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THERMODYNAMIC STUDY OF THE BINDING OF LEAD BY PECTIN

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Abstract. *Thermodynamic and computerized equilibrium modeling studies demonstrate up to 75% reduction in the amount of lead complexed when used pectate. This finding is in good agreement with the clinical results on the content of lead in blood of children in the Bac Ziang city of Vietnam. The calculation of the diagram of repartition of lead containing species and the conditional constant of stability show that the complex of* Pb^{2+} *with pectin is more stable within the range of pH 5-7. The developed approach could be successfully used for estimation of the binding other toxic heavy metals with pectins for their eliminating from animal and human organisms.*

Keywords: *Blood of children, equilibrium modelling, lead, pectin, thermodynamics*

UDC: 615.9

Introduction

There are many published investigations suggesting pectic substances as efficient antidotes for heavy metal poisoning because of the insolubility of the compounds formed with a series of metals [1, 2, 3]. Thus, the toxic metal ions are complexed by pectins intensified their elimination from human organisms. Pectins are very stable under acidic conditions in a pH range from 2 - 4.5. [1]. At higher pH values, between 4.5 and 10, pectin chains are split by β-elimination. However, pectic acid and pectates are stable in this pH range because they lack any methyl ester groups. Still higher pHs lead to the saponification of pectin. It was proved that binding of Pb^{2+} to carboxyl groups does not depend on the esterification degree (ED) of pectin within ≤ 50%, in contrast to other bivalent cations and at a higher ED the values log β_{PbPECT} slightly decrease [4]. A still relatively high value of the stability constant of lead pectinates was found even at a high ED of pectin.

Ions Pb^{2+} are very firmly bound to carboxyl groups of pectin, what is evidenced by precipitation of a highly esterified pectin with Pb^{2+} ions Evidently, the removal of lead could be enhanced by increasing the ratio of sodium pectate to lead. If the ratio of sodium pectate was 1:1, some 10-fold greater amount of lead was found to be bound in the lumen of the intestinal segments as compared to controls; when the ratio was 3:1, the difference was almost 20-fold [4]. Complexation is also influenced by pH, ionic strength and the concentration and affinity of the other cations present [5]. The importance of pH on the binding of a series of heavy metals to pectin was proven by author [5] *in vitro* investigations. The highest complex formation constants are in range of pH 4-6, except for iron which occurs at around pH 7. In the case of Pb^{2+}, pectin considerably increases elimination in both animals and humans. The obtained results in [6, 7] showed significant decreases in blood Pb levels from 760 to 530 ng Pb per mL. Even with high ED, Pb ions form relatively stable complexes [8].

The aim of this paper is to study the complex formation of lead ions with pectins by computerized calculations of the conditional constant and reparation of formed complexes as a function of chemical composition of mixture and acidity of medium in order to determine the maximal stability of complex Pb^{2+} - pectin and the degree of removal of lead by complexation. The obtained results are compared with the data of clinical trial for the content of lead in blood of children in the Bac Ziang city in Vietnam, treated with pectins, obtained by Ukrainian coauthors of this paper.

Theoretical part

The protonation constants for pectins (L ≡ pectin, a monomer unit of the polymer chain), the hydrolysis constants of the lead ions, and the complex formation constants for the Me^{2+} - L species are generally given according to the equilibria of the following equations respectively (the charges for simplicity are omitted):

$$L + iH = H_iL, \qquad \beta_i \tag{1}$$

$$pM + qH_2O = M_p(OH)_q + qH, \qquad \beta_{pq} \tag{2}$$

$$iM + L + jH = M_iLH_j \qquad \beta_{ij} \tag{3}$$

The mass balance (MB) in these systems is described by the system of equations:

$$C_M^0 = \sum_{p=1}\sum_{q=0}[M_p(OH)_q] + \sum_{i=1}\sum_{j=0}[M_iLH_j] \tag{4}$$

$$C_L^0 = \sum_{i=0}[H_iL] + \sum_{i=1}\sum_{j=0}[M_iLH_j], \tag{5}$$

where C_M^0 and C_L^0 are the initial (analytical) concentrations of the metal ion and ligand respectively.

Solving the system of two MB equations (4)-(5), by using the corresponding equilibrium constants β_i, β_{pq} and β_{ij} , the equilibrium concentrations of all the species can be calculated by the typical methods [9, 10]. With these calculated data, one can plot the diagram of distribution of the Pb^{2+}-containing species versus pH ($f_{ij} = f(pH)$) at different initial compositions (C_M^0 and C_L^0) of the system. For this step, the molar fraction of each species is computed by the following equations:

$$f_{10} = \frac{[M]}{C_M^0},\ f_{pq} = \frac{[M_p(OH)_q]}{C_M^0},\ f_{ij} = \frac{[M_iLH_j]}{C_M^0}.\ \text{Obviously,}\ f_{10} + f_{pq} + f_{ij} = 1.$$

The percent of bonded (sequestered) Pb^{2+} is calculated as a sum of equilibrium concentrations of all the lead-containing species:

% of bonded Pb^{2+} = $100\% \cdot \sum_{i=1} \sum_{j=0} [Pb_i LH_j] \ / C_M^0$ (6)

