Environment Protection Engineering

Vol. 14 1988 No. 3–4

Š. CERJAN-STEFANOVIĆ*, M. KAŠTELAN-MACAN*, M. BLANUŠA**, L. BOKIĆ*

SEPARATION OF CADMIUM FROM HOT WATERS BY ION EXCHANGE RESINS

The relationship between the ion exchange reaction in a column and temperature was examined in the system cadmium-ion exchanger resin Lewatit S 1080. Cadmium was bound by 0.02 M HNO_3 and then eluted by 2.0 M HCl. Working temperature was gradually increased from 273 to 333 K. Cadmium concentrations were determined by atomic absorption spectrometry. Thermostated columns were of our own construction. The distillation plate theory was applied for the same ion eluted at different temperatures. It was necessary to determine graphically the following parameters: c_{ex}, c_{max}, V_{max}, and the width of elution band. These parameters obtained for elution curves were related to temperature. The elution curves were found to be temperature specific. Deviations from Gauss normal distribution are larger at higher temperatures. The width of elution band is essential for comparing elutions at different temperatures. This value can be determined from the segment of the elution curve with the ordinate $c_{max/e}$. Consequently, we suggest the width of elution curve to be a measure of elution conditions at higher temperatures.

1. INTRODUCTION

In waters of a high salt content and very low concentrations of toxic heavy metals, direct determination of lead and cadmium is impracticable to carry out by means of common analytical techniques. Therefore before determination, the metals have to be concentrated or extracted. Cadmium is easily concentrated by ion exchange resins or chelating celluloses [1]–[10]. The literature data always refer to the working temperature of 293 K. The effect of temperature on ion exchange is, however, very scarce [11]–[14].

Previously [15], [16] we investigated the relationship between the static equilibrium of ion exchange of toxic metals and temperature. In this work we examined the dynamic equilibrium of cadmium exchange as a function of temperature rising from 293 to 333 K.

* Department of Analytical Chemistry, Technological Faculty, Marulićev trg 20, Zagreb, Yugoslavia.

** Institute for Medical Research and Occupational Health, Moše Pijade 158, Zagreb, Yugoslavia.

2. EXPERIMENTAL

The exchange of cadmium ions was performed in an equipment of our own construction. The ion exchanger was housed in two columns fitted with glass sinter. The diameter and the height of the columns were 1.35 and 3.5 cm, respectively. For ion exchange there was used Lewatit S 1080 resin of 8 mmol/g capacity and particle size range from 0.1 to 0.2 mm. The columns were heated by the thermostat water (ultra-thermostat type NBE, VEB Prüfgerate Werk) passing through a coil. A pump and a mixer were connected to the thermostat to enable the water circulation through both columns. By means of a contact thermometer connected to a heater, the temperature in the system was maintained constant. Control thermometers served to show the temperature in the thermostat and in the columns.

The resin was transferred to the H^+ form by means of 2 M HNO_3. For sorption of metal ions the resin was prepared by adding solutions in the following sequence: 15 cm^3 of thermoregulated HNO_3, 10 cm^3 of metal solution, and deionized water up to pH 7 using pH-mV meter MA 5730 (Iskra YU). Metal stock solution (1–20 mg/dm^3) were made by dissolution of cadmium in mineral acid. Elution of cadmium was carried out by means of 2 M HCl. The eluates were collected by fraction collector LKB Bromna-7000. Cadmium concentrations higher than 2 ppm were determined by flame AAS using a Varian AA 375 instrument. Lower concentrations were measured by electrothermal atomization in a graphite furnace using Varian CRA-90.

3. RESULTS AND DISCUSSION

The mechanism of the exchange process can be explained in terms of the distillation plate concept [8] pertaining to elution curves for various ions. This theory was applied to the same ion eluted at different temperatures. Elution curves could be approximated to normal distribution which meant that the elution conditions fulfilled the statistical law.

