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IONIC SILVER ZEOLITE, METHOD OF ITS PRODUCTION AND ITS USE FOR MEDICAL PURPOSES

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Abstract: The invention relates to ionic silver zeolite, which represents zeolite with particle size of $60 - 100 \, \mu \text{m}$ and size of pores of $3 - 4 \, \text{Å}$, containing silver ions from $0.03 \, \text{mg/g}$ up to $3 \, \text{mg/g}$.

The method of its production, in accordance with the invention, is as follows:

A) deionized water is saturated through electrolysis with silver ions by application of electricity with voltage of 8-10 V on silver electrodes for a duration of between 0,5 and 2 hours until silver ion concentration of between 0,03 mg/l and 3 mg/l is reached.

B) natural zeolite is subjected to grinding and sieving down to a fraction with particle size of $60-100~\mu m$. After that, it is rinsed with a 5%-solution of Sodium Chloride. A second rinsing through deionized water follows until the Chloride ions are removed. The so cleaned zeolite is thermally activated by heating it at 400°C - 450°C for 2-3 hours until the full release of the zeolite water.

C) Then follows the mixing of the zeolite 3-4 $^{\rm A}$ with the water saturated with ionic silver for a duration of 1 to 2 hours with intensive stirring at a ratio of silver water from 0,03 mg/l up to 3 mg/l: zeolite 1 g. The mixture filtered under vacuum with a 50 μ m filter. The drying is performed at 25 $^{\circ}$ C until the complete removal of moisture.

The ionic silver zeolite, in accordance with the invention, is intended for use in human and veterinary medicine as an antibacterial and antimicrobial agent. For internal use with maximum saturation of ionic silver from 0,03 mg/g up to 0,1 mg/g and for external use from 1 mg/g up to 3 mg/g, as one part of the zeolite pores remain free, which multiplies its drying effect and its enhances its ability for additional ion-exchange, by detaching its Sodium and Calcium ions, to gether with a sufficient quantity of silver ions.

Advantages of this method-inexpensive, as there is no application of high temperatures, no additional agents are used, which makes it environmentally friendly. The method provides the possibility to control the quantity of silver ions, adsorbed in the zeolite, and it also ensures the obtaining of a product, which is suitable for medical application, as it possesses the property to release the biocidal agent with a predetermined speed and achieve optimal biological availability in the treated organism.

Keywords: Zeolite, Ionic silver zeolite

INTRODUCTION

The application of metal ions as antibacterial and antimicrobial agents is well known. For example, silver ions, copper ions and zinc ions are used as antimicrobials. Usually, these metal ions are incorporated into a carrier system where the carrier releases the antimicrobial active ingredient in the environment in which it is placed.

In the Japanese patent application Nr. 1-172301, filed on 26.12.1987, a number of different compositions of mineral carrier are proposed for medical use, where alumosilicate zeolites are used as adsorbents in which the Na + ions are replaced by Ag +, Cu +, Zn² + or NH⁴ + cations.

Methods for preparing a carrier/antimicrobial agent system are known, including as a rule, the mixing of the crushed or milled carrier with a solution containing a metal ion possessing antimicrobial activity, after which the resulting particles are dried, for example [JP patent appl. Nr. 3275627], [WO 97/23594]. A disadvantage of these known methods is that the antimicrobial agent undergoes rapid desorption from the carrier, resulting in a decrease in antimicrobial activity for a short time, as well as the introduction of high levels of the antimicrobial agent into the respective region of the body.

Another type of methods for incorporating silver into a carrier material involves adding a reducing agent to the mixture of carrier and silver salt in order to achieve the reduction of the silver salt, for example [US 4396512, US 5824267]. None of these methods mentions the benefits of drying and/or heating the carrier and the silver salt prior to contact with the reducing agent.

In U.S. Pat. Nr. 6383273, a method is described that is intended to achieve the desired rate of release of the antimicrobial agent, the prolonged release and provision of an optimal concentration of the antimicrobial agent. The method includes (a) mixing the carrier with a biocidal agent,

- b) heating of the resulting mixture from 80 to 180°C; and
- c) contacting the mixture heated in step b) with a reducing agent to reduce at least a known portion of the first biocidal agent to obtain a first reduced biocidal/carrier composition;

A variant of the method is described wherein, after step c) follows the oxidation of at least a portion of the biocidal agent in the first reduced biocidal/carrier composition to yield an oxidized biocidal/carrier composition.

The method involves: step a) mixing a carrier, a binding substance containing colloidal metal oxide or colloidal non-metal oxide, a biocidal agent and an acid; b) separating a sufficient portion of the water to achieve binding of the binding substance to the carrier and/or biocidal agent;

- c) contacting the resulting composition containing a bound biocidal agent to the binding substance, with a reducing agent; and
- in a variant of the method, there follows step d) oxidation of the composition obtained in step c).