In order to establish how the secondary (competitive) reactions (1) and (2) affect the stability of the complex of composition *PbL*, especially in function of pH, the conditional stability constant of the complex β_{PbL}^{cond} has been computed using the formula:

$$\beta_{PbL}^{cond} = \beta_{PbL} \frac{\alpha_{PbL}}{\alpha_{Pb}\alpha_L} \quad (7)$$

Here where α_{Pb}, α_L, and α_{PbL} are concentration coefficients that depend on the nature of the species and on the experimental conditions. According to the IUPAC, they must be called *parasitic reaction constants* [11]. These coefficients are calculated for the system (1)-(3) in the absence of polynuclear complexes (i=1) by the expressions:

$$\alpha_{PbL} = 1 + \sum_{j=1} \beta j [H]^j \ ; \ \alpha_{Pb} = 1 + \sum \sum \beta_{pq} [Pb]^{p-1} [OH]^q \ ; \ \alpha_L = 1 + \sum_{i=1} \beta_i [H]^i \ .$$

1. Results and Discussions

Values of the stability constant β_{PbL} of lead pectinate and the constant of protonation of pectin β_{HL} are taken from [12]. Fig. 1 shows the conditional constant of stability of the complex Pb^{2+} - *pectin* as a function of pH. Conditional stability constants of type (7) allow, from a theoretical standpoint, to treat complex formation equilibria (3) as if it were alone, to which other equilibria of any nature as (1) and (2) are superimposed. Using conditional constants permits simply and quickly to quantitatively forecast the course of complexes formation reactions that would occur in the experimental conditions. The complex Pb^{2+} - *pectin* is most stable within the region of pH 5-7. The complex is less stable for pH < 5 due to the concurrent reaction $PbL + H+ = HL + Pb^{2+}$, while for pH > 7 the more stable hydroxocomplexes are formed.

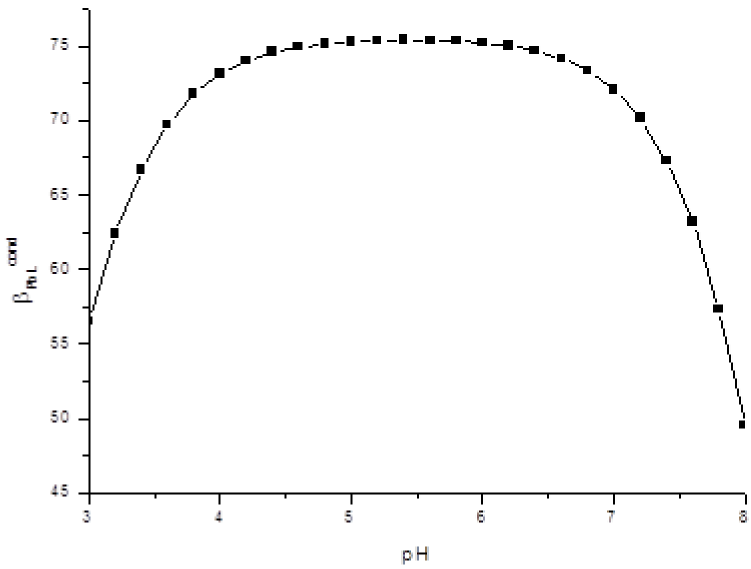

Figure 1. Conditional constant of stability of the complex Pb^{2+} - *pectin* versus pH.

From Fig. 2 one can observe that lead ions are bond to pectate even at relatively low pH of solution (pH ≈ 3). In addition, the diagram shows that the complex of Pb^{2+} with pectin is the most stable within the range of pH 5-7. At pH < 5 this complex is less stable because of concurrent reaction of ligand protonation (Eq.(1)), while at pH > 7 the stability of the complex decreases due to formation of stable hydroxocomplexes (see Eq. (2)) according to the following reaction schemes:

$$PbL + H_2O = PbOH^+ + H^+$$
$$3PbL^+ + 4H_2O = Pb_3(OH)_4^{2+} + 3L^- + 4H^+$$

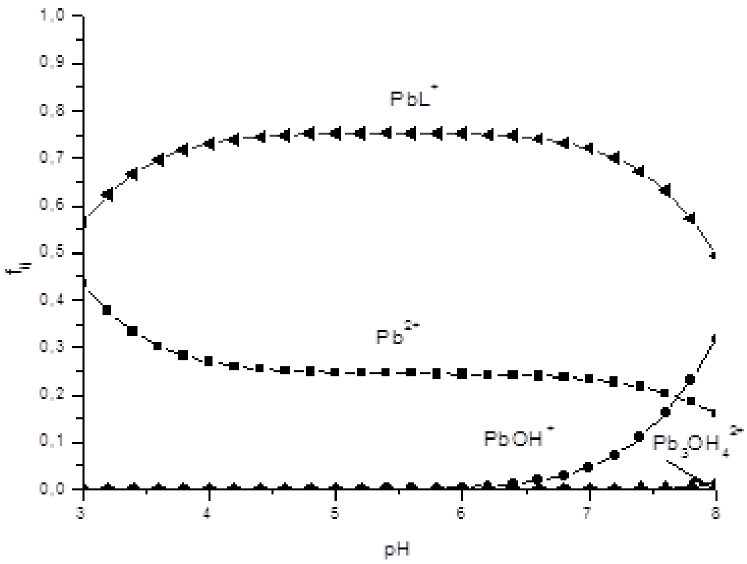

Figure 2. Diagram of repartition of the lead-containing species as a function of pH, $C^0_{Pb2+} = 1 \cdot 10^{-4}$ mol/L, $C^0_L = 1 \cdot 10^{-5}$ mol/L.