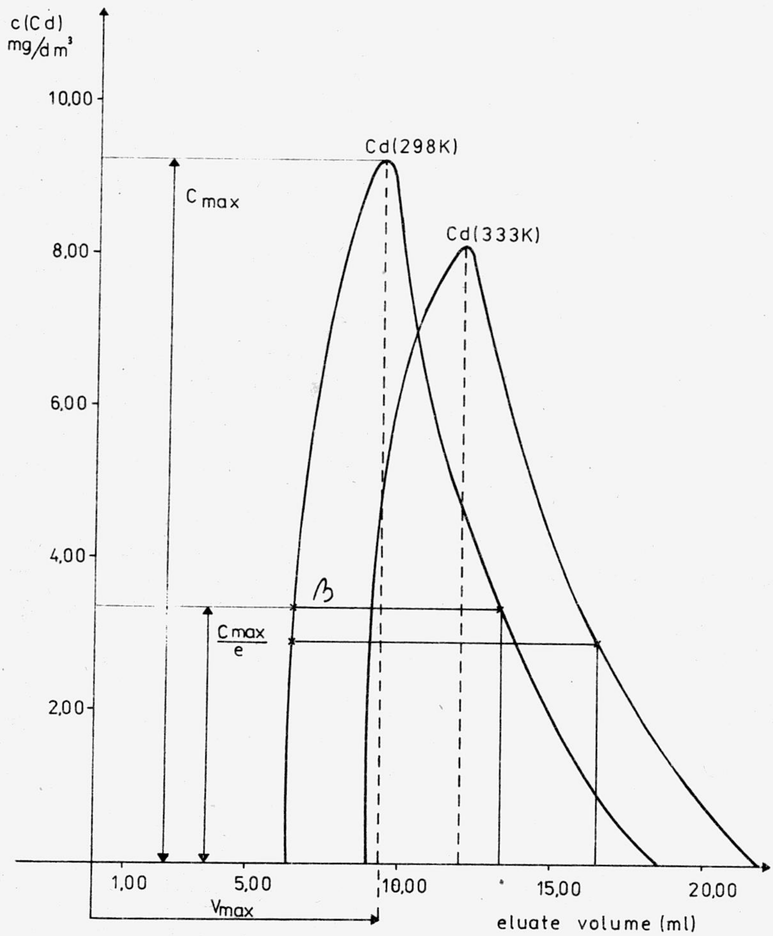
For precise designing the elution conditions it was necessary to determine graphically or by calculation the following parameters: c_{ex} (mg/dm^3) – total cadmium concentration after elution, α – elution factor, c_{max} (mg/dm^3) – maximal cadmium concentration after elution, V_{max} (cm^3) – calculated maximal volume, and β – width of elution band (table).

Optimum conditions of elution at different temperatures or in the presence of other ions in solution could be determined. The areas under the curve obtained by integration of elution curves [18] corresponded to the c_{ex} obtained experimentally. Area under the elution curves (c_{ex}), which corresponds to the values of total cadmium eluting, decreases with a temperature rise. The ratio of cadmium concentrations before elution (c_1) to cadmium concentration after elution (c_2) does not depend on temperature.

Table

Parameters of cadmium elution at different temperatures

T K	α cm^3	V_{max} cm^3	c_{ex} mg/dm^3	c_{max} mg/dm^3	$\beta = \frac{c_1}{c_2}$
298	13.30	9.60	13.69	9.09	1.02
303	13.85	9.80	13.55	9.00	1.03
308	14.22	9.85	13.46	8.91	1.04
313	14.91	10.30	13.31	8.66	1.05
318	15.13	10.73	13.61	8.54	1.03
323	15.71	11.15	13.07	8.44	1.07
328	16.00	11.85	12.93	8.21	1.08
333	16.50	12.00	12.77	8.10	1.09



Influence of temperature on elution curves

The peak values of elution curve obtained graphically and statistically (table) corresponded to c_{max}. Peak values were lower when the temperature increased. The results of elevated temperature were broader elution curves and a lower ability to separate ions. The V_{max} is the calculated volume of solution which was needed for elution of maximal cadmium concentration. The V_{max} was determined graphically on the basis of elution curves. V_{max} was abscissa which corresponded to ordinate of c_{max}.

