

SORPTION OF CADMIUM AND LEAD BY CHELATING ION EXCHANGERS OSTSORB OXIN, OSTSORB DETA, AND OSTSORB DTTA

Ladislav SVOBODA and Petr VORECHOVSKY

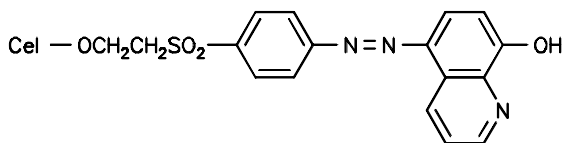
*Department of Inorganic Technology,
University of Pardubice, 532 10 Pardubice, The Czech Republic*

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The properties of cellulose chelating ion exchangers Ostsorb have been studied in the sorption of cadmium and lead from aqueous solutions. The Cd(II) and Pb(II) ions are trapped by the Ostsorb OXIN and Ostsorb DETA ion exchangers most effectively in neutral and alkaline media but at these conditions formation of stable hydrolytic products of both metals competes with the exchange equilibria. From this point of view, Ostsorb DTTA appears to be a more suitable sorbent since it traps the Pb(II) and Cd(II) ions in acidic media already. Chloride ions interfere with the sorption of the two metals by Ostsorb DTTA whereas the ionic strength adjusted by the addition of sodium perchlorate does not affect the exchange capacity of this ion exchanger.

The importance and application examples of chelating ion exchangers were discussed in earlier communications dealing with study of properties of cellulosic sorbents with diethylenetriamine functional groups¹, phosphoric acid², H-acid², and diethylenetriaminetetraacetic acid^{3,4}. The Ostsorb ion exchangers based on spherical pearl cellulose modified with diethylenetriamine (DETA) or diethylenetriaminetetraacetic acid (DTTA) groups in the side chains are dealt with in detail in the previous communications^{1,3,4} investigating the physical properties and studying the sorption of Pb(II) ions. Further information can be found in commercial leaflets^{5,6} and other papers^{7,8}. The Ostsorb OXIN ion exchanger is a cellulose modified in side chains by 8-hydroxyquinoline groups (*I*) which predetermine the exchanger to sorb a number of metals. Their partition coefficients can reach as high as $D \approx 10^5$ on this sorbent. The pH dependence of this quantity can be utilized for selective or group elution of the cations trapped⁵. Pieces of information about cellulosic ion exchangers with oxine groups can be en-



countered in literature only sporadically. Valuable data are found in the manufacturers' leaflets⁶ giving the results of investigation of sorption of Ni(II), Co(II), Zn(II), Pb(II), and last but not least Cu(II) ions by Ostsorb OXIN. The complex-forming properties of this ion exchanger were utilized for isolation of heavy metals from some pharmaceutical preparations⁷.

The present communication gives the properties of the Ostsorb OXIN ion exchanger in the sorption of Cd(II) and Pb(II) ions and those of Ostsorb DETA and Ostsorb DTTA in the sorption of cadmium.

EXPERIMENTAL

Apparatus and Reagents

The sorption experiments were carried out by the batch process method. The ion exchanger was mixed with the solution of metals by means of a magnetic stirrer MM 2A (Laboratorni pristroje, The Czech Republic) and longitudinal vibrator LT 1 (Kavalier, The Czech Republic). The pH values of solutions were determined by means of a recording pH meter OP-207 with a combined glass electrode OP-8083 (Radelkis, Hungary). The lead and cadmium concentrations in solutions were determined with the help of an atomic absorption spectrophotometer Atomspek-H 1550 (Hilger and Watts, U.K.) in acetylene-air flame at 217.5 nm (Pb) and 229.0 nm (Cd) using the method of calibration curve.

The lead and cadmium solutions for use in the sorption experiments with the concentrations of 1 mg ml⁻¹ were prepared by dissolving the corresponding amount of Pb(NO₃)₂ (pre-dried at 110 °C) and/or 3 CdSO₄ · 8 H₂O in deionized water acidified with 1 M HNO₃ to pH 4 – 5. Precise concentrations of the two metals in stock solutions were determined by means of AAS, the calibration solutions being prepared by dissolution of the standard solutions for AAS (Analytika, The Czech Republic). The pH values of selected sorption solutions were maintained by means of an acetic acid-sodium acetate buffer. The ion exchangers Ostsorb DETA, Ostsorb OXIN, and Ostsorb DTTA are products of Spolek pro chemickou a hutni výrobu, The Czech Republic.