The described carriers include mixtures of oxides, including zeolite.

The described method is complex, energy-intensive, cost-ineffective in terms of the use of various reducing and oxidizing agents and other substances assisting the fulfilment of the operations.

The problems that need resolution are the creation of an ion-silver zeolite that contains a stable and optimal amount of silver ions in order to achieve quality healing, for example of wounds, especially extensive burn wounds, as well as for the treatment of infections of the gastrointestinal tract and detoxification of organisms, and also to develop a method for its preparation which is cost-efficient, easy to carry out, with the implementation of accessible technical equipment, and achieving the adsorption of silver ions without rapid desorption, which provides an optimum rate of silver ion release throughout the treated region and optimum bioavailability.

MAIN THESIS

The problem is resolved by the creation of ion-silver zeolite, characterized by particle size of 60-100 µm and pore size of 3 - 4 Å, containing silver ions from 0,03 mg/g to 3 mg/g.

The production method according to the invention consists of the following:

- A) Deionized water is saturated using electrolysis with silver ions by applying current with voltage of 8-10V on silver electrodes for 0,5 to 2 hours until reaching concentrations from 0,03 mg/l to 3 mg/l.
- B) natural zeolite is subjected to grinding and sieving to a fraction of $60\text{-}100~\mu m$. It is then washed with 5% sodium chloride solution. A second rinse with deionized water follows until the chloride ions are removed. The zeolite washed in such a way is then thermoactivated by heating at 400°C 450°C for 2-3 hours until the complete separation of the zeolite water.
- C) mixing follows of the so obtained zeolite with the silver-saturated water for 1 to 2 hours with vigorous stirring at a ratio of silver water 1l: zeolite 1 g. The mixture is filtered under vacuum through a 50 μ m filter. Drying is carried out at 25°C until the complete moisture removal.

The silver-ionized zeolite, in accordance with the invention, is intended for use in human and veterinary medicine as an antibacterial and antimicrobial agent. For internal use it should be with maximum ionic silver saturation from 0,03 mg/g to 0,1 mg/g and for external use from 1 mg/g to 3 mg/g, while some of the zeolite pores remain free, which multiplies its drying effect and the possibility for additional ion exchange separating its sodium or calcium ions, together with a sufficient amount of silver ions.

The advantages of the method are that it is economical, no high temperatures are applied, no additional agents are used, which makes it environmentally friendly, it allows for the control of the amount of silver ions adsorbed into the zeolite, provides a product that is suitable for use in medicine as having the ability to release the biocidal agent at a predetermined rate and to achieve optimum bioavailability in the treated organism.

With the use of silver-ionized zeolite, silver ions more quickly and effectively decontaminate and kill germs in the wound surface. Unlike colloidal silver, which in order to react has to be converted to an ionic state, in the silver-coated zeolite according to the invention, silver is adsorbed into an ionic state, ready to penetrate the wound surface, which is why the proposed method of saturation is more effective in terms of use of the resulting product. Such a silver ion content is achieved which is most effective for the treatment of wounds - extensive burn wounds, postoperative lesions, as well as oral administration for bacterial infections of the gastrointestinal tract.

EXAMPLES OF POSSIBLE APPLICATIONS Example 1.

The method for producing ionically silver-coated zeolite is as follows:

- A) Deionized water with electrical conductivity of $0.055 \mu S/cm$ is saturated electrolytically with silver ions by passing an electricity current of 8 volts between two silver electrodes immersed in water with 90% of their useful surface. The silver electrodes are with 99.99% purity of silver metal.
- B) The natural zeolite extracted from the ground deposit is subjected to milling and sieving to a fraction of $80~\mu m$. It is then washed with 5% sodium chloride solution. A second rinse with deionized water follows until the chloride ions are removed The zeolite washed in such a way is then thermoactivated by heating at 450° C for 2 hours until the complete separation of the zeolite water.
- C) Mixing follows of the zeolite with the ion-saturated water for 1 hour with vigorous stirring in a ratio of ionic silver water of 0.03~mg/l: zeolite-1g. The mixture is filtered under vacuum through a 50 μ m filter. Drying is carried out at 25°C until the complete removal of moisture. The ionized silver zeolite obtained by the method contains 0.03~mg/g silver ions as separate positive ions.

Example of application:

In the treatment of Acne: the face is powdered with silver-ionized zeolite 0,03 mg/g; the treatment starts by first washing the face with soap /or other washing agent/ after which the face is dried a little, but left moist. The powder is applied by powdering. It stays for 10 - 15 minutes, after which it is washed with water. The procedure is repeated 3 times a day in the morning, noon and evening until the acne starts to dry out within 2-3 days. For prophylactic purposes, the same procedure is performed every night.

