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SORPTION OF STRONTIUM ON THE COMPOSITE SORBENT BASED ON CELLULOSE AND HYDRATED ANTIMONY PENTOXIDE

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In this study cellulose-inorganic sorbents based on bleached cotton fibres and hydrated antimony pentoxide were prepared and used for strontium ions sorption from model aqueous solutions. The adsorption of strontium ions was determined by the radiotracer method using radioisotopes. A comparative analysis was made of sorption properties of the obtained sorption materials with different contents of hydrated antimony pentoxide towards strontium ions. The efficiency of strontium sorption increases with the increase in the modifier content in the composite cellulose-inorganic sorbents. The maximum efficiency of strontium sorption from solution (99 %) and the maximum distribution coefficient (1400 ml/g) correspond to the sorbents with the hydrated antimony pentoxide content 2.9 %. The effect of pH on the density of ions sorption on the cellulose-inorganic sorbent and the distribution coefficient was investigated. The experimentally determined density of ions sorption and distribution coefficient for strontium varied between 0.045 and 0.076 µmol/m² and between 100 and 1400 ml/g respectively depending on pH of model aqueous solutions. Chemical and structural properties were investigated by the low temperature nitrogen adsorption–desorption method, X-ray diffraction, infrared spectroscopy, differential thermal analysis. Surface area of the sorbents was determined by Brunauer, Emmett and Teller method. All composite cellulose-inorganic sorbents were characterized by a low specific surface area (1 m²/g). Hydrated antimony pentoxide characterized by amorphous structure and modification process does not affect cellulose crystallinity.

Keywords: cellulose-inorganic sorbent, antimony pentachloride, hydrated antimony pentoxide, strontium, removal efficiency

INTRODUCTION

Strontium is present in the environment as a decay product from nuclear power plants, and is also produced in the reprocessing of nuclear fuels, such as ⁸⁹Sr and ⁹⁰Sr with half-life of 51 and 29 years respectively. Strontium is chemically similar to calcium and tends to deposit in human body causing different illnesses. Removal of radioactive strontium from liquids ensures health security and environmental protection.

Variety of methods are applied to remove radioactive elements from liquid wastes. Nowadays, such methods as coagulation, extraction, precipitation, membrane filtration, etc. are widely used in order to purify contaminated water from different compounds. Adsorption is one of the most important techniques in separation and purification processes used in water conditioning and waste water industry for the removal of different pollutants. The importance of adsorption comes from the separation of trace amounts of elements from the large volume solutions. Because of its easy use and low cost, adsorption is the preferred method.

Different types of organic and inorganic materials have been proposed for the removal or concentration of strontium ions from aqueous solutions. These are activated carbon [1, 2], hydrous metal oxides [3] or titanates and silicotitanates [4, 5], hydroxyapatite [6], zeolites
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To increase selectivity of natural minerals towards radionuclides, several methods have been proposed. The most widely used are acid and alkali treatment, thermal and hydrothermal treatment, mechanical activation [12–14]. In the last few years it has been proposed to impregnate the carriers with specific inorganic compounds which show selectivity for certain ions. It is known that hydrated antimony pentoxide (HAP) is also characterized by high sorption capacity with the respect to strontium. For preparation of HAP, mainly hydrolysis of SbCl₅ is considered. It can be obtained either in an amorphous or in a crystalline form. HAP is highly dispersed substances making their application difficult connected under individual condition for radioactive water decontamination. In order to improve the operational performance, the immobilization of such sorption materials on different carriers can take place or binding materials can be used. It is appropriate to use fibrous materials as a carrier-matrix for HAP that allows us to improve kinetic and sorption characteristics. In this regard, bleached cotton fibres (BCF), which are widely used as the technologically suitable material for the production of the filter and membrane materials, could be also considered as a carrier of HAP. Another advantage of using plant materials as sorbents is a possibility of their utilization by the thermal degradation that can reduce the volume of solid wastes by a thousand times with the formation of ash residue [15].

The aim of this study is to prepare cellulose-inorganic sorbents based on the bleached cotton fibres and hydrated antimony pentoxide, to study structural characteristics and sorption of strontium ions from aqueous solutions as a function of modifier content and pH.

