BIOSORBENTS IN SURFACE WATERS TREATMENT FROM RADIONUCLIDES

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Abstract
Method is presented of water purification from radionuclides using biosorbents.
Given method is based on natural watercourse hydrobiocenoses, immobilized on capron fibrous carrier of the "VIYA"type. For this purpose the carrier was placed into natural water flow with sufficient water aeration (Content of O_2 > 4,5 mg/L). Accumulated biomass represents a developed trophic chain including worms and mollusks. The mass of animalcular protein biofouling (dry weight) achieves 10g per kg of carrier. Periphyton developed on the carrier can absorb radionuclides from water and retain them. The activity of absorbed radionuclides is 3-5 orders greater than that of water. In laboratory conditions accumulate biomass provided 90,5% of deactivation. The proposed method differs favorably by its ecological compatibility. Besides, it doesn't require complicated expensive equipment for biosorbent production and enables decontamination of large volume of running waters.

Introduction
The technology of preliminary purification of natural waters using hydrobiocenoses immobilized on artificial (capron) fibrous carrier "VIYA" was developed in the A.V. Dumansky Institute of Colloid and Water Chemistry (1). Since the problem of radioactive ^{90}Sr removal with surface runoff out of the Chernobyl Exclusion Zone still persists, we were set the task to determine effectiveness of given method for natural water deactivation.
The fact is that extraction from water of Chernobyl-derived ^{90}Sr, whose major part is dissolved in the free cation form (up to 91-97%), is very complicated process. Up to 6% of average ^{90}Sr concentration in surface waters falls at conditionally dissolved organic matters and up to 10-12% - at organogenic colloids and suspension. At present given radionuclide is carried over during destruction of fallouts fuel matrixes and is washed out from upper soil layer while infiltration of rainfalls and floodwater are present. Annual ^{90}Sr transport by Prypiat River to the Kyiv reservoir fully depends on the annual precipitation value (dryness of the year) and spring flood probability. Since 1995 the years with high spring flood (1999) and high summer flood (1998) were distinctly distinguished by annual ^{90}Sr transport equaled 10,2 TBq and 6,37 TBq, respectively at average annual value of 4,27 TBq.

Strontium passed into soluble or exchange form is not practically retained by mineral constituent of soil. The Chernobyl Exclusion Zone is located in the wooded zone (Polessie-Woodland) in the absence of effective natural barriers for ^{90}Sr, which is caused by low calcium and other cations content in the exchange soil complex, that essentially retards neutralization of humus acids. Weak-acid reaction of soil water solutions at high humidity facilitates migration of metals and their carry over into surface waters. Since solutions are characterized by high acidity and buffering as well as high content of organic matter, deactivation of natural waters reagent methods is ineffective and using mineral sorbents becomes rather complicated.
Thus, biosorption methods of water decontamination can be the most acceptable for given conditions. In given paper we consider the fibrous carrier of "VIYA"-type as a basis for biosorbent. Each "VIYA" bundle consists of 160-170 fibers with specific surface about 550cm^2/g. Just due to great specific surface the fibrous nozzle is capable to accumulate large amount of microscopic hydrobionts responsible for water purification.

The studies were divided into two stages – laboratory and field ones. The results of studies are presented in given paper.
Prior to laboratory tests the fibrous carrier was placed into natural watercourse for 12-40 days to achieve full immobilization of microorganisms.

In summer 2002 the *full-scale test* of technique for biological sorption on hydrobiocenoses fixed in "VIYA"-type carriers was performed at the watercourses within the Chernobyl Exclusion Zone.
Three rows of carriers were mounted at different distance from one another along the communicating channels, of which the last one drained into the Prypiat River. The first and second row were mounted in the channel section covered with concrete, the third row was mounted at 45m down of the second one in the uncoated channel with sandy-gravel bottom. Carriers with periphytonic hydrobiocenoses accumulated previously in the Nivka River (Kyiv City) were used at the 2nd row.

Methods
Quantitative assessment of hydrobiocenoses immobilization was made through determination of protein content using Loury methods (in modification of N.S. Egorov) with preliminary hydrolysis of biofouling in the alkaline solution. Spectroscopic determination of protein in the hydrolysate showed presence of 622 mg of protein of microscopic organisms in 1g of biomass washed away from carrier.
Control over radionuclides accumulation on the hydrobiocenoses was realized by total β-activity and separately by ^{137}Cs and ^{90}Sr. The volumetric activity of ^{137}Cs and ^{90}Sr in the watercourse up and down of mounted "VIYA" rows was also determined. Discharge rate of channel directly before the second "VIYA" row was measured by hydrometric spinner while sampling of biosorbent and additionally 3-4 times a month – weekly.
During laboratory analyses of biosorption efficiency in *dynamic regime* model radioactive solutions in the column were run through biosorbent layer (23 $\cdot 10^{-2}$m) with velocity of 3,0.10^{-9}m/s.

Total β-activity of samples was measured by β-radiometer KRK 1-01A. To determine volumetric and specific activities of ^{137}Cs in dried biosorbent sample (direct measuring) and water (after evaporating) γ-spectrometers of two types were used: γ-spectrometer based on the analyzer AI-1024-97 and γ-spectrometer SBS-55 with semiconductor detectors DGDK-80B3 and DGDK-80B. ^{90}Sr content in biosorbent samples was measured with the help of selective β-spectrometer RUB-91 produced by "Ardani". Within the range of measured activities (2-2000Bq/kg) inaccuracy of measurements didn't exceed 35%. For determination of ^{90}Sr volumetric activity in water samples and external verification of analyses results liquid-scintillation α-β-spectrometer "Quantulus-1220^{TM}" was used. Given device enables measuring of ^{90}Sr activity in the range of 10^{-2} -10^{6}Bq/kg (l). The basic measurement inaccuracy for analyzed solutions was 4-5%. For narrow tint range (from transparent to brown) of water samples the calibration procedure was performed, which enabled measurements to be made without exceeding of given inaccuracy.

Results

Laboratory experiment In the *dynamic regime* using the biocenoses accumulated on the "VIYA"carrier as a biosorbent led to essential decrease of ^{137}Cs and ^{90}Sr in artificial solution. Initial water activity was $4{,}4 \cdot 10^8$ Bq/m^3 for ^{137}Cs and $4 \cdot 10^7$ Bq/m^3 for ^{90}Sr. Activity of decontaminated water (at specific consumption of biosorbent = 1,2kg/ m^3 of water) equaled $4{,}2 \cdot 10^7$ Bq/m^3 -for ^{137}Cs and $3{,}92 \cdot 10^6$ Bq/m^3 – for ^{90}Sr, with decontamination degree 90,5% and 90,2%, respectively (Table 1). At that, specific activity of spent sorbent equaled $1 \cdot 10^7$Bq/kg and $9 \cdot 10^5$ Bq/kg for ^{137}Cs and ^{90}Sr, respectively.

Carrying out of experiment in *circulation regime* resulted in higher degree of deactivation. Thus, at ^{137}Cs activity of 80 Bq/dm^3 in initial water, the subsequent decrease in activity was observed down to 2 Bq/dm^3 and less.

In the channels within the Chernobyl Exclusion Zone sampling of "VIYA" fibers were made in fixed time intervals: at first –in five days, further - in a week, in two weeks, in three weeks and once a month. At the same time the water and air temperature as well as discharge rate of the channel were measured, which allowed comparing the dynamics of radionuclides sorption by biomass with environmental conditions of hydrobiocenoses vital activity (Fig.1).

Table 1. Volumetric activity of solution after decontamination (A_{fin}), specific activity of spent biosorbent (C_{sb}), degree of water decontamination (DD) from ^{137}Cs and ^{90}Sr, %, obtained in laboratory conditions

Biomass accumula-ted on the carrier, g/kg	Period of biomass accumula-tion, days	^{137}Cs			^{90}Sr		
		$A_{fin,}$ Bq/m^3	C_{bs}, Bq/kg	DD, %	$A_{fin.,}$ Bq/m^3	C_{sb}, Bq/kg	DD, %
10	12	$0{,}84 \cdot 10^8$	$0{,}9 \cdot 10^7$	81,0	$0{,}84 \cdot 10^7$	$7{,}8 \cdot 10^5$	78,8
15	36	$0{,}42 \cdot 10^8$	$1{,}0 \cdot 10^7$	90,5	$0{,}39 \cdot 10^7$	$9{,}0 \cdot 10^5$	90,2
20	40	$0{,}21 \cdot 10^8$	$1{,}05 \cdot 10^7$	95,2	$0{,}30 \cdot 10^7$	$9{,}2 \cdot 10^5$	92,4

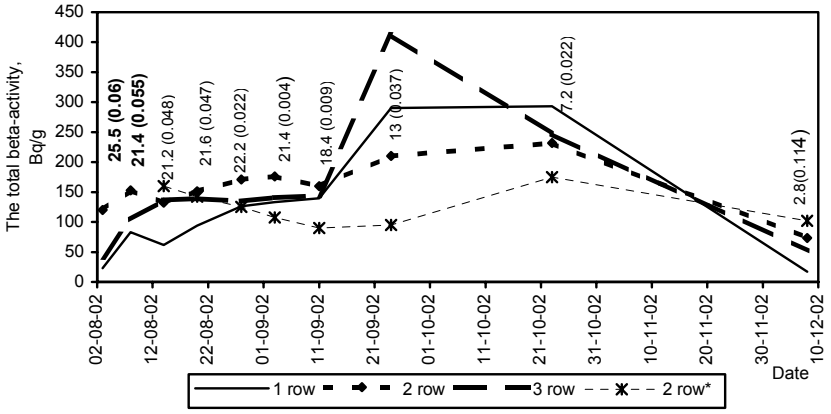

Fig.1. Changes of total β-activity of biosorbent in the course of full-scale test, 2002. Values above sampled points indicate: water temperature, ^oC (discharge rate of the channel, m^3/s); * - "VIYA" with previous biofouling.

Total β-activity of water sampled from the channel K-90A while mounting of "VIYA" carriers (end of July) was about 36Bq/l (19,77 Bq/l – in solution + 17,24 Bq/l –in suspension). At that time ^{90}Sr and ^{37}Cs activities in solutions accounted to 15Bq/l and 5,4 Bq/l, respectively. Water in the channels has hydrocarbonate-calcium chemical composition. The value of permanganate oxidation varried from 30 to 18 mg O/l (maximal allowable concentration is 4-5 mg O/l, according to Standards of Ukraine and EC-98) over the period of July-September.

At completion of testing (8.12.2002) maximal specific activity of ^{90}Sr and ^{137}Cs in autochtonous biofoulings was fixe at 580Bq/g and 700 Bq/g, respectively (2nd row). As compared to initial stage of test (August 3 and 8), by December ^{90}Sr and ^{137}Cs specific activity in biomass increased, namely: at the 1st row – by 5 and 7 times, at the 2nd row – by 3 and 2 times, respectively. At the 3rd row ^{90}Sr and ^{137}Cs specific activity remained practically unchanged over given period.

Down of the 3rd row decrease of ^{90}Sr volumetric activity in water was fixed, as compared to that sampled before the 1st and 2nd rows. Maximal degree of decontamination from ^{90}Sr was achieved at the flow rