Study Regarding the Presence of Zn(II) in Thermal Waters for Cosmetic Use

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The experimental investigations aimed to determine the optimal conditions for the process of zinc removal from thermal waters with the PUROLITE S920 ion exchange resin. It was determined the residual zinc concentration dependence on the amount of ion exchanger at different initial zinc concentrations in solution and different stirring times. The optimum conditions for achieving a residual concentration below 1 mg/L are: ion exchange rate 1.6 g/L, stirring time about 45 min. The PUROLITE S920 ion exchanger can be successfully used to remove very small amounts of zinc ions from the solution

Keywords: zinc, ion exchange resin, thermal water

Zinc is one of the most essential biometals. In nature, it is involved in multiple biological processes from protein biosynthesis, cell proliferation, to defense against free radical [1-9]. It participates in metabolism of lipids, proteins and carbohydrates. Zinc acts as a key structural component in many proteins; thereby it binds with nucleic acids with beneficial effect on active transport or transcription. Zinc plays metabolic functions as a co-enzymatic or activator of about 300 enzymes.

Zinc is an essential trace element for the human organism. It acts like cofactor for the metalloenzymes involved in many cellular processes.

Approximately 30% of zinc (Zn) in the diet is absorbed in the small intestine [1]. Of the absorbed Zn, 80% and 20% are bound to blood albumin and a 2-macroglobulin, respectively [2,3]. However, this protein-bound Zn comprises only 0.1% of the total body Zn, indicating that only this amount is replenished daily [4]. This serum Zn is delivered and stored in peripheral tissues including skeletal muscle (60%), bones (30%), liver (5%), and skin (5%) [5]. Thus, the skin is the third among tissues with the most abundance of Zn in the body.

In the human skin, Zn localizes more in the epidermis than in the dermis [6, 7]. The Zn concentration is 60 mg/g in the epidermis and 40 mg/g in the dermis [6]. The human epidermis consists of four layers (basal layer, stratum spinosum, stratum granulosum, and stratum corneum) that are categorized in accordance with the degree of differentiation and keratinization. Although the differential distribution of Zn in these four layers may be a clue to understand the functions of Zn in keratinocytes (KCs). Metallothioneins (MTs) are localized in actively dividing cells such as epidermal basal layer KCs, outer hair roots, and hair matrix in healthy human skin [8]. MTs are localized in the cytoplasm and have a characteristic aminoacid composition with cysteine-rich residues, allowing them to bind to heavy metals including Zn. Thereby, MTs contribute to the storage of Zn and are associated with an increased Zn concentration in tissues [9].

Zn deficiency is organized into two categories: acquired and inherited. The latter is known as acrodermatitis enteropathica (AE). Acquired Zn deficiency occasionally develops in individuals with malabsorption syndrome, total parenteral nutrition, chronic liver or renal dysfunction, or malignancy. Additionally, a low dietary intake of Zn is estimated to affect 17% of the world's population, especially in developing countries. Even in developed countries, some populations such as vegetarians, alcoholics, pregnant women, infants, and the elderly, are at risk of Zn deûciency [10-14].

Experimental part

The initial zinc concentration present in thermal waters for cosmetic use was determined by atomic absorption spectrophotometry using a VARIAN SpectrAA110 spectrophotometer [15-17].

The experimental investigations aimed to determine the optimal conditions for the process of zinc removal from thermal waters with the PUROLITE S920 ion exchange resin [17-21]

In a laboratory vessel was added 25 mL thermal water with zinc concentration determined in accordance with table 1 to which a certain amount of exchange ion was

No.	Thermal water	Amount of Zn, µg/l
1.	I	159.8
2.	II	79.6
3.	III	20.1
4.	IV	21.7

 Table 1

 INITIAL ZINC CONCENTRATION

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Structure of the polymer	Styren-divynilbenzene macroporous
Physic shape of the polymer	Spherical beads
Functional groups	Thyoronics
Ionic form	H ⁺
Total capacity	1.6 eq/L min
Humidity	48 - 54 %
Size of beads	0.3 – 1.2 mm
Density	700 – 730 g/L
Temperature max of work	60 °C
pH domain	1 – 9