EXPERIMENTAL

BCF were used as a raw material and the content of the main components was as follows: cellulose – 95.5 %; lignin – 0.45 %; ash - 0.05 %; ethanol-benzene extractives, hot-water and 1 % NaOH solubility are absent. The chemical composition of the initial material was determined according to the corresponding TAPPI standards for the different components: T-222 for lignin, T-211 for ash, T-204 for ethanol-benzene extractives, T-257 for hot-water solubility, T-212 for 1 % NaOH solubility. The Kurschner-Hoffer method was used for cellulose determination: BCF was extracted with a mixture of nitric acid and ethanol (1:4) four times in a hot water bath and then filtered and dried. The content of cellulose was determined gravimetrically. BCF used for modification with the moisture content of 5 % were stored in desiccators for permanent humidity and chemical composition.

All chemicals of analytical grade were used. Deionised water from a Millipore-MilliQ system (ρ = 18 MΩ·cm) was also used throughout the experiments.

The preparation of the cellulose-inorganic sorbents was made by impregnation of cellulose material in deionised water during 10 min at 100 °C followed by the addition of SbCl₅ under continuous stirring. Antimony pentachloride consumption was 1–10 %. Then the solution was heated for 30 min at 100 °C. The ratio of solids to liquids was 10:1. The product was then separated from the solution by filtration, washed with deionised water at 80 °C to achieve a neutral medium, dehydrated and dried at 50 °C to a constant moisture content of 5–7 %.

The specific surface area of the obtained sample was determined by Brunauer, Emmett and Teller method. To determine parameters of sample surface porous structure, the low temperature nitrogen adsorption–desorption method was used. The measurements were made by means of an automatic adsorption analyzer of the ASAP 2405 type (Accelerated Surface Area and Porosimetry) by the Micromeritics Instruments, Co firm.

Infrared (IR) spectra of the samples in the range 4000–300 cm⁻¹ were performed in KBr pellets and were recorded on a spectrophotometer Specord M80 (Carl Zeiss). Preparation of cellulose samples for research was done by rubbing materials with KBr at the ratio 1:100.

X-ray diffraction (XRD) patterns of the samples were recorded at room temperature on a DRON-4-07 diffractometer using Ni-monochromated CuKα radiation. The crystallinity index of cellulose samples was calculated from the heights of the (200) peak (I₀₀₂, 2θ = 22.6°) and the intensity minimum between the (200) and (110) peaks (I₁₁₀, 2θ = 18°) following Segal method [16], Cᵢ (%):

\[ Cᵢ = \frac{1 - (Iᵢ / I₀₀₂)}{100}, \]  

ISSN 2079-1704. CPTS 2017. V. 8. N 4
where \( I_{am} \), \( I_{002} \) are the amorphous and crystalline materials respectively.

The differential thermal analysis (DTA) of the initial and modified samples was performed in air atmosphere using a Q-1500D device with digital recording of the thermography data, the heating rate of 10 °C/min. The HAP, BCF and BCF-HAP samples of 50 mg were used for the analysis. The samples were heated to 950 °C.

The adsorption of strontium ions was determined by the radiotracer method using radioisotopes. The initial concentration of the cations was \( 1 \times 10^{-6} \) mol/l. The NaCl solution of the concentrations 0.001 mol/l was used as a background one. The adsorption of Sr ions was determined by the radiotracer method using radioisotopes \(^{90}\)Sr. Adsorption also was studied as the function of pH. The radioactivity of electrolyte solution before and after adsorption was measured using a liquid scintillation counter LS5000D by Beckman. Based on the changes of radioactivity before and after adsorption, the removal efficiency \( S(\%) \), the distribution coefficient \( K_d \) (ml/g), the specific distribution coefficient \( S_{Kd} \) (ml/g) and the density of ions sorption on the cellulose-inorganic sorbent \( \Gamma \) (\( \mu \)mol/m\(^2\)) were calculated:

\[
S = \frac{C_i - C_e}{C_i} \cdot 100, \quad (2)
\]

