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## Fabrication and Evaluation of Compound enterosorbents for Removing Excess Amounts of Metals in the Environment.

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**ABSTRACT**

The results of development and evaluation of sorption capacity of a number of combinations of biopolymer enter sorbents combined with an inorganic matrix. The possibility of using whey for modeling sorption processes occurring in the body. Proposed the most effective combination of contributing selective removal of an excess amount of accumulated metals from the body.
**Keywords:** enterosorbtion, metals, biopolymers, sorption capacity, whey.

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## INTRODUCTION

A resident of the modernity is exposed to the effects of various polymetallic anthropogenic sources of pollution. The danger of a constant exposure to metals from the environment caused by the long half-life of the body (5 years or more, if the absorption predominates over breeding), followed by a toxic effect on the whole body. In order to protect the body from the effects of polymetallic influence using the method of enterosorbtion – therapeutic step in order terminate effect of the toxins of various origins and their elimination from the body. Due to the simplicity and efficiency, the method of enter sorption actively used both in clinical practice in the treatment of various diseases and health programs of environmental remediation by the correction of micro elements. Accordingly, a drug used as enter sorbents, special requirements will vary depending on the specific goals and objectives of their scope. A consequence of this is the development of new enter sorbents, different structure and composition, exercising binding metals in the gastrointestinal tract by means of adsorption, ion exchange, complexation, and deriving them from the organism [1- 3].

Recent studies show that a combination of several enters sorbents with different mechanisms of sorption, can significantly increase the adsorption activity of the combination compared to monosorbents, to achieve selectivity of action and to provide the maximum therapeutic effect. The greatest selectivity and safety steps for the researchers note enter sorbents on the foundations of the biopolymers [3-5].Because the consumer market represented biopolymer enter sorbents of different classes, the aim of our study was to determine their relative effectiveness to create the most effective combinations. At the same time, it seems tons of interest and research of sorption capacity sorption materials which have appeared in the pharmaceutical market in recent years, as in the descriptions of these preparations typically contains only evaluate of the clinical efficacy, while the information on their sorption capacity is not given [4,5].

The aim of this study is a research for optimal combinations of biopolymer and mineral enterosorbents's, which are capable for the most effective and selective excretion of metals from the body. One of the objectives of the experiment is the problem of simulating the conditions of the internal environment of the human body, to assess the sorption capacity with respect to a number of different combinations of the metals inorganic and biopolymer sorbents. For modeling complex composition of the internal environment was used whey, which is a multi-component matrix consisting of water with dissolved minerals and organic fraction in it (proteins, carbohydrates, fats, and vitamins). Whey proteins are globular proteins, which are shown on 65% β-lacto globulin, 25% α-lactalbumin and 8% albumin. In [6, 7] turned out that the same multicomponent solution can adequately simulates complex composition of various fluids of the human body and the conditions of the internal environment.

As inorganic enter sorbents were used for creation combinations the most accessible and is often used to the moment: dioctahedralsmectite ("Spectra"), fumed silica ("Polysorbate").

As biopolymers polysaccharides were used, a unique feature which is the ability to absorb large amounts of water and in the presence of divalent metal captions to form gels. In the ability of non-starch polysaccharides to sorption of metal captions is gelatin mechanism [8].From biopolymers to create combinations were used:

- Polymer β- (1 → 4) -2-acetamido-2-deoxy-D-glucopyranose (enter sorbent "Chitosan") whose molecule contains a large number of free amino groups, which allows it to bind hydrogen ions and acquire excess positive charge.

- Polymer constricted from the residues of N-acetyl-β -D-glucosamine 1→4 bonds between them(chitin)andβ-glucans (β-1,3- and β-1,6) (enter sorbent "Microtone").

