) was achieved on filter paper impregnated with dithizone^{10,11}. The third possibility of preparation of selective ion exchangers consists in binding the chelating functional groups to a surface of solid phase by means of a chemical reaction.

The dithizone sorbents based on cross-linked dextrans¹² and carboxymethylcellulose¹³ were synthesized in this way. Due to the very low solubility of dithizone in water, the complex-forming metals can effectively be extracted from acid solution with powdered dithizone alone. A concentrate of the metals trapped is obtained by dissolving the reagent (collected by filtration) in concentrated HNO₃. The method was elaborated for concentrating silver from nitric acid media¹⁴⁻¹⁶. The dithizone-modified sorbents were also used to isolate and concentrate mercury^{4,5,8-10}, copper^{6,7,10,13}, gold^{12,13}, lead and zinc^{7,13}, platinum and palladium¹², and manganese, cobalt, and cadmium⁷.

Selective sorbents with the functional grouping of salicylic acid have not yet found such broad applications as compared with the dithizone sorbents: the published reports deal mainly with their preparation and properties. Vernon and Eccles¹⁷ prepared four types of complex-forming resins, the salicylic acid being one of the components in the polymerization reaction, or it was attached to the diazotized poly(aminostyrene) matrix by means of azo coupling reaction. The sorbents exhibited selective sorption of Fe(III), UO₂²⁺, Al(III), and Cu(II); moreover, the authors also studied the behaviour with respect to Ni(II), Zn(II), and Co(II) ions. A study of ion exchange kinetics of Cu(II), Ni(II), Cd(II), Zn(II), and Ca(II) on a macroporous resin containing salicylate groups showed that the exchange rate increased with increasing porosity of the polymer¹⁸. Cellulose ion exchangers with chemically bound residues of salicylic acid were used to study the sorption of Fe(III) ions¹⁹ and Cu(II), Ni(II), Co(II), and Zn(II) ions²⁰. A number of further valuable pieces of information about chelating sorbents inclusive of the dithizone and salicylic ones are given by Myasoedova and Savvin²¹.

The foreign matter which endangers man and environment, and which is most often monitored, involves heavy metals in general, and lead and cadmium in particular. The present communication describes and discusses the experiments in which sorption of Pb(II) and Cd(II) ions has been studied using the selective ion exchangers Ostsorb DITHIZON and Ostsorb SALICYL having the functional groups of diphenylthiocarbazon and salicylic acid, respectively, bound in side chains of pearl cellulose. The work forms a continuation of our earlier research²²⁻²⁶ studying the properties of other cellulosic sorbents Ostsorb with the aim of finding a ion exchanger suitable for isolations and concentrations of trace amounts of the above-mentioned metals from aqueous solutions with potential applications to analytical and technological practice.

EXPERIMENTAL

Apparatus and Chemicals

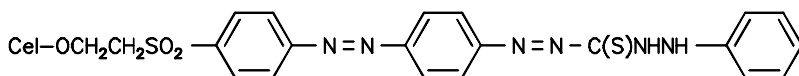
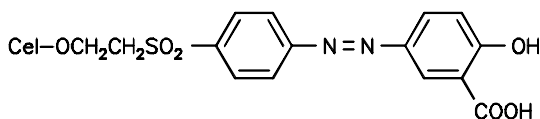
Lead and cadmium were determined in solution by means of the method of atomic absorption spectrometry using an Atomspek H 1550 apparatus (Hilger and Watts, U.K.) with acetylene-air flame at the wavelengths of 217.5 nm (Pb) and 229.0 nm (Cd). The pH values of solutions were determined with the help of an OP-207 apparatus with a combined glass electrode OP-8083 (Radelkis, Hungary).

For stirring we used electromagnetic stirrers MM 2A (Laboratorni pristroje, Prague, The Czech Republic) and shakers LT 1 (Kavalier, The Czech Republic).

The solutions of lead and cadmium of 1 mg ml^{-1} concentration were prepared by dissolving the corresponding amounts of $\text{Pb}(\text{NO}_3)_2$ and $3 \text{ CdSO}_4 \cdot 8 \text{ H}_2\text{O}$, respectively, in deionized water acidified with 1 M HNO_3 (pH 4 – 5).

The ion exchangers tested involved Otsorb DITHIZON and Otsorb SALICYL, sorbents based on pearl cellulose with functional groups of diphenylthiocarbazono (*I*) and salicylic acid (*II*), respectively, chemically bound through an azo group to the cellulose side chains. They are products of Spolek pro chemickou a hutni vyrobu (Company of Chemical and Metallurgical Production, The Czech Republic). The dithizone ion exchanger used is no standard product, whereas Otsorb SALICYL is commercially available already. The content of functional groups, as specified by the producer, is at least 0.2 mmol g^{-1} (DITHIZON) and 0.5 mmol g^{-1} (SALICYL). For the experiments, the ion exchangers were used in swollen H^+ form, the estimated water content was 70% (DITHIZON) and 74% (SALICYL). The physical properties of the Otsorb sorbents are described in detail in a booklet²⁰ by the producer.