The content of functional groups in dry ion exchangers as given by the manufacturer is 1.5, 0.2, and 1 mmol g⁻¹ for DETA, OXIN, and DTTA, respectively. The physical properties of Ostsorb DETA and Ostsorb DTTA were described in our earlier papers^{1,3}, those of Ostsorb OXIN are summarized in Table I. The ion exchangers were transferred to the H⁺ form and dried at room temperature to constant weight before use.

All the chemicals used were of p.a. purity grade (Lachema, The Czech Republic).

Procedures

Time dependence of sorption of cadmium by Ostsorb OXIN. Aqueous solution of cadmium (25 g l⁻¹, 100 ml) was stirred with ion exchanger (1 g) in a beaker, and pH was continuously potentiometrically monitored and adjusted at pH 7 by addition of 0.2 M NaOH. At chosen time intervals, 2 ml samples were withdrawn from the solution and, after diluting, analyzed by means of AAS.

pH Dependence of the ion exchanger capacity. An 0.1 g sample of the ion exchanger pre-dried at room temperature was stirred with cadmium solution (250 mg l⁻¹, 100 ml) 2 h, and pH of solution was monitored potentiometrically and maintained at the required value by adding either 0.2 M HCl or 0.2 M NaOH solution. Then the sorbent was separated, washed with 10 ml liquid of the given pH

value, and shaken with 20 ml 1 M HCl in a 50 ml calibrated flask 1 h. The cadmium concentration of desorbate was determined by means of AAS.

Dependence of exchange capacity of Ostsorb DTTA on ionic strength of solution. An 0.1 g sample of ion exchanger was shaken with lead or cadmium (initial concentration 250 mg l⁻¹, 100 ml) solution in acetate buffer of pH 4. The ionic strength was adjusted at $I = 0.04 - 4.00$ by addition of solid sodium perchlorate. Then the sorbent was filtered off, the metals trapped were desorbed by means of 20 ml 1 M HCl, and their concentration in solution was determined with the help of AAS. The same procedure was adopted also in the experiments with the ionic strength adjusted with potassium chloride.

Determination of yields of cadmium and lead in the sorption-desorption processes. In a 1 000 ml calibration flask, Ostsorb DTTA (0.1 g) was shaken with cadmium or lead solution (500 ml) in acetate buffer of pH 4, ionic strength $I = 0.04$, and initial concentration of metals $\rho_0(\text{Cd}) = 0.6 \text{ mg l}^{-1}$ and $\rho_0(\text{Pb}) = 1 \text{ mg l}^{-1}$. After two hours, the ion exchanger was filtered off, washed with 10 ml buffer, and extracted with 20 ml 1 M HCl in a 50 ml calibrated flask. The experiment described was repeated five times with solutions containing lead or cadmium or none of the metals.

RESULTS AND DISCUSSION

The ion exchangers used contained almost constant amounts of water per gram when dried at room temperature, but with a swollen exchanger kept in deionized water it is impossible to obtain the same amounts of retained water (i.e. content of dry matter) after each filtration, which results in a worse reproducibility of results in repeated determinations of the exchange capacity. Therefore the experiments were carried out with the ion exchangers which were converted to their H⁺ form and then left to dry to constant weight at 19 – 21 °C in spite of the fact that such a procedure could affect the complex formation kinetics in an unfavourable way.

If not otherwise stated, the data given in the text and tables are arithmetic mean values of two repeated experiments each.

TABLE I
Properties of Ostsorb OXIN

Property	Value
Density, g cm ⁻³	1.19 ^a
Specific weight, g cm ⁻³	0.76 ^a , 0.84 ^b
Specific volume, cm ³ g ⁻¹	1.31 ^a , 1.19 ^b
Mass swelling capacity, g H ₂ O/g	1.43 ^a
Volume swelling capacity, cm ³ g ⁻¹	3.22 ^a
Water content, %	10.1 ^b
Particle size ^a , μm	80 – 340

^a In swollen state. ^b Dried at 20 °C.