\[
K_d = \frac{C_e - C_i}{C_i} \cdot \frac{V}{m_s}, \quad (3)
\]

\[
S_{Kd} = \frac{C_e - C_i}{C_i} \cdot \frac{V}{m_s}, \quad (4)
\]

\[
\Gamma = \frac{C_i \cdot V}{m \cdot S_w} \cdot \frac{1}{1 - \frac{N_e}{N_0}}, \quad (5)
\]

where \( C_i, C_e \) – the initial and equilibrium concentrations, respectively, mol/l; \( V \) – the solution volume, l; \( m_s \) and \( m_m \) – the masses of sorbent and modifier in the composite sorbent (HAP), respectively, g; \( S_w \) – the specific surface area, m\(^2\)/g; \( N_0 \) – the number of counts from the source taken up before adsorption and \( N_e \) is that during titration.

RESULTS AND DISCUSSION

During treatment of the BCF in aqueous solution, the hydrolysis SbCl\(_5\) with the formation of Sb\(_2\)O\(_5\)\(\times\)nH\(_2\)O and its sedimentation on the cellulose fibres took place. Thus the modification of initial organic material under such conditions with heating leads to the immobilization of inorganic phase on the cellulose surface with the formation of composite BCF-HAP sorbents. The effect of modifier consumption in the modification process on the modifier content in BCF-HAP is presented in Fig. 1. The values given in Fig. 1 are averaged over three replicate runs and the relative error does not exceed 10 %.

![Fig. 1. Effect of antimony pentachloride consumption in the modification process on the modifier content in the BCF-HAP sorbents](image)

Increasing the consumption of antimony pentachloride during modification leads to an increase in modifier content in the samples of obtained materials. As can be seen (Fig. 1), an increase in the modifier consumption to 8 % leads to the increasing content of HAP in the carrier bulk and its further increase does not affect the modifier content. According to the results of low-temperature nitrogen adsorption experiments, increasing of HAP in cellulose-inorganic sorbents does not influence on the specific surface area values. All obtained sorbents are characterized by a low specific surface area \( \sim 1 \) m\(^2\)/g.

The IR spectra of the modifier, initial and modified BCF are shown in Fig. 2. As follows from the obtained results, the IR spectrum of individual HAP is characterized by the bands about 766 and 552 cm\(^{-1}\) attributed to the Sb-O stretching modes of Sb-O-Sb and Sb-OH, respectively [17]. The peak at 1170 cm\(^{-1}\) indicates the presence of Sb-O-H bending vibration. The band at 1618 cm\(^{-1}\) is due to the bending vibration of molecular water. The band
at 3402 cm\(^{-1}\) indicates the presence of O-H stretching in the hydrogen bonds.

The broad absorption in the region 3000–3700 cm\(^{-1}\) of initial and modified BCF also indicate the presence of O-H stretching involved in hydrogen bonds, while the band at 1636 cm\(^{-1}\) is attributed to the bending vibration of H-O-H of absorbed water [18]. The adsorption band at 1428 cm\(^{-1}\) is assigned to symmetric CH\(_2\) bending vibrations. The bands at 1030 and 1060 cm\(^{-1}\) for both samples are assigned to C-O stretching in the secondary and primary alcohol groups of cellulose elementary units. The absorption band at 898 cm\(^{-1}\) is assigned to the C-O-C stretching at \(\beta\)-(1\(\rightarrow\)4)-glycosidic linkages. Analysis of the IR spectra of initial and modified materials with the HAP content 2.9 % points out no difference between the spectra because of the low modifier content.

As known commonly, the more crystalline a sorbent material is, the less sorption capacity it has for metal. The structure of initial HAP powder was investigated by X-ray diffraction and the pattern is presented in Fig. 3. Based on the XRD pattern, the HAP sample exhibits poor crystallinity.