All the chemicals used were of p.a. purity grade (Lachema, The Czech Republic) and their solutions were prepared in deionized water.

*I**II*

Procedures

Measurement of pH dependence of exchange capacity of ion exchangers. A mixture of 0.5 g swollen ion exchanger and 100 ml solution of lead or cadmium (initial concentration $\rho_0 = 50 \text{ mg l}^{-1}$) was stirred 2 h and pH was continuously potentiometrically measured and adjusted at the required value by adding 0.2 M HCl or 0.2 M NaOH . Then a 1 ml sample was taken from the liquid and, after diluting and possible adjusting the pH 4 – 5 by addition of 0.2 M HCl , the content of lead and/or cadmium was determined by means of AAS using the method of calibration curve.

Measurement of dependence of exchange capacity of ion exchangers upon ionic strength of solution. A mixture of 0.5 g swollen ion exchanger and 100 ml solution of lead or cadmium with initial concentration $\rho_0 = 50 \text{ mg l}^{-1}$ was shaken 2 h; the ionic strength was adjusted at $I = 0 - 5 \text{ mol l}^{-1}$ by addition of sodium perchlorate. pH was adjusted by adding 0.1 – 0.4 ml 0.2 M NaOH . After finishing the sorption process, the pH value was determined with a pH meter and the metal concentration with AAS.

RESULTS AND DISCUSSION

The data given in the following text are arithmetical means of two repeated experiments each.

pH Dependence of Exchange Capacity of Ion Exchangers

Table I presents the values of analytical mass exchange capacity Q_a of both the ion exchangers tested in the sorption of Pb(II) and Cd(II) ions from solutions of pH 4 – 9 and the order of magnitude of ionic strength $I \approx 10^{-4} - 10^{-3} \text{ mol l}^{-1}$ (the ionic strength resulted from the metal salts present and the sodium hydroxide used to adjusting pH). The Q_a values can be considered to be equilibrium values: if the time of contact of ion exchanger with the sorption solution was increased above 2 h, the amount of the metal trapped did not increase any further.

The results show that Ostsorb DITHIZON reaches its maximum capacity for both the metals in a relatively narrow region about pH 7.5: the functional group of ion exchanger is completely ionized (pK_1 (dithizone) 5.6 – 6.3, ref.²⁷), however, the interfering effect of the hydrolytic process giving stable hydroxo complexes of lead and

TABLE I

The pH dependence of exchange capacity Q_a (mmol g^{-1}) of Ostsorb DITHIZON and Ostsorb SALICYL in sorptions of Pb(II) and Cd(II) ions^a

pH	Q_a			
	Ostsorb DITHIZON		Ostsorb SALICYL	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
4.0	–	–	–	0.53
4.5	–	–	0.11	–
5.0	–	–	0.10	0.63
5.5	–	–	1.21	–
6.0	–	–	1.01	0.61
6.5	0.13	0.02	0.92	0.62
7.0	0.70	0.60	0.47	1.06
7.5	0.75	0.97	–	–
8.0	0.05	0.74	0.21	2.58
8.5	0.05	0.29	–	–
9.0	–	0.33	0.12	4.30

^a $I \approx 10^{-4} - 10^{-3} \text{ mol l}^{-1}$.

cadmium becomes significant. The stability constants of these compounds are comparable with or even greater than those of the two metals and the dithizone ligand, which of course has an unfavourable effect on the complex-forming reaction of the metal ions with the functional group of ion exchanger. The stability constants given in tables²⁷ for the dithizone complexes of lead and cadmium have the following values: $\log K_1(\text{Cd}) = 7.81$, $\log \beta_2(\text{Cd}) = 15.10$, $\log K_1(\text{Pb}) = 7.31$, $\log \beta_2(\text{Pb}) = 14.16$; for the hydroxo complexes: $\log \beta_2(\text{Cd}) = 7.64$, $\log \beta_4(\text{Cd}) = 8.64$, $\log \beta_{44}(\text{Cd}) = 23.13$, $\log \beta_2(\text{Pb}) = 10.87$, $\log \beta_3(\text{Pb}) = 13.93$, $\log \beta_{44}(\text{Pb}) = 35.1$. The data given apply to zero ionic strength of solution. They show (and the results in Table I confirm it) that the formation of hydroxo complexes affects more strongly the sorption of lead ions, which form more stable hydroxo complexes and a less stable dithizone complex than cadmium ions. Moreover, the low values of solubility products of both metal hydroxides²⁸ ($pK_s(\text{Pb}(\text{OH})_2) 14.9$, $pK_s(\text{Cd}(\text{OH})_2) 14.35$) made themselves felt by the formation of corresponding precipitates in neutral and alkaline pH regions at the concentrations as low as (in the order of magnitude) $10^{-1} - 10^0 \text{ mg l}^{-1}$, which brought concomitant experimental difficulties in separating the ion exchanger from the sorption solution with the precipitate. This problem was solved by using a filter extension with sintered glass attached to the end of pipette used for taking the sample of sorption solution with potential precipitate for analysis. In spite of that, the reproducibility of these measurements was worse than that with clear solutions. The relative standard deviation of four repeated determinations of lead in suspension of pH 8 with initial metal concentration $\rho_0 = 50 \text{ mg l}^{-1}$ was $s_r = 8.3\%$, being $s_r = 3.4\%$ for a solution of pH 5.