Time Course of Sorption of Cadmium with Ostsorb OXIN Ion Exchanger

The title time course is given in Fig. 1 wherefrom it is obvious that the exchange equilibrium was established approximately 2 h after the beginning of sorption. This contact time of exchanger and metal was used in the rest of experiments. A longer time of establishing of equilibrium on Ostsorb OXIN as compared with those on Ostsorb DETA (ref.¹) and Ostsorb DTTA (ref.³) (where it was shorter than 1 h) can particularly be ascribed to the fact that the ion exchanger has been used in dry state now, whereas the earlier tested sorbents were used in their swollen states providing better conditions for fast exchange kinetics. The kinetic properties of exchanger can also be affected in an unfavourable way by bulky oxine functional groups bringing hydrophobic aromatic structures into the cellulosic skeleton⁵.

pH Dependence of Ion Exchanger Capacity

Most often the ion exchanger capacity is expressed in the amount of ions (in millimoles) exchanged by one gram of dry ion exchanger at the given conditions, and it is referred to as analytical mass exchange capacity Q_a . The theoretical mass exchange capacity Q_0 gives the amount of active functional groups in mmol per 1 g ion exchanger in the given form⁹. The trapped ions are usually desorbed with solutions of mineral acids, and on the basis of earlier studies¹⁻³ and found pH-dependences of exchange capacity we have chosen 1 M HCl.

From the data of Table II it is obvious that the most efficient sorption of Pb(II) and Cd(II) ions by the Ostsorb OXIN ion exchanger only occurs in alkaline medium at $\text{pH} \geq 8$ where the nitrogen atom of the oxine moiety is fully deprotonated already (the corresponding dissociation constants are $\text{p}K_1$ 4.91 and $\text{p}K_2$ 9.81)¹⁰ and can take part in chelate bond formation with the metal ion. The significant difference between the

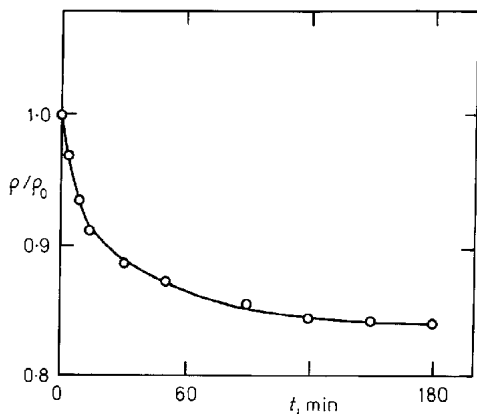


FIG. 1
Time dependence of sorption of cadmium with Ostsorb OXIN at pH 7, ρ/ρ_0 ratio of actual and initial weight concentrations of cadmium

values of exchange capacities Q_a of lead and cadmium is obviously due to different stabilities of hydroxy compounds of lead and cadmium which are formed in solutions of these metals at $\text{pH} \geq 7$ and thus compete with the exchange equilibrium between the cations and ion exchanger. This interpretation is also supported by the magnitude of stability constants of hydroxo complexes of lead and cadmium whose logarithms have the following values¹⁰: $\log \beta_2(\text{Cd}) = 7.7$, $\log \beta_2(\text{Pb}) = 10.9$, $\log \beta_{44}(\text{Cd}) = 23.2$, $\log \beta_{44}(\text{Pb}) = 35.1$.

Also the stability constant of complex of cadmium with 8-hydroxyquinoline is somewhat lower than that with lead ($\log \beta_1(\text{Cd}) = 7.78$, $\log \beta_1(\text{Pb}) = 9.02$). With regard to the reasons given, physical sorption of hydrolytic products from Pb(II) and Cd(II) salts cannot be excluded either, being supported primarily by the high exchange capacity $Q_a(\text{Cd}) = 0.98 \text{ mmol g}^{-1}$ at pH 8, which is five times higher than the minimum content of complex-forming groups given by the manufacturer. The formation of insoluble hydroxy compounds of the two metals, whose solubility products have the values of $\text{p}K_s(\text{Pb}(\text{OH})_2) 14.9$ and $\text{p}K_s(\text{Cd}(\text{OH})_2) 14.35$, can unfavourably affect the reliability of determination of exchange capacity in this pH region. The relative standard deviations of five estimations of exchange capacity $Q_a(\text{Pb})$ at pH 8 was $s_r = 7.6\%$, being 3.2% at pH 5. With respect to separation of large amounts of precipitates of lead and cadmium

