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## Collection of Traces of Cadmium(II)-Ion on 2(3)-Alanine-*N,N*-Diacetic Acid Cellulose

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2(3)-alanine-*N,N*-diacetic acid cellulose represents a non-selective sorbent for a series of metal ions. It can be utilized for quantitative collection of traces of Cd(II)-ion from aqueous solutions, proving to be more efficient than Dowex A-1 (Na<sup>+</sup>) resin. The influence of pH, mass of the sorbent, metal ions concentration, ionic strength and contact period are discussed.

### INTRODUCTION

A remarkable increase in pollution of air, soil, plants, animals, waste and natural waters has been registered over the last few years, making environmental protection and pollution control one of the most important tasks of today<sup>1-9</sup>. Although opinions are divided, the majority of authors consider cadmium even in trace amounts to be a contaminant<sup>4,5,10</sup>. Based on toxicity data<sup>4,10</sup> some criteria for cadmium content in food, water, air, paints etc. have been drawn up<sup>1,10,11</sup>.

Cadmium pollution control requires sensitive, accurate and precise analytical methods. Preliminary concentration and separation of cadmium from the matrix is also necessary. The most important procedures used are based upon ion-exchange and/or chelating reactions of cadmium with synthetic or natural sorbents<sup>12-23</sup>.

For this reason laboratory prepared chelating 2(3)-alanine-*N,N*-diacetic acid cellulose, ADA-cell (H<sup>+</sup>)<sup>12,24,25</sup>, as well as chelating resin Dowex A-1 (Na<sup>+</sup>)<sup>14,15,18,23</sup>, were examined as sorbents for the Cd(II)-ion. The results obtained are given in this paper.

### EXPERIMENTAL

#### Chemicals

All the chemicals used were of »analytical grade«, except Dowex A-1(Na<sup>+</sup>) resin of purity »purum«. Also, redistilled water was used throughout.

#### Sorbents

i) *Chelating 2(3)-alanine-*N,N*-diacetic acid cellulose, ADA-cell (H<sup>+</sup>)*: was laboratory prepared by the recommended procedure<sup>24,25</sup>. The synthesized sorbent was characterized on the basis of IR-spectra and sorption capacity<sup>25,26</sup>. The presence of bands at 1725 and 1630 cm<sup>-1</sup> belonging to the carbonyl group and carboxylate ion, respectively, showed that —OCH<sub>2</sub>CH[N(CH<sub>2</sub>COOH)<sub>2</sub>]COOH anchor groups had been successfully introduced.

ii) *Dowex A-1(Na<sup>+</sup>) chelating resin*: represents a commercially available resin of the styrene-divinylbenzene type with aminoacetic acid functional groups (Fluka, Switzerland).

### *Metal Ions Solutions*

Stock solutions of Cd(II)-, Cu(II)-, Ag- and Cr(VI)-ions were prepared from  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$  by their dissolution in 1% HCl or 1%  $\text{HNO}_3$ , so as to contain 100.0  $\mu\text{g}$  of metal ion per 1 ml. From these solutions some further dilutions as well as standards were prepared.

In order to alter the ionic strength of the solution, solid sodium-chloride was added. For pH-adjustments dilute  $\text{H}_2\text{SO}_4$  or KOH were utilized.

### *Apparatus*

The pH-measurements were performed with an Orion combined pH-electrode and an Orion digital 701 pH-meter (Orion, USA).

Flame atomic-absorption spectrophotometric determinations were performed using a Perkin-Elmer 305B atomic-absorption spectrophotometer and a Perkin-Elmer 56 recorder (Perkin-Elmer, USA), under standard conditions for cadmium determination:

light source type	hollow cathode lamp
wavelength (nm)	228.8
source current (mA)	8
slit regulation	4 (0.7 nm)
flame type	air (205.9 kPa)-acetylene(54,9 kPa)
burner type	single slot of 10.6 cm
instrumental regulations	INT 2, 3X

A laboratory centrifuge (Tehtnica, Yugoslavia) and shaker Kinetor m (Elektro-medica, Yugoslavia) were also used.

