TROCA IÔNICA DE TÁLIO (I) E CÉSIO NA DROGA “FERROCINUM” E EM UM MATERIAL COMPOSTO BASEADO EM “FERROCINUM”

THALLIUM (I) AND CAESIUM ION EXCHANGE ON THE “FERROCINUM” DRUG AND ON THE COMPOSITE MATERIAL BASED ON “FERROCINUM”

ОБМЕН ИОНОВ ТАЛЛИЯ (I) И ЦЕЗИЯ НА ПРЕПАРАТЕ «ФЕРРОЦИН» И КОМПОЗИЦИОННОМ МАТЕРИАЛЕ НА ЕГО ОСНОВЕ

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RESUMO

Foi determinado que o fármaco "Ferrocium" e o material compósito à base de ferrocium extraem com eficiência íons de tálio (I) e cézio. Foi apresentada a dependência da capacidade de troca de íons extraídos da em solução concentrada.

Palavras-chave: *Troca iônica, Tálio, Materiais compósitos.*

ABSTRACT

It was determined that the drug "Ferrocium" and the ferrocium-based composite material efficiently extract ions of thallium (I) and caesium. The dependence of the exchange capacity from the extracted ions concentration in solution is presented.

Keywords: *Ion Exchange, Thallium, Composite materials.*

АННОТАЦИЯ

Было установлено, что с помощью препаратов на основе композиционного материала "Ferrocium" и ferrocium можно эффективно извлекать ионы таллия (I) и цезия. В статье представлена зависимость обменной емкости из экстрагированной концентрации ионов в растворе.

Ключевые слова: *Ионный Обмен, Таллий, Композиционные Материалы*

INTRODUCTION

Currently, the use of synthetic organic ionites commonly called ion exchange resins far exceeds the scale of the inorganic ionites use. However comparing to organic ion exchangers the inorganic ones have their peculiar features such as a large variety of composition (and consequently a wide variety of selectivity types), more rigid structure, higher radiation and thermal stability. These features provide the inorganic ionites with a high interest of researchers (Nikol'skiy & Romankov (Eds), 1982; Clearfielda, 2000) and certain application areas. In particular, inorganic ion exchangers are used in medicine (Nikol'skiy & Romankov (Eds), 1982; Belinskaya, 2000; Pharmacopeia article, 1978) where they allow to efficiently remove toxicants from biological environments.

Ferrocyanides are the inorganic ion exchangers of high interest. Ferrocyanides are the substances whose anionic polymeric frame $[MFeII(CN)_6](4-Zm^+)$ (where M is Fe, Zn, Co, Ni, Cu, Cd, etc.; Zm^+ is the charge of a metal) is built of alternating $FeII$ and $M Zm^+$ situated in the lattice sites and connected with CN-bridges (Fig. 1). The medicinal product "Ferrocinum" is among ferrocyanides. "Ferrocinum" is suitable for the first aid and further treatment of intoxications with caesium-137 and rubidium-87 radioisotopes and the uranium fission products containing these isotopes (Romankov, 1982; Pharmacopeia article, 1978). It was actively used in the Chernobyl accident affected areas for the removal of radionuclides and heavy metals from organisms of people, pets and farm animals (Belinskaya, 2000).

Figure 1. The structure of Berlin blue (ferric ferrocyanide).

In June 2004, the head of the Laboratory of Ion Exchange of Saint Petersburg State University N. S. Grigorova handed over 8 kg of the "Ferrocinum" medicinal preparation to the Military Therapy Clinic of the Saint Petersburg Military Medical Academy to give a course of detoxication treatment for twenty-seven soldiers who were poisoned by thallium salts. The treatment was successful (Bobovitch, 2004).

The powdered forms of inorganic ion exchangers are suitable only for oral administration. Neither powder nor granules of irregular form are not suitable for the hemosorption and hemodialysis processes because they create too high impedance during dynamic use, injure the corpuscles of blood and other biological fluids, and are easily peptized (Tananaev *et al.*, 1971). To circumvent these shortcomings, one can use composite materials consisting of an inorganic ion exchanger and an organic polymeric binder (Kolodezeva, 2010a, 2010b). These materials are notable for their plasticity and can be formed as membranes, granules, particles of various sizes and shapes. Previous investigations allowed to establish the optimal ratio between the amounts of an ionite and a binder (Kolodezeva, 2010a, 2010b).