The XRD patterns of initial and modified cellulose (Fig. 4) are characterized by strong reflections. A narrow intense peak at \(2\theta = 22.61^\circ\), including those of 14.64\(^\circ\) and 16.13\(^\circ\), and a pronounced reflection at 34.5\(^\circ\) are attributed to the diffraction planes of (002), (101), (10-1) and (040) which were believed to represent typical cellulose I crystal form [19, 20]. The same peaks are observed for BCF and BCF-HAP. The crystallinity of each sample is 75 %.

Sorption properties of the obtained cellulose-inorganic sorbents are shown in Fig. 5.

The study of sorption properties of the obtained materials towards strontium ions shows that the value of efficiency of strontium ion sorption is doubled and the distribution coefficient increases five times with the increasing HAP content in the bulk of BCF from 0.6 to 1.8 % (Fig. 5 a, b). The maximum efficiency of strontium sorption from solution 99 % and the maximum distribution coefficient 1400 ml/g correspond to BCF-HAP with the modifier content 2.9 %.

According to the literature data, the distribution coefficient of strontium on bentonite is 1400 ml/g [21], clinoptilolite – 850 ml/g, synthetic zeolites such as erionite, NaA, NaY and NaX are 283, 471, 220 and 520 ml/g respectively [22]. Comparing the values of the
distribution coefficient of strontium on BCF-HAP with the literature data, it is possible to argue about high effectiveness of the obtained sorbents. It is known that pure cellulosic and lignocellulosic materials show no affinity to radionuclides so the values of distribution coefficient of strontium can be calculated not for the mass of composite sorbent but on the mass of modifier in it [23], and the specific distribution coefficient has been calculated and is presented in Fig. 5 b. As can be seen, the value of specific distribution coefficient of strontium on HAP in the bulk of composite sorbents reaches $4.7 \times 10^4$ ml/g.

The pH of a solution is an important parameter that controls the adsorption process because of alteration of the solution composition and ionization of surface functional groups. Sorption of strontium ions on BCF-HAP was studied using the pH values from 3.5 to 7.5. Dependence of Sr$^{2+}$ ions adsorption density on pH is presented in Fig. 6 for the concentration $1 \times 10^{-6}$ mol/l of Sr$^{2+}$ ions and the BCF-HAP sample with the modifier content 2.9% was used.

Fig. 5. Sorption properties of composite sorbents towards strontium ions: (a) removal efficiency, (b) distribution coefficient

Fig. 6. Dependence of the density of Sr$^{2+}$ adsorption from the solution ($0.001$ mol/l NaCl + $1 \times 10^{-6}$ mol/l Sr$^{2+}$) on pH

Strontium ions belong to those which in the range from 3 to 11 can be present in the form of Sr$^{2+}$ and SrOH$^+$. Up to the pH value 10.5, the predominant form of strontium ions is Sr$^{2+}$. SrOH$^+$ increases only in the alkaline solution. The composition of the surface phase of cellulose-inorganic sorbents is not constant in the solution with the value pH in the range 3.5–10.5. The metal oxide surface can exist as negative, positive or neutral charge state in an aqueous solution depending on the pH value. Typically cation adsorption increases with the increasing pH.

As the experiment proceeded, it was found out that the sorption capability of BCF-HAP towards strontium ions essentially depends on pH. As can be seen from Fig. 6, adsorption of Sr$^{2+}$ ions in the pH function increases. A characteristic feature of strontium ions adsorption on BCF-HAP is a relatively slow decrease of strontium ions concentration from the solution due to adsorption, e.g. the concentration of Sr$^{2+}$ ions $1 \times 10^{-6}$ mol/l quickly decreases with the increasing pH from 3.5 to 6.3, with the further increase of pH up to 10.5, the adsorption value changes slowly.

The HAP, BCF and BCF-HAP samples were subjected to the DTA analysis and the results are
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illustrated in Fig. 7. The HAP powder loses about 18% mass in the heating range 50–800 °C and exhibits two exothermic effects that represent the partial dehydration (up to about 400 °C) with the following concurrent evolution of crystallization water and lattice oxygen, as well as with the resultant formation of Sb₂O₄ which can be seen from the XRD pattern of ash residue in Fig. 8.