Our calculations of the degree of elimination of lead by pectin, % versus pH (Fig. 3) demonstrate up to 75% reduction in the amount of lead complexed when used pectate. This finding is in good agreement, for the same level of lead ion concentration, with the clinical results concerning the content of lead in blood of children in the Bac Ziang city of Vietnam (Table 1). Therefore, our developed approach could be successfully used as a reliable tool for assessment of the binding lead and other toxic heavy metal ions with pectins for their eliminating from animal and human organisms.

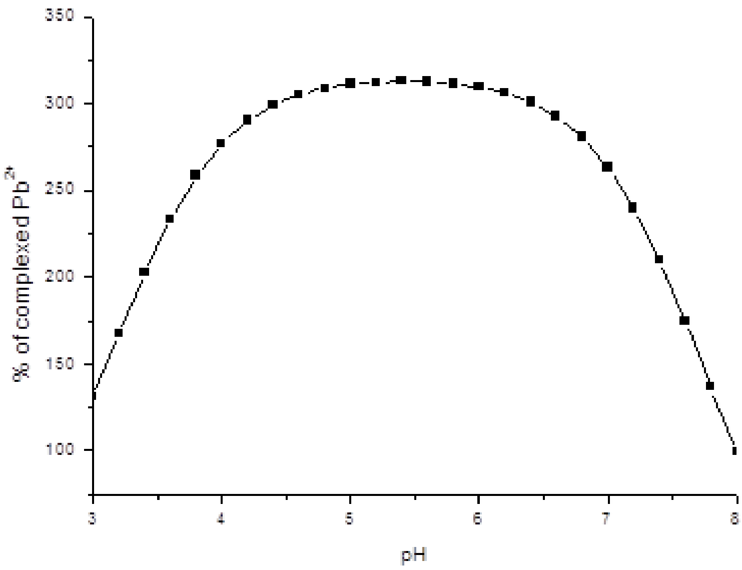

Figure 3. Degree of elimination of lead by pectin, % versus pH, $C^0_{Pb2+} = 1 \cdot 10^{-4}$ mol/L, $C^0_L = 1 \cdot 10^{-5}$ mol/L.

Table 1. Test results for the content of lead in blood of children in the Bac Ziang city of Vietnam

No	Name	Gender	Age	Pb^{2+} content in blood before taking pectin, ug/100 mL (May 2017)	Pb^{2+} content in blood after 3 months of taking pectin with breaks, ug/100 mL (October 2017)	% of reduction of Pb^{2+} content in blood
1	Patient 1	Male	6	13.43	4.84	63.96
2	Patient 2	Male	3	11.88	4.51	62.04
3	Patient 3	Female	6	13.52	3.48	74.26
4	Patient 4	Male	5	10.44	3.48	68.58
5	Patient 5	Female	8	11.81	4.25	64.01
6	Patient 6	Female	9	13.97	5.21	62.71
7	Patient 7	Female	6	16.47	6.28	61.87
8	Patient 8	Female	9	15.02	3.89	74.10
9	Patient 9	Female	8	16.51	5.65	65.78
10	Patient 10	Female	5	11.91	3.29	72.38
11	Patient 11	Male	2	12.79	3.58	72.01
12	Patient 12	Male	2	17.05	5.51	67.68
13	Patient 13	Male	6	12.6	4.06	67.78
14	Patient 14	Female	2	13.23	3.60	72.79
15	Patient 15	Female	4	12.40	3.51	71.69
16	Patient 16	Male	2	12.58	3.69	70.75

**(1 g/L = 1000 ug/mL).*

Conclusions

- Pectin is a suitable binding agent for lead as an antidote against poisoning of living organisms.
- The most suitable pH conditions for sequestration of lead ions have been identified using the computerized calculations of the conditional constant of complex formation and the diagram of distribution of lead-containing species versus pH. It has been established that the complex of Pb^{2+} with pectin is more stable within the range of pH 5-7.
- The ability of pectin to sequester lead have been defined using different modeling techniques and the experimental stability parameters of the complex species formed in the investigated systems. Modeling study demonstrate up to 75% reduction in the amount of lead complexed when used pectate. This finding is in good agreement with the clinical results concerning the content of lead in blood of children in the Bac Ziang city of Vietnam.
- The developed approach could be successfully used as a reliable tool for assessment of the binding other toxic heavy metal ions with pectins for their eliminating from animal and human organisms.
- The practical utilization of pectin in protection of people working with lead and its salts as well as children is the consumption of a diet rich in pectin. In the acute cases a direct use of sodium pectate would need.

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