The varying V_{max} values show that at higher temperatures maximal eluate concentrations are shifted towards higher values. The width of elution band β is essential in comparison of elution processes at different temperatures. This value denotes the volume of eluate needed for elution of total cadmium quantity. Graphically, according to the distillation plate theory, the band width can be determined from the segment of the elution curve (figure) with the ordinate $c_{max/e} = c_{max} \cdot 0.368$ [17]. SMIT [19] suggests the ordinate at 1/10 of peak height. The volume needed for cadmium elution rises with rising temperature. Elution curves do not correspond to Gauss normal distribution. Deviations from normal distribution are larger at higher temperatures. Consequently, we suggest that the width of the elution curve β is a measure of elution conditions at higher temperatures.

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SEPARACJA KADMU Z WODY O PODWYŻSZONEJ TEMPERATURZE ZA POMOCĄ ŻYWIC JONOWYMIENNYCH

Określono zależność reakcji wymiany jonowej od temperatury. Badania wykonywano dla układu kadm–żywica jonowymienna Lewatit S 1080. Jony kadmu były wiązane przez 0,02 molowy roztwór HNO_3, następnie wypłukiwane 2,0-molowym roztworem HCl. Temperaturę reakcji zwiększano stop-

niowo od 273 do 333 K. Stężenie kadmu określano za pomocą absorpcyjnej spektroskopii atomowej. Termostatowane kolumny zostały skonstruowane przez autorów. W opisie procesu wypłukiwania jonów w różnej temperaturze wykorzystano teorię destylacji warstwowej. Należało określić następujące parametry: c_{ex}, c_{max}, V_{max} i szerokość pasma wypłukiwania. Te parametry uzyskane dla krzywych wypłukiwania odniesiono do temperatury. Stwierdzono, że przebieg krzywych wypłukiwania zależy od temperatury. Odchylenia od rozkładu normalnego Gaussa są większe w wyższej temperaturze. Szerokość pasma wypłukiwania jest ważnym parametrem w porównywaniu procesów wypłukiwania w różnych temperaturach. Wartość ta może być określona na podstawie odcinka krzywej wypłukiwania o rzędnej $c_{max/e}$. W konsekwencji autorzy sugerują, że szerokość krzywej wypłukiwania jest miarą warunków wypłukiwania w wyższej temperaturze.

СЕПАРАЦИЯ КАДМИЯ И ВОДЫ ПОВЫШЕННОЙ ТЕМПЕРАТУРЫ ПРИ ПОМОЩИ ИОНООБМЕННЫХ СМОЛ

Определена зависимость реакции ионообмена от температуры. Исследования проведены для системы кадмий–ионообменная смола Lewatit S 1080. Ионы кадмия связывались 0,02 молярным раствором HNO_3, а затем вымывались 2,0 молярным раствором HCl. Температуры реакции повышали постепенно от 273 до 333 K. Концентрацию кадмия определяли при помощи абсорбционной атомной спектроскопии. Термостатируемые колонки были конструированы авторами. В описании процесса вымывания ионов при разных температурах использовали теорию слоевой дистилляции. Следовало бы определить следующие параметры: c_{ex}, c_{max}, V_{max} и ширину полосы вымывания. Эти параметры, полученные для кривых вымывания, отнесли к температуре. Было установлено, что ход кривых вымывания зависит от температуры. Отклонения от нормального распределения Гаусса больше в высших температурах. Ширина полосы вымывания является важным параметром в сравнении процессов вымывания в разных температурах. Это значение может быть определено на основе отрезка кривой вымывания ординаты $c_{max/c}$. В результате, авторы внушают, что ширина кривой вымывания является мерой условий вымывания при высших температурах.