The position of adsorption maximum of lead at the curve of pH dependence of exchange capacity agrees with the results published by Bauman et al.¹³ and Carrit⁷ who recommend pH 8 and 7, respectively, for its sorption by dithizone ion exchangers.

Ostorb SALICYL attains its maximum exchange capacity for Pb(II) ions in mildly acidic medium of pH 5.5 – 6.5, which corresponds to the acidity of the functional group of ion exchanger. The respective dissociation constants²⁸ have the values of $pK_1 2.29$ and $pK_2 13.74$. It is particularly favourable that an efficient sorption of Pb(II) ions takes place in such pH region where the lead salts are not hydrolyzed and do not form precipitates of hydroxides.

Cd(II) ions were trapped by the Ostorb SALICYL at pH 4 already, but, in contrast to the sorption of lead, the pH dependence of exchange capacity does not exhibit any maximum: it monotonously increases also in alkaline medium to finally reach values which many times exceed the declared content of ligand functional groups in the ion exchanger. This fact can be interpreted by physical adsorption of the hydroxo complexes; Vernon and Eccles¹⁷ ascribe an analogous behaviour of Cu(II) ions to interactions of metal with nitrogen atoms of azo group which connects the ligand to the support.

Dependence of Exchange Capacity of Ion Exchangers on Ionic Strength of Solution

As shown by the data of Table II the concentration of indifferent salt NaClO_4 affects significantly the exchange capacities of both ion exchangers, particularly in the sorption of bulky lead ions. With the Ostsorb DITHIZON the exchange capacity in Pb(II) sorption decreased from 100% at $I = 0 \text{ mol l}^{-1}$ to 5.3% at $I = 5 \text{ mol l}^{-1}$, the steepest decrease being observed in the interval of $I = 0 - 0.01 \text{ mol l}^{-1}$. Cd(II) ion was effectively sorbed even from a medium of $I = 5 \text{ mol l}^{-1}$ when the exchange capacity of ion exchanger decreased to 50% as compared with its value at $I = 0 \text{ mol l}^{-1}$. If we consider $Q_a = 0.3 \text{ mmol g}^{-1}$ to be a sufficient exchange capacity, then Ostsorb DITHIZON can be used for the sorption of lead from solutions of $I = 0 - 1 \text{ mol l}^{-1}$ and for that of cadmium from solutions of $I = 0 - 5 \text{ mol l}^{-1}$.

A decrease in exchange capacity for lead and cadmium in the sorption from solutions of increasing ionic strength was also observed with Ostsorb SALICYL. The same recommendation applies to the practical use of this ion exchanger like that for the dithizone sorbent. The sorbent Ostsorb SALICYL has the advantage in its higher exchange capacity in the whole interval of NaClO_4 concentrations investigated. With regard to the complexity of the systems studied, in which acid-base, complex-forming, and precipitation equilibria exist side by side, the data obtained are insufficient for any unambiguous interpretation of the dependences found. However, that was not the aim of the present paper.

The reproducibility of measurement of exchange capacity of ion exchangers was determined by four repeated experiments with Ostsorb SALICYL and with lead and cadmium solution of the ionic strength $I = 1 \text{ mol l}^{-1}$ and pH 5.9 (Pb) or 8.9 (Cd). The

TABLE II
The dependence of exchange capacity Q_a (mmol g^{-1}) of Ostsorb DITHIZON and Ostsorb SALICYL in sorptions of Pb(II) and Cd(II) ions from solutions of various ionic strength I

$I, \text{ mol l}^{-1}$	Q_a			
	Ostsorb DITHIZON		Ostsorb SALICYL	
	Pb(II)^a	Cd(II)^a	Pb(II)^b	Cd(II)^c
0	0.75	0.60	1.01	4.30
0.01	0.43	0.41	0.59	3.23
0.1	0.40	0.39	0.57	3.18
1.0	0.37	0.37	0.36	2.42
5.0	0.04	0.31	0.11	2.11

^a pH 7; ^b pH 6; ^c pH 9.

relative standard deviation of measurement of Q_a (Pb) was $s_r = 7.3\%$, 95% confidence interval $L_{1,2} = 0.67 \pm 0.08$ mmol g⁻¹; the corresponding values for determination of Q_a (Cd) were $s_r = 4.9\%$, $L_{1,2} = 2.42 \pm 0.18$ mmol g⁻¹.

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