The amount of ion	Residual zinc concentration, µg/L							
exchanger, g	15 min		30 min		45 min		60 min	
0.4	20.8		10.3		5.	9	3.	4
0.8	16.5		9.2		3.	6	2.	1
1.2	14.8		7.0		4.	3	2.	0
1.6	12.4		3.3		2.	0	1.	0
2.0	10.6		2.1	1.		5	0.9	
	Residual zinc concentration, µg/L					1		
The amount of ion	Res	sidu	al zinc co	ncent	ration,	µg/L		
The amount of ion exchanger, g	Res 15 min	sidu	ial zinc co 30 min	ncent 45	ration, min	μg/L 60) min	
The amount of ion exchanger, g 0.4	Res 15 min 18.5	sidu	ual zinc co 30 min 17.0	ncent 45	ration, min 3.8	μg/L 60) min 1.5	
The amount of ion exchanger, g 0.4 0.8	Res 15 min 18.5 14.6	sidu	ual zinc co 30 min 17.0 11.4	45	ration, min 3.8 5.0	μg/L 60) min 1.5 1.1	
The amount of ion exchanger, g 0.4 0.8 1.2	Res 15 min 18.5 14.6 9.3	sidu	al zinc co 30 min 17.0 11.4 7.7	45	ration, min 3.8 5.0 5.5	μg/L 60) min 1.5 1.1 1.0	
The amount of ion exchanger, g 0.4 0.8 1.2 1.6	Res 15 min 18.5 14.6 9.3 8.3	sidu	al zinc co 30 min 17.0 11.4 7.7 4.2	45	ration, min 3.8 5.0 5.5 2.1	μg/L 60) min 1.5 1.1 1.0 0.9	

Table 2 MAIN CHARACTERISTICS OF THE ION EXCHANGE RESIN PUROLITE S920

Table 3

RESIDUAL ZINC CONCENTRATION DEPENDENCE ON THE AMOUNT OF ION EXCHANGER AT DIFFERENT STIRRING TIMES, IN THERMAL WATER IV, WITH INITIAL CONCENTRATION 21.7 µgZn/L

Table 4RESIDUAL ZINC CONCENTRATIONDEPENDENCE ON THE AMOUNT OF IONEXCHANGER AT DIFFERENT STIRRING TIMES,IN THERMAL WATER III, WITH INITIALCONCENTRATION 20.1 µgZn/L

Table	5
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RESIDUAL ZINC CONCENTRATION DEPENDENCE ON THE AMOUNT OF ION EXCHANGER AT DIFFERENT STIRRING TIMES, IN THERMAL WATER II, WITH INITIAL CONCENTRATION 79.6 µgZn/L

					_		
The amount of ion	Residual zinc concentration, µg/L						
exchanger, g	15 min	30 min	45 min	60 min	1		
0.4	137.5	113.5	83.0	68.0	1		
0.8	120.5	52.0	50.2	49.5	1		
1.2	106.3	58.1	1.6	7.9	1		
1.6	26.1	5.0	1.6	1.3	1		
2.0	26.8	1.4	0.8	0.5	1		

30 min

95.3

79.2

67.0

4.3

3.1

Residual zinc concentration, µg/L

45 min

24.9

18.6

14.3

1.1

0.8

60 min

13.4

12.1

10.2

0.9

0.4

Table 6

RESIDUAL ZINC CONCENTRATION DEPENDENCE ON THE AMOUNT OF ION EXCHANGER AT DIFFERENT STIRRING IMES, IN THERMAL WATER I, WITH INITIAL CONCENTRATION 159.8 µgZn/L

added. The samples so prepared were subjected to stirring well-defined time period in a MTA Kutesz Type 609/A shaker. After that, the residual zinc concentration was determined by atomic absorption spectroscopy using a Varian Spectr AA110 spectrophotometer.

15 min

97.8

88.5

74.8

21.4

12.6

Results and discussions

The amount of ion

exchanger, g

0.4

0.8

1.2

1.6

2.0

Experimental data to determine the residual zinc concentration dependence on the amount of ion exchanger at different initial zinc concentrations in solution and different stirring times are shown in tables 3 to 6.

Conclusions

From the experimental data, the residual concentration of zinc in solutions decreases as the amount of ion exchanger increases for the same volume of solution and the same stirring time. With the same amount of ion exchanger, the zinc residual concentration in the solution decreases with increasing stirring time for all concentrations of the initial solutions.

Based on the experimental data, the optimal conditions of the zinc elimination process with the PUROLITE S920 ion exchanger were determined. Regardless of the initial concentration of zinc in solutions, the optimum conditions for achieving a residual concentration below 1 mg/L are: ion exchange rate 1.6 g/L, stirring time about 45 min.