Allergic skin reactions: In various manifestations of rashes, the affected areas are sprinkled with silver-ionized zeolite, if there is rash fluid, it is not dried first but the powder is sprinkled directly, if the rash is dry, then it is moistened without rubbing with a cotton swab moistened and then sprinkled with powder. This operation is repeated 3 times a day for 2-3 days.

Example 2

In another application of the method, silver-ionized zeolite with particle size of 80 μ m and pore sizes of 4 Å, containing 0,1 mg/g silver ions is obtained by means of:

- A) Deionized water with a electrical conductivity of $0,055~\mu\text{S/cm}$ is saturated electrolytically with silver ions by passing an electrical current of 9 volts between two silver electrodes immersed in water for 90% of their useful surface. The silver electrodes are with 99,99% purity of silver metal.
- B) The natural zeolite extracted from the ground deposit is milled and sieved to a fraction of 90 μ m. It is then washed with 5% sodium chloride solution. A second rinse with deionized water follows until the chloride ions are removed. The zeolite washed in such a way is then thermoactivated by heating at 450°C for 2 hours until the complete separation of the zeolite water.
- C) mixing follows of the zeolite with the ionic silver-saturated water for 1 hour with vigorous stirring at a ratio of ionic silver-saturated water 0.1 mg/l: zeolite-1g. The mixture is filtered under vacuum through a 50 μ m filter. Drying is carried out at 25°C until the complete removal of moisture.

Example application:

In the prevention of gastritis and ulcer of the stomach and duodenum: One teaspoon in the morning and evening in fasting state, 20-30 minutes before meals. Duration of administration from 1 to 3 months.

For influenza prevention in flu-carriers environment: A teaspoon of silver-ionized zeolite is placed into a teacup and then covered with water (low-mineral water, if possible), then it is drunk by holding it for a few seconds in the mouth, gargle on the throat is made, after which it is swallowed. The procedures are repeated in the morning and evening 20-30 minutes before eating.

Example 3

Silver-ionized zeolite, representing zeolite with particle size of 90 µm and pore size of 4 Å containing 1 mg/g silver ions is obtained by means of:

- A) Deionized water with electricity conductivity of $0.055~\mu\text{S/cm}$ is saturated electrolytically with silver ions by passing electrical current of 9 volts between two silver electrodes immersed in water for 90% of their useful surface. The silver electrodes are with 99,99% purity of silver metal.
- B) The natural zeolite extracted from the ground deposit is milled and sieved to a fraction of 90 μ m. It is then washed with 5% sodium chloride solution. A second rinse with deionized water follows until the chloride ions are removed. The zeolite washed in such a way is then thermoactivated by heating at 400°C for 2 hours until the complete separation of the zeolite water.
- C) mixing follows of the zeolite with the ionic silver-saturated water for 1 hour with vigorous stirring in a ratio of silver ionized-water 1 mg/l: zeolite-1g. The mixture is filtered under vacuum through a 50 μ m filter. Drying is carried out at 25°C until the complete removal of moisture.

Example application:

In the case of burn wounds: the burned area is disinfected with oxygen water, then sprinkled with powder from silver-ionized zeolite, a crust is formed, which after a few days falls on its own, then, if the wound has not healed, the washing with oxygen water is repeated as well as the sprinkling of the burned place with powder.

In the case of cut wounds, abrasions, scratches: the wound is washed with oxygen water and then sprinkled with powder, this is repeated in the morning and evening for several days, depending on the size and depth of the wound until it has healed.

In the treatment of Herpes: the site is cleaned with water, then in the morning, at noon and evening, it is sprinkled with silver-ion powder, which is left in place for 10 -15 minutes. If applied in a timely manner, the herpes wilts and is healed.

CONCLUSIONS

- 1. A method for producing of silver-ionized zeolite comprising the following steps:
- A) Deionized water with electricity conductivity of 0,055 to 1 μ S/cm is electrolytically saturated with silver ions by passing an electrical current of 8 to 10 V between two silver electrodes for 0,5 to 2 hours until a concentration of 0,03 mg/l to 3 mg/l is reached.
- B) natural zeolite undergoes grinding and sieving to a fraction of $60-100 \mu m$, then it is washed with 5% sodium chloride solution, followed by a second washing with deionized water until the chloride ions are removed, and then the washed zeolite is thermoactivated by heating at 400° C for 2 hours until the complete separation of the zeolite water.
- C) mixing follows of the 3 Å zeolite with the ionic silver-saturated water for 0,5 to 2 hours with vigorous stirring in a ratio of silver water 1 l: zeolite 1 g, the mixture is then filtered under vacuum though a 50 µm filter and dried at 25°C until the complete moisture removal.
- 2. Silver-ionized zeolite, characterized by having particle size of $60 100 \, \mu m$ and pore size of $3 4 \, \text{Å}$, and containing silver ions $0.03 \, \text{mg/g}$ to $3 \, \text{mg/g}$.

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