THE INVEATIGATION PURPOSE, OBJECTS, AND METHODS

The work purpose was to determine the correlation between the quantity of absorbed ions and ions in solution for the case of thallium and caesium ions being adsorbed on the drug "Ferrocinum" and a composite material. The latter consisted of "Ferrocinum" and the organic fluoropolymer "F-26" (polytetrafluoroethylene (PTFE)) which were taken in the ratio of 3:2 by weight. The investigations were carried out in static conditions: the weighted samples of the ion exchanger and the composite material were placed in contact with aqueous solutions of $TiNO_3$ and $CsCl$ having different concentrations; after a certain while the filtrate was separated from the solid phase. The content of metals ions was determined in the filtrate and the ion exchanger exchange capacity G (mEq/g) was calculated according to Equation 1.

$$G = (C_{init} - C^*) \cdot V / m \quad (Eq.1)$$

where C_{init} and C^* are the concentrations of Me^+ in the solution before and after contact with the ion exchanger correspondingly (mEq/cm^3); V is the solution volume (cm^3); m is the mass of the ion exchanger (g).

The distribution coefficient K_D (cm^3/g) was also calculated according to Eq. 2.

$$K_D = G / C^* \quad (Eq.2)$$

The "Ferrocium" weighted amount was 0.5 g and the composite material one was 0.83 g. In the latter case, the amount of the exchanger itself was also 0.5 g while the remainder (0.33 g) is accounted for the polymer. The contact time was 7 days (168 hours) as the previous investigations have shown that this period can be considered to be sufficient to achieve the steady state. The initial concentrations of salts ranged from 0.01 to 0.23 mEq/cm^3 .

The thallium ions concentration was determined by the atomic-emission analysis using the "AAS-1N" spectrophotometer and by the x-ray fluorescence analysis using the "EDX - 800P" spectrometer (purchased from "Shimadzu") in the Saint Petersburg State University Resource Centre "Methods of the substance composition analysis". The atomic-emission analysis method was used to determine the caesium concentration.

EXPERIMENTAL RESULTS AND DISCUSSION

Experiments performed with the drug "Ferrocium" showed that with the increase of the initial $TiNO_3$ solution concentration the resulting exchange capacity and the equilibrium Ti^+ concentration also increased. The dependence of G from S^* has a peculiar look and reaches rather high values (Fig. 2). However these values are consistent with the available literature data (Tananaev *et al.*, 1971). The results obtained for the contact of $CsCl$ solutions and the ionite were of a similar character but the higher values of capacity and distribution coefficients were achieved (Figs. 2 and 3).

Figure 2. The dependence of the exchange capacity from the Me^+ equilibrium concentration for "Ferrocium".

Figure 3. The dependence of the distribution coefficient from the Me^+ equilibrium concentration for "Ferrocium".

In the case of the composite material, the values of the exchange capacity and of the distribution coefficients are decreased comparing to "Ferrocium" but the type of the dependence is retained (Figs. 4 and 5). The absorption of thallium ions is significantly reduced (especially in the area of relatively high concentrations) while the absorption of caesium ions reduces considerably less. The obtained capacity values in the case of caesium ion for the initial "Ferrocium" ionite and for the ferrocium-based composite are often comparable (Figs. 6 and 7).

Figure 4. The dependence of the exchange capacity from the Me^+ equilibrium concentration for the composite material.

Figure 5. The dependence of the distribution coefficient from the Me^+ equilibrium concentration for the composite material.

It is worth mentioning that in all the cases considered, the dependences of K_d from the equilibrium concentrations are of extreme character: initially they decline and then begin to increase.

Figure 6. The dependence of the exchange capacity from the Me^+ equilibrium concentration:

1 and 2 are Tl^+ and Cs^+ absorbed on "Ferrocium"; 3 and 4 are Tl^+ and Cs^+ absorbed on the composite material.

Figure 7. The dependence of the distribution coefficient from the Me^+ equilibrium concentration: 1 and 2 are Tl^+ and Cs^+ absorbed on "Ferrocium"; 3 and 4 are Tl^+ and Cs^+ absorbed on the composite material.

The observed effects are apparently connected with the following two aspects.

1. The first aspect relates to the changes of the ion exchanger structure. The fluoropolymer "F-26" does not possess ion-exchange properties (Pachkovet al., 1970) but its presence in the composite hampers the movement of ions. In addition, "F-26" is more hydrophobic than "Ferrocium".

2. The second aspect relates to the size and the hydration degree of Tl^+ and Cs^+ ions. The crystallographic radius is 0.149 nm for Tl^+ and 0.165 nm for Cs^+ (Nikol'skiy(Ed), 1982) but thallium is more hydrated in aqueous solutions. As a consequence, it is the Tl^+ ion that must experience great difficulties when switching from "Ferrocium" to the composite material owing to both the steric reasons and the increasing hydrophobicity of the phase.

CONCLUSIONS

1. The composite material consisting of the inorganic ion exchanger "Ferrocium" and the organic fluoropolymer is able to absorb Tl^+ and Cs^+ ions from aqueous solutions of their salts.

2. The composite material shows in general a smaller exchange capacity than the original ion exchanger.

3. The capacity change is more pronounced for Tl^+ adsorption than for Cs^+ adsorption. Apparently this is connected with the ion exchanger structural features and with the state of both ions in solution.

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