The PUROLITE S920 ion exchanger can be successfully used to remove very small amounts of zinc ions from the solution

References

1. MAILLOUX, R. J., YUMVIHOZE, E., CHAN H. M., Chemico-Biological Interactions, **239**, 2015, p. 46 2. BELYAEVAA E. A., KOROTKOVA S. M., SARIS N.E., Journal of Trace Elements in Medicine and Biology, **25S**, 2011, p. S63

3. HU X.F., LAIRD B.D., CHAN H.M., Environmental Research, 152, 2017, p.470

4. LI, G., SHEN, B., LU F., Chemical Engineering Journal, **273**, 2015, p. 446

5. HA, E., BASU, N., BOSE-O'REILLY, S., DOREA, J., MCSORLEY, E., SAKAMOTO, M., CHAN, H.M., Environmental Research, **152**, 2017, p.419

6. TAMÁS, L., ZELINOVÁ, V., Journal of Plant Physiology, **209**, 2017, p.68

7.AHMAD, I., MOHMOOD, I., PACHECO, M., SANTOS, M. A., DUARTE, A. C., PEREIRA, E., Chemosphere, **92**, 2013, p.1231

8. KARIMI, R., VACCHI-SUZZI, C., MELIKER, J. R., Environmental Research, **146**, 2016, p.100

9. LOHREN, H., BLAGOJEVIC, L., FITKAU, R., EBERT, F., SCHILDKNECHT, S., LEIST, M., SCHWERDTLE, T., Journal of Trace Elements in Medicine and Biology, **32**, 2015, p. 200

10. SYVERSENA, T., KAURB, P., Journal of Trace Elements in Medicine and Biology, **26**, 2012, p. 215

11. SUTA, L.M., VLASE, G., VLASE, T., SAVOIU-BALINT, G., OLARIU, T., BELU, I., LEDETI, A., MURARIU, M.S., STELEA, L., LEDETI, I., Rev.

Chim. (Bucharest), 67, no.1, 2016, p. 84

12. SUTA, L.M., VLASE, G., VLASE, T., OLARIU, T., LEDETI, I., BELU, I., IVAN, C., SARAU, C.A., SAVOIU-BALINT, G., STELEA, L., LEDETI, A., Rev. Chim. (Bucharest), **67**, no.1, 2016, p. 113

13. SAVOIU-BALINT, G., PETRUS, A., MIHAESCU, R., IONESCU, D., CITU, C.,

MARINCU, I., TOMA, C.C., Rev. Chim. (Bucharest), 66, no.6, 2015, p. 833

14. BORUGA, O., SAVOIU, G., HOGEA, E., HEGHES, A., LAZUR, E.V., Rev. Chim. (Bucharest), **66**, no.10, 2015, p. 1651

15. ANDONI, M., IOVI, A., NEGREA, P., NEGREA, A., CIOPEC, M., Rev. Chim. (Bucharest), **59**, no. 6, 2008, p. 653

16. ANDONI M., IOVI, A., NEGREA, P., LUPA L., NEGREA, A., CIOPEC, M., Rev. Chim. (Bucharest), **59**, no. 7, 2008, p.779

17. ANDONI, M., DRAGOMIRESCU, A., URSOIU, I., IOVI A., NEGREA P., LUPA L., NEGREA, A., CIOPEC, M., Rev. Chim. (Bucharest), **60**, no.4, 2009, p.424

18. POP, R., ANDONI, M., PAUSESCU, I., MEDELEANU, M., Rev. Chim. (Bucharest), **64**, no. 9, 2013, p. 942

19. POP R., ANDONI M., VAN STADEN J., PU^ ESCU I., MEDELEANU M., Dig. J. Nanomater. Biostruct., **8**, no. 4, 2013, p. 1739

20.POP, R ILICI, M., ANDONI, M., BERCEAN, V.N., MUNTEAN, C., VENTER, M.M., JULEAN, I., Acta Chim. Slov., **62**, no.1, 2015, p.8

21. SAVOIU BALINT, G., BORZA, C., CRISTESCU, C., ANDONI, M., SIMU, G. M., MALITA, D., MALITA, I., CHEVERESAN, A., Rev. Chim. (Bucharest), **62**, no. 6, 2011, p. 680

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