Model solutions of metal salts were prepared appropriate dilution of standard samples of metals in whey. Prepared two series solutions of salts of the most common in antropogenically loaded metals (Cd, Zn, Fe, Cu) in concentrations calculated 0,5 (a);1,0 (b);2,0 (c);3,0 (d) -5,0 (e) mg / L for each metal. The concentrations of metals in the solution is selected so that firstly, it was possible to fix the probable fluctuation of concentrations, and secondly, that these concentrations were close to physiological [9].

Selection of specific biopolymer enters sorbents due to their highest sorption capacity (Table. 1), compared with the other classes of biopolymer enter sorbents:

—Pectin (Citrus Pectin) – complex of colloid polysaccharides based on galacturonic acid side chains of ramose, arabinose, xylose and fructose;

—Alginate (Calcium alginate) - salts of agonic acid molecules which are presented polyatomic acid polymers;

—Microcrystalline cellulose (MCC) -product of hydrolytic cleavage of the polymer of D-glucose.

**Table 1: The effectiveness of sorption of metals enter sorbents different in terms of 1 g sorbent (μg/g)**

| Biopolymerenterosorbent | Cd | Fe | Cu | Zn |
|---|---|---|---|---|
| Citrus Pectin(a) | 3,7 | 3,3 | 2,9 | 13,4 |
| Citrus Pectin (b) | 7,4 | 6,3 | 6,6 | 18,2 |
| Citrus Pectin (c) | 14,5 | 13,7 | 14,2 | 28,2 |
| Citrus Pectin (d) | 21,1 | 18,9 | 22,4 | 38,1 |
| Citrus Pectin (e) | 33,4 | 32,7 | 41,2 | 62,1 |
| Calcium alginate (a) | 3,7 | -18,9 | -14,2 | 12,7 |
| Calcium alginate (b) | 7,5 | -16,9 | -10,7 | 17,6 |
| Calcium alginate (c) | 14,6 | -10,7 | -3,0 | 27,0 |
| Calcium alginate (d) | 21,2 | -5,5 | 3,9 | 36,3 |
| Calcium alginate (e) | 33,9 | 9,1 | 22,4 | 60,0 |
| Chitosan (a) | 3,8 | 5,9 | 3,4 | 14,5 |
| Chitosan (b) | 7,5 | 9,5 | 7,3 | 19,3 |
| Chitosan (c) | 15,1 | 17,1 | 15,7 | 30,2 |
| Chitosan (d) | 21,5 | 22,8 | 23,9 | 39,5 |
| Chitosan (e) | 64,8 | 68,5 | 81,6 | 121,4 |
| MCC (a) | 2,5 | 3,4 | 2,3 | 9,4 |
| MCC (b) | 5,1 | 6,2 | 5,1 | 13,0 |
| MCC (c) | 9,8 | 10,8 | 10,3 | 19,3 |
| MCC (d) | 14,2 | 14,8 | 16,2 | 25,4 |
| MCC (e) | 22,9 | 24,1 | 29,1 | 42,3 |
| Microtone (a) | 3,8 | 5,5 | 3,5 | 14,6 |
| Microtone (b) | 7,6 | 9,4 | 7,5 | 19,6 |
| Microtone (c) | 14,9 | 16,2 | 15,6 | 29,6 |
| Microtone (d) | 21,7 | 22,9 | 24,3 | 39,8 |
| Microtone (e) | 34,7 | 37,1 | 43,9 | 64,9 |

The results of the analysis, shown in Table 1, had revealed that "Chitosan" was 1.5-2 times more active than other enter sorbents related to all metals, preceded by. "Microtone". Calcium alginate has a high sorption capacity with respect to cadmium and zinc, and totally ineffective with respect to iron and copper. This could be explained by the content of these metals in the enter sorbent itself, so the concentration of iron and copper in the solution increases.

The combination of enter sorbents was based on a mix of pre-readied solutions of inorganic enter sorbents ("POLYSORB", "Spectra") and of a biopolymer, taken in proportion to the volume of a single application, recommended by the manufacturer. Thus, the sample totaled enter sorbents "POLYSORB" - 1 g, "Spectra" - 3 g, "Chitosan" - 0.45 g, "Microtone" - 0.5 g.