### *Procedure*

To determine the amount of cadmium sorbed, the indirect procedure was applied. The air equilibrated sorbent was weighed accurately to  $10^{-4}$  g and suspended in a definite volume of metal ion solution of known concentration and pH. The suspension was shaken for a definite time at room temperature. These experiments were performed in PVC-bottles of low sorption capacity<sup>27</sup>, previously rinsed with distilled water and dried in air. After the sorption was completed, the suspension was centrifuged for 15 minutes at 1500—2000 revolutions  $\cdot \text{min}^{-1}$  in glass centrifuge cuvettes of low affinity for cadmium<sup>27</sup>. The amount of cadmium remaining was determined by atomic-absorption spectrophotometric analysis of the transparent centrifugate.

Atomic-absorption measurements were always performed with respect to a standard solution of 0.7  $\mu\text{g}$  Cd  $\cdot \text{ml}^{-1}$  (pH = 6.4). Redistilled water was used as a blank.

## RESULTS AND DISCUSSION

### *i) Qualitative Evidence of Cd(II)-Ion Sorption*

The IR-spectrum of the Cd-ADA-cell chelate was recorded by the recommended procedure<sup>25,26</sup>. On comparison with the spectrum of chelating cellulose itself, some differences were found. Thus, the band at  $1725 \text{ cm}^{-1}$  assignable to the free carboxyl group of ADA-cell ( $\text{H}^+$ ) nearly completely disappeared, while the band at  $1630 \text{ cm}^{-1}$  assignable to the salified carboxyl group was strongly intensified as well as shifted to  $1616 \text{ cm}^{-1}$ . Similar effects have been observed by other authors<sup>28</sup>.

### ii) Influence of pH on Cd(II)-Ion Sorption

The results obtained (Figure 1) are in agreement with data from the literature<sup>14,19,29</sup> and show that metal ion sorption increases with increased pH at levels below those at which precipitation of the metal-hydroxy species takes place. The ion-exchange reaction is very slow in acid medium which is due to imino nitrogen protonation (e.g. in the case of Chelex 100, iminodiacetic acid cellulose and ADA-cell), while the increase of sorption by alkalization is the consequence of increased ionization of weakly acidic functional groups. Hydrolysis might explain the decrease of sorption efficiency at high pH-levels. These remarks are in accordance with the assumption that the basic step of cadmium sorption is deprotonation of functional groups with variation of pH<sup>19</sup>.

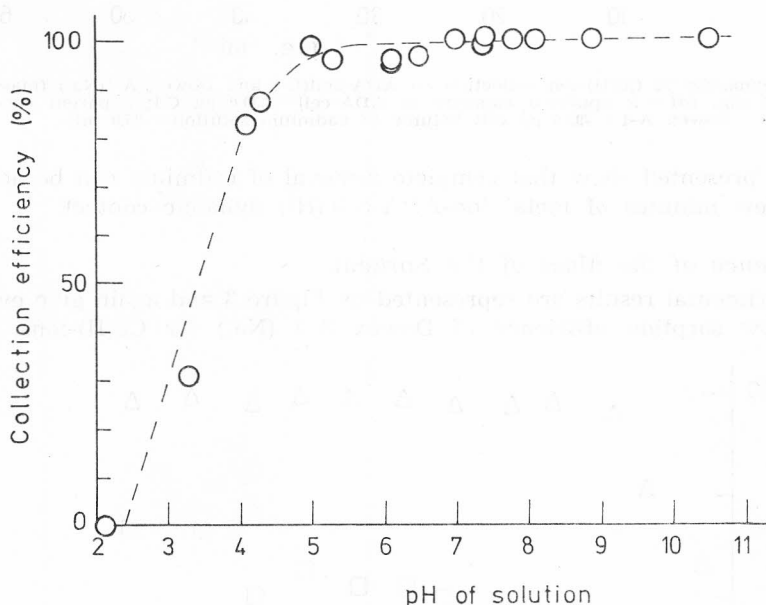


Figure 1. Dependence of Cd(II)-ion collection onto ADA-cell(H<sup>+</sup>), on pH of the solution (mass of ADA-cell = 10 mg; concentration of Cd = 0.81  $\mu\text{g ml}^{-1}$ ; volume of cadmium solution = 25.0 ml; time of dynamic contact = 60 min.)

From our experimental data as well as from the experiences of other authors<sup>14,15,18</sup> we have accepted pH = 7 as the optimal pH-level. It represents the pH of natural water as well as the pH-level at which cadmium is still present in its ionic form<sup>30</sup>.

### iii) Dynamics of Cd(II)-Ion Sorption

These investigations were performed by variation of dynamic contact time, ion concentration, sorbent type and amount of sorbent. The slow exchange as well as the effect of »latent« time of sorption on chelate resin which can be due to the swelling of the resin (Figure 2), were observed.