Based on the obtained results, the TG curve for the BCF sample can be divided into two main parts representing the loss of water and thermal decomposition. The dehydration of BCF due to desorption of physically and chemically bound water occurs in the range 100–250 °C. A rapid depolymerisation of the cellulose chain proceeds only at the temperature higher than 300 °C. Oxidative thermal decomposition to CO and CO₂ as well as and formation of carbonaceous char also starts. The stage of BCF thermal decomposition characterized by the maximum mass loss (93 %) occurs in the temperature range of 300–500 °C. At the same time, two exothermic peaks at 365 and 480 °C are observed in the DTA. A thermolyzed cellulose leaves a small portion of the ash residue (less than 0.5 %) at 500 °C. The final temperature for dehydration and decomposition processes of BCF-HAP is lower than that of the initial BCF and the ash residue is nearly 8%.

The thermal destruction of composite BCF-HAP sorbents can be used for the effective disposal of spent materials. This process results in the formation of only inorganic (ash) residue

Fig. 7. DTA results of HAP (a), BCF (b), BCF-HAP (c)

Fig. 8. XRD pattern of ash residue after HAP DTA
CONCLUSIONS

Composite cellulose-inorganic sorbents based on the bleach cotton fibres and hydrated antimony pentoxide have been prepared. The strontium sorption investigation confirmed that the efficiency of strontium removal depends on the modifier content in the bulk of cellulose carrier. The maximum efficiency of strontium sorption from solution of BCF-HAP with the modifier content 2.9 %. The maximum pH for efficient sorption of strontium on the cellulose-inorganic sorbents is 6.5.

The structural properties of initial HAP and on the fibre surface were determined by the results of XRD analysis and IR spectroscopy.

ACKNOWLEDGEMENT

This research was supported by the “Fine Chemicals” Programme of the National Academy of Sciences of Ukraine (No. 0114U003532).

The XRD analysis indicated that BCF retained the cellulose I crystalline structure with a crystallinity 75 %. It was concluded that modification of BCF with HAP did not affect cellulose crystallinity. The DTA results showed that the decomposition temperature of composite sorbents was decreased.

As follows from the above cellulose-inorganic sorbents might be potentially applied in various fields, such as ecology, radiochemistry, and analytical chemistry.
Сорбция стронция на композитном сорбенте на основе целлюлозы и гидратированного пентаоксида сурьмы

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В этой работе были получены целлюлозно-неорганические сорбенты на основе беленных хлопковых волокон и гидратированного пентаоксида сурьмы для сорбции ионов стронция из модельных водных растворов. Адсорбцию ионов стронция изучали с помощью радиоактивных индикаторов с использованием радиоизотопов. Проведен сравнительный анализ сорбционных свойств полученных сорбционных материалов с различным содержанием гидратированного пентаоксида сурьмы относительно ионов стронция. Эффективность сорбции стронция растет с увеличением содержания модификатора в составе целлюлозно-неорганических сорбентов. Максимальная эффективность сорбции стронция из раствора (99 %) и максимальный коэффициент распределения (1400 мл/г) соответствуют сорбентам с содержанием гидратированного пентаоксида сурьмы 2.9 %. Исследовано влияние рН на плотность сорбции и коэффициент распределения. Экспериментально установлено, что плотность сорбции и коэффициент распределения ионов стронция варьируются от 0.045 до 0.076 мкмоль/м² и от 100 до 1400 мл/г в зависимости от рН модельных водных растворов. Химические и структурные свойства исследовали методом низкотемпературной адсорбции-десорбции азота, рентгеновской дифракции, инфракрасной спектроскопии, дифференциального термического анализа. Площадь поверхности сорбентов определяли методом Брунауэра, Эммета и Теллера. Все композитные целлюлозно-неорганические сорбенты характеризуются низкой удельной поверхностью (1 м²/г). Гидратированный пентаоксид сурьмы характеризуется аморфной структурой и процесс модификации не влияет на кристалличность целлюлозы.

Ключевые слова: целлюлозно-неорганический сорбент, пентахлорид сурьмы, гидратированный пентаоксид сурьмы, стронций, эффективность удаления

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Received 26.06.2017, accepted 30.10.2017