The following combinations of enter sorbents were considered: "Spectra" + "Chitosan» (№1), «Spectra" + "Microtone» (№2), «POLYSORB" + "Chitosan» (№3), «POLYSORB" + "Microtone" (№4), «Spectra" + "chitosan" + "Microtone» (№5) and "POLYSORB" + "chitosan" + "Microtone» (№6).

The combination was extracted by mixing the recommended daily doses of each enter sorbent. The uniformity (equability) of mixing was reached by preparing the aqueous suspensions of enter sorbents. The mixed suspension was filtered through "blue tape" filter, and then its precipitate was dried and used in the test.

In order to evaluate the sportive capacity of enter sorbents, the obtained combination samples were placed into a volumetric flask and filled by the 10-fold volume (50 ml) model solutions of the predetermined concentration. The concoction was blending for 1 hour and then filtered through cashless "blue tape" filter.
The residual concentration of metal salts in the solution is determined by atomic absorption spectrometry on the A Analyst 400 device. The result was converted to an absolute amount of adsorbed metal (Me), according to [10]:

$$Me = (C1 \times V1 - C2 \times V2) / m,$$

Where C1, C2 - concentration of the metal salt solution before and after the sorption μg/ ml;
V1, V2 - volumes of the solutions before and after the adsorption, ml;
m - Massenterosorbent (weighed portion), g.

The statistical manipulation of data was performed using the statistical package Statistical 6.0. Langmuir isotherm was built according to the obtained data. The formation of isotherms, reflecting the relationship between the amount of adsorbed metal and the equilibrium concentrations of metal salt in solution, was conducted in accordance with the act [11]. The sportive capacity of obtained enter sorbents combinations for different metals in whey was evaluated first of all. The results are shown in Table 2.

**Table 2: The sorption capacity of different metals combinations enter sorbents, in terms of 1 g sorbent (μg/g)**

| № combinations | the concentration of test solution, μg / ml | Cd | Zn | Fe | Cu |
|---|---|---|---|---|---|
| №1 | 0,5 | 5,9 | 5,9 | 2,8 | 6,1 |
| | 1,0 | 26,2 | 25,5 | 24,7 | 27,1 |
| | 1,5 | 39,1 | 38,9 | 38,5 | 38,0 |
| | 2,0 | 54,8 | 55,2 | 56,5 | 56,9 |
| №2 | 0,5 | 6,5 | 6,3 | 4,9 | 6,6 |
| | 1,0 | 12,2 | 12,0 | 10,8 | 12,9 |
| | 1,5 | 17,1 | 17,5 | 16,0 | 19,4 |
| | 2,0 | 24,3 | 24,3 | 24,4 | 25,9 |
| №3 | 0,5 | 4,2 | 4,8 | 6,5 | 6,5 |
| | 1,0 | 10,4 | 11,1 | 15,7 | 16,3 |
| | 1,5 | 18,9 | 15,9 | 24,3 | 24,7 |
| | 2,0 | 24,2 | 24,1 | 31,6 | 32,2 |
| №4 | 0,5 | 12,5 | 12,1 | 11,5 | 12,3 |
| | 1,0 | 26,1 | 25,2 | 21,6 | 25,6 |
| | 1,5 | 36,4 | 33,7 | 34,8 | 37,8 |
| | 2,0 | 34,5 | 33,5 | 47,6 | 49,4 |
| №5 | 0,5 | 5,0 | 4,8 | 4,2 | 5,1 |
| | 1,0 | 10,7 | 10,5 | 9,97 | 10,8 |
| | 1,5 | 15,8 | 16,0 | 15,2 | 16,1 |
| | 2,0 | 21,3 | 20,9 | 20,6 | 21,4 |
| №6 | 0,5 | 6,8 | 6,7 | 7,1 | 7,3 |
| | 1,0 | 18,9 | 18,7 | 17,8 | 19,1 |
| | 1,5 | 28,4 | 28,3 | 28,3 | 28,6 |
| | 2,0 | 37,3 | 37,0 | 37,4 | 37,4 |

For all investigated combinations the deviation from the classical adsorption isotherms for all four metals was found in a given deviation range of concentrations (Fig. 1, 2), with different feature of the isotherms.