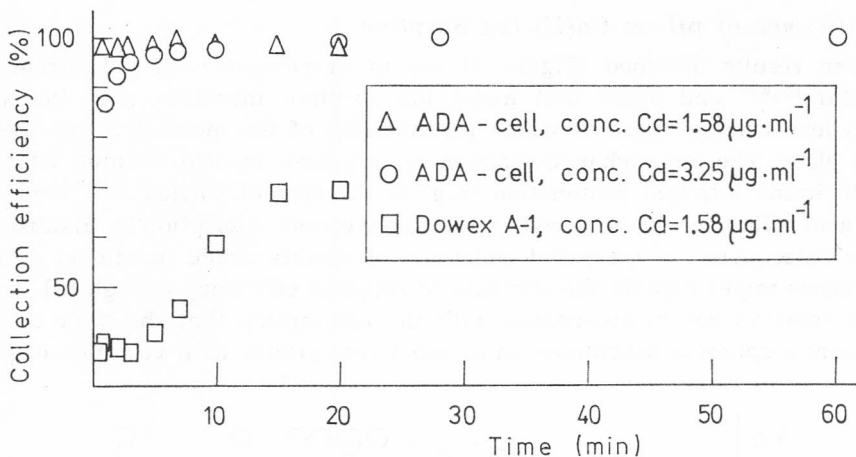


Figure 2. Dynamics of Cd(II)-ion collection on ADA-cell( $H^+$ ) and Dowex A-1( $Na^+$ ) (mass of the sorbent = 15 mg; pH = 7; apparent capacity of ADA-cell = 330.0  $\mu g$  Cd; apparent capacity of Dowex A-1 = 792.0  $\mu g$  Cd; volume of cadmium solution = 25.0 ml)

The data presented show that complete removal of cadmium can be achieved after a few minutes of metal ion-ADA-cell( $H^+$ ) dynamic contact.

#### iv) Influence of the Mass of the Sorbent

Experimental results are represented by Figure 3 and again give evidence of the low sorption efficiency of Dowex A-1 ( $Na^+$ ) for Cd(II)-ions. Better

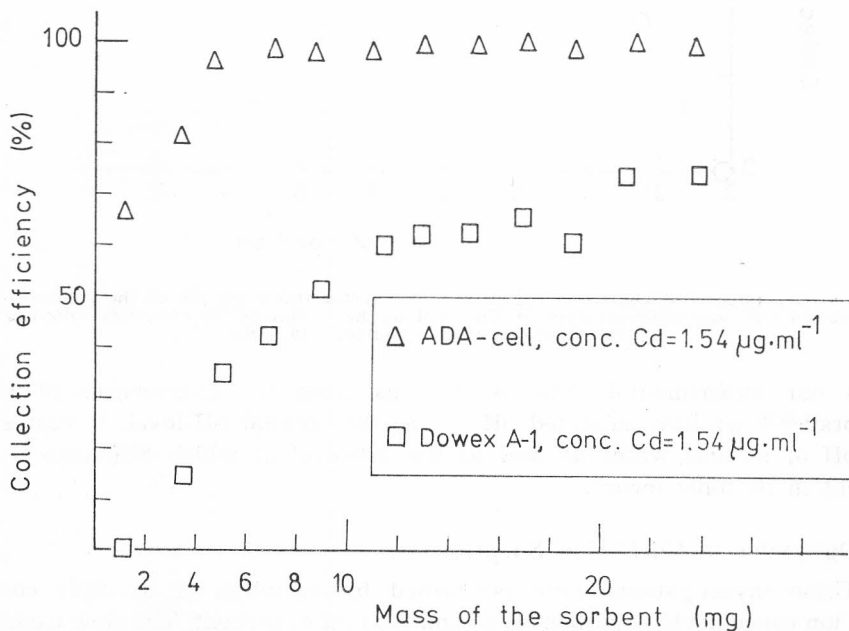


Figure 3. Dependence of Cd(II)-ion collection on the mass of the sorbent (pH = 7; apparent capacity of ADA-cell = 28.6–501.6  $\mu g$  Cd; apparent capacity of Dowex A-1 = 63.4–1261.9  $\mu g$  Cd; volume of cadmium solution = 25.0 ml; time of dynamic contact = 10 min.)

sorption characteristics of ADA-cell ( $H^+$ ) resulted from its larger active surface, wide capillary spaces, hydrophilicity with momentary swelling, in sum, from the great accessibility of reactive functional groups.