TABLE II
pH Dependence of exchange capacity Q_a of Ostsorb OXIN, Ostsorb DETA, and Ostsorb DTTA in sorption of Cd(II) and Pb(II) ions

pH	$Q_a, \text{ mmol g}^{-1}$			
	OXIN ^a	OXIN ^b	DETA ^a	DTTA ^a
0.8	–	–	–	0.10
1.0	–	–	–	0.12
2.0	–	–	–	0.46
2.7	–	–	–	0.75
3.3	–	–	–	0.81
4.0	0.04	0.03	0.00	1.17
5.0	0.10	0.04	0.01	1.23
6.0	0.09	0.03	0.02	–
7.0	0.21	0.03	0.06	–
7.5	0.69	0.08	0.12	–
8.0	0.98	0.13	0.22	–
8.5	–	–	0.69	–
9.0	–	0.12	0.92	–

^a Sorption of Cd(II) ions. ^b Sorption of Pb(II) ions.

compounds from the solutions of $\text{pH} > 8$ it was impossible to reliably determine the value of the maximum ion exchanger capacity. The pH dependence of exchange capacity of Ostsorb DETA in Cd(II) ion sorption has a similar course to that of Ostsorb OXIN (see Table II). The $Q_a(\text{Cd})$ values reach their maximum at pH 8 (the dissociation constants of protonated diethylenetriamine are $\text{p}K_1$ 3.64, $\text{p}K_2$ 8.74, $\text{p}K_3$ 9.80), and like with Ostsorb OXIN it was impossible to determine the maximum attainable exchanger capacity due to separation of the precipitate of hydrolytic products of cadmium. According to the manufacturer, the value of theoretical exchange capacity is $Q_0 = 1.5 \text{ mmol g}^{-1}$, the value found at pH 9 being $Q_a(\text{Cd}) = 0.92 \text{ mmol g}^{-1}$. For the reproducibility of determination of $Q_a(\text{Cd})$, similar conclusions are valid as those for Ostsorb OXIN. The sorption of lead with Ostsorb DETA was described earlier¹; the estimated maximum capacity of ion exchanger $Q_a(\text{Pb})$ was distinctly lower (like that with Ostsorb OXIN) than the capacity for Cd(II) ion, which agrees with the presumed high stability of hydroxy compounds of lead. The negative steric effect of bulky Pb(II) ion cannot be excluded either. The stability constants of the diethylenetriamine complexes have the following values¹⁰: $\log \beta_1(\text{Cd}) = 8.4$, $\log \beta_2(\text{Cd}) = 13.8$, $\log \beta_1(\text{Pb}) = 8.50$, $\log \beta_2(\text{Pb}) = 13.37$.

The pH dependence of analytical exchange capacity of Ostsorb DTTA for Cd(II) ions is practically identical with that for Pb(II) ions³ (see Table II). The ion exchanger retains the ions of both the metals to a small extent at as low as pH 1 ($Q_a(\text{Cd}) = 0.12 \text{ mmol g}^{-1}$, $Q_a(\text{Pb}) = 0.25 \text{ mmol g}^{-1}$), the maximum exchange capacity being reached at $\text{pH} \geq 4$: $Q_a(\text{Cd}) = 1.2 \text{ mmol g}^{-1}$, $Q_a(\text{Pb}) = 1 \text{ mmol g}^{-1}$. Although the dissociation constants and stability constants of complexes of diethylenetriaminetetraacetic acid have not been published, they can be presumed to be close to those of diethylenetriaminopentaacetic acid¹⁰ viz. $\text{p}K_1$ 1.82, $\text{p}K_2$ 2.66, $\text{p}K_3$ 4.30, $\text{p}K_4$ 8.59, $\text{p}K_5$ 10.55, which means that the complexes of Pb(II) and Cd(II) ions with polyaminopolycarboxylic ligands (inclusive of DTTA) can be formed in acid media already, the competitive hydrolytic reactions being insignificant here. Also favourable are the high values of stability constants of chelates of both metals ($\log \beta_1(\text{Cd}) = 19.2$, $\log \beta_1(\text{Pb}) = 18.80$) and the value of analytical exchange capacity corresponding to the declared value $Q_0 = 1 \text{ mmol g}^{-1}$. The reproducibility of five parallel estimations of $Q_a(\text{Cd})$ at pH 4 is expressed by the corresponding relative standard deviation $s_r = 2.8\%$.