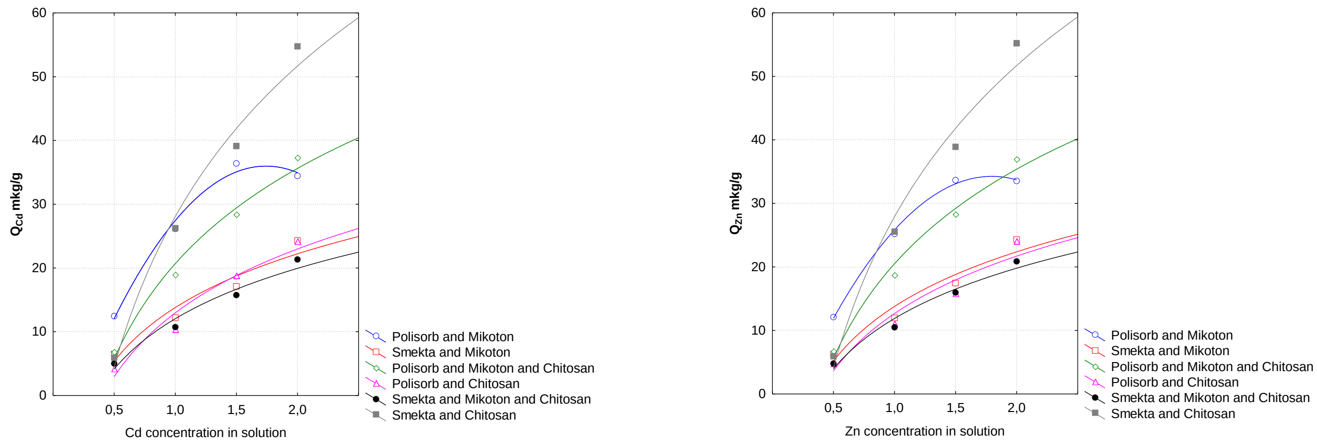


**Figure 1: The sorption capacity of the combinations of enter sorbents against Cd and Zn in the model environment.**

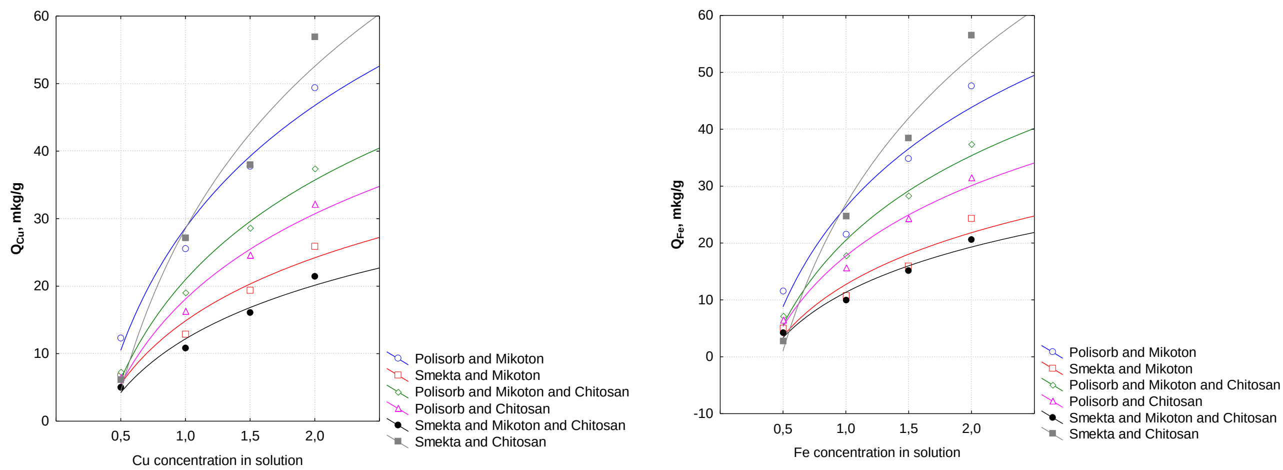


**Figure 2: The sorption capacity of the studied combinations of enters sorbents against Fe and Cu in the model environment.**

Linear plot is typical for sorption isotherms of Cd and Zn at the low concentrations, but at high concentrations the amount of adsorbed substances is not changed with increasing concentration, which corresponds to saturation of sorbent surface by molecules of adsorbed substance (Fig. 1). For isotherm shown in Fig. 2 there is a deviation from the classical Langmuir isotherm – which is almost directly proportional relationship between the concentration of Fe and Cu in solution and the amount of sorbet metals.

The combinations of "Spectra" + "Microtone" and "Spectra" + "Microtone" + "Chitosan" showed their low efficiency with respect to all of the metals. It should be noted that, contrary to expectations, the sorption capacity of the combination "Spectra" + "Microtone" + "Chitosan" was lower than that of the combination of "Spectra" + "Microtone." We assume that the interaction of enter sorbents "Microtone" and "Chitosan" with each other in the presence of "Spectra" is inactivated multimolecular layer, formed at the site of contact enter sorbents and inert with respect to metal captions. However, when replacing enters sorbent "Spectra" on other inorganic sorbent "POLYSORB", this combination shows better performance in relation to the studied metals.

The most significant effect of metal adsorption was obtained in blending the combination of "Spectra" фтв "Chitosan". The adsorption of metals by these enter sorbents was close to the lineal in all range of analyzed concentrations. Therefore, the combination of "Spectra" + "Chitosan" is most effective and can be used for selective removal from the body of all studied metals, in the case of concentrations exceeding the safe range of content. It can be assumed that the porous, leaf–like structure of the enter sorbent "Spectra" ensures the homogeneity of the mixture, distributing "Chitosan" uniformly throughout the volume of the combination, thereby increasing the adsorption surface and improving conditions for gelling.

It is also found that the combination of enter sorbents "POLYSORB MP" + "Microtone" absorbs Fe (sorption capacity of 47.6 μg / g) and Cu (sorption capacity of 49.4 μg / g) good enough and absorbs Cd and Zn significantly worse. Consequently, it could be used for the selective removal of these metals from the organism.

## CONCLUSION

Thus, the whey turned to be really effective indicator unit when preparing the model solutions. In whey milieu the sorption capacity of enter sorbents to metals varies. This experimental method of producing combinations of enter sorbents by blending the pre-readied mix of colloidal solutions of mineral sorbent and one or another biopolymer allows to obtain a homogeneous mixture at their optimum, with qualitatively new properties. And the use of whey as a background solution allowed bringing the experiment into proximity with the physiological conditions.

The received combinations of enter sorbents were of higher adsorption capacity in relation to the investigated metals as compared with mono- biopolymer enterorbentams. This fact allows us to hypothesize the idea of improving the efficiency of sorption of metals by creating a sorption layers with a higher sorption capacity by combining several sorbents (a combination of an inorganic porous structure of the sorbent and the molecular layer active ligands biopolymer) as compared with separate enter sorbents. With increasing concentration of the metal ions only two combinations (№1 and №4) are distinguished, which have a considerably higher sorption capacity. The research will allow to create and improve the adequacy assessment of the sorption capacity combinations of enter sorbents for selective removal of excess metal content of the human body.

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