Chelating cellulose was regenerated by treatment with 0.1 M HCl. Regenerated cellulose partly lost its sorption potential; each further regeneration induced a greater decrease in sorption capacity. These effects could be assigned to decarboxylation of ADA-cell ( $H^+$ ). This is in accordance with the results of other authors<sup>31</sup>.

#### v) Influence of Cd(II)-Ion Concentration

From the results obtained sorption isotherms were plotted (Figure 4), with the linear region reaching some critical value defined by the amount of metal ion and sorbent, as well as by the sorbent capacity<sup>32</sup>.

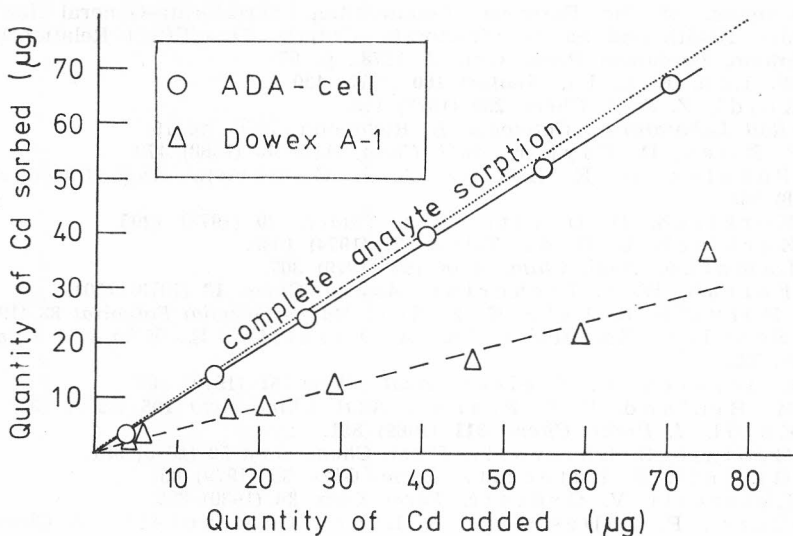


Figure 4. Sorption isotherms for Cd-ADA-cell and Cd-Dowex A-1 systems (mass of the sorbent = 5 mg; pH = 7; apparent capacity of ADA-cell = 110.0 µg Cd; apparent capacity of Dowex A-1 = 264.0 µg Cd; volume of cadmium solution = 25.0 ml; time of dynamic contact = 10 min.)

#### vi) Influence of Ionic Strength

Some examinations of Cd-solutions containing NaCl in a concentration range of up to 5.5 M were done. Greatly decreased sorption of cadmium onto ADA-cell ( $H^+$ ) but practically no change in the case of Dowex A-1 ( $Na^+$ ) were observed in the concentration range of up to 1M NaCl; above this value enhanced sorption was noticed in both cases. These effects are partly in agreement with the results of other authors<sup>29,32,33</sup>.

Sorption of Cd(II)-ion was also examined in the presence of Ag-, Cu(II)- and Cr(VI)-ions and indicated the nonselectivity of ADA-cell ( $H^+$ ). It should be emphasized that none of ions mentioned hinder cadmium sorption at a mass ratio of 1 : 1, but the completeness of the sorption is lost. This can be avoided by the use of larger amounts of the sorbent. The slightly depressive

action of added metal ions may be explained on the basis of increased ionic strength of the system and or the competition of Ag-, Cu(II)- and Cr(VI)-ions with Cd(II)-ion for reactive sites on the ADA-cell (H<sup>+</sup>) sorbent.

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## SAŽETAK

**Sakupljanje tragova kadmij(II)-iona na 2(3)-alanin-N,N-diocteno kiseloj celulozi**

*S. Luterotti i V. Grdinić*

2(3)-alanin-N,N-diocteno kiselja celuloza predstavlja neselektivni sorbens za niz metalnih iona. Ona se može uspješno primijeniti za kvantitativno sakupljanje tragova Cd(II)-iona iz vodenih otopina, te se u tom smislu pokazala boljim sorbentom od Dowex A-1(Na<sup>+</sup>) smole. Razmatrani su utjecaji pH, mase sorbensa, koncentracije metalnih iona, ionske jakosti i vremena kontakta.