With respect to the advantages mentioned with Ostsorb DTTA, the further experiments verifying the effect of ionic strength of solution upon the sorption of cadmium and lead and recovery yields of sorption-desorption processes of traces of both metals were only carried out with this ion exchanger.

Effect of Ionic Strength on Sorption of Cadmium and Lead by Ostsorb DTTA

Table III presents the Q_a values of Ostsorb DTTA for the sorptions of Cd(II) and Pb(II) ions from a medium of acetate buffer of pH 4 and varying ionic strength adjusted by

addition of sodium perchlorate or potassium chloride. The values of both $Q_a(\text{Cd})$ and $Q_a(\text{Pb})$ estimated for the solutions with NaClO_4 show no systematic dependence on ionic strength, being randomly distributed around the mean value of $\overline{Q_a}(\text{Cd}) = 0.94 \pm 0.04 \text{ mmol g}^{-1}$ and $\overline{Q_a}(\text{Pb}) = 0.93 \pm 0.02 \text{ mmol g}^{-1}$, respectively. On the other hand, increasing concentration of chloride ions in solution results in a distinct decrease of exchange capacities for both lead and cadmium, the latter being practically not trapped by the ion exchanger from a solution with $c(\text{KCl}) = 4 \text{ mol l}^{-1}$ ($I = 4$). This phenomenon can be explained by the ability of a number of metals, inclusive of Pb and Cd, to form anionic complexes with chloride ions, the different stabilities of these complexes forming a basis of, inter alia, a method of separation of these metals from hydrochloric acid media of different concentrations on strongly basic anion exchangers⁹.

Recovery in Concentration Processes of Cd and Pb Traces on Ostsorb DTTA

The above-mentioned experiments were carried out with solutions of high cadmium and lead concentrations but in analytical practice much more dilute samples are encountered. Therefore the following measurements were accomplished with solutions containing the two metals at concentrations as low as the limit of direct detectability by the AAS method, and the overall recovery of the sorption-desorption processes was examined. The statistical treatment of five repeated experiments showed that acceptable recovery values $R(\text{Pb}) = 93.6 \pm 0.8\%$ and $R(\text{Cd}) = 94.3 \pm 0.7\%$ were obtained by

TABLE III

Dependence of exchange capacity Q_a (mmol g^{-1}) of Ostsorb DTTA on ionic strength I in sorption of Cd(II) and Pb(II) ions^a

I	Cd(II)		Pb(II)	
	A	B	A	B
0.04 ^b	0.94	0.94	0.96	0.96
0.15	0.92	0.33	0.92	0.93
0.25	0.94	0.30	0.91	0.90
0.65	0.87	0.22	0.93	0.86
0.90	1.00	0.19	0.89	0.79
1.50	0.93	0.15	0.94	0.62
3.0	0.96	0.05	0.95	0.46
4.0	0.82	0.00	0.93	0.35

^a In acetate buffer of pH 4, the ionic strength was adjusted by adding sodium perchlorate (A) or potassium chloride (B). ^b In a buffer without added salts for ionic strength adjustment.

twentyfold concentrating 500 ml original lead and cadmium solutions, respectively (pH 4, $I = 0.04$, initial concentrations $\rho_0(\text{Pb}) = 1 \text{ mg l}^{-1}$, $\rho_0(\text{Cd}) = 0.6 \text{ mg l}^{-1}$). The mean values of estimated amounts of metal were $m(\text{Pb}) = 0.468 \text{ mg}$ and $m(\text{Cd}) = 0.283 \text{ mg}$, the relative standard deviations of determination of m being $s_r(\text{Pb}) = 1.63\%$, $s_r(\text{Cd}) = 2.43\%$. The metals were not found in the reference solutions without added lead and cadmium. Provided the detection limits of AAS apparatus are $0.5 \text{ mg l}^{-1} \text{ Pb}$ and $0.02 \text{ mg l}^{-1} \text{ Cd}$, the concentration procedure suggested will enable determination of lead and cadmium present in original samples at the concentrations $\rho(\text{Pb}) = 25 \text{ } \mu\text{g l}^{-1}$ and $\rho(\text{Cd}) = 1 \text{ } \mu\text{g l}^{-1}$. When analyzing real samples one will have to verify the recovery of concentration procedure e.g. by the method of standard addition because such solutions often contain a variety of more or less interfering compounds whose presence will result in a decreased efficiency of sorption by the ion exchanger of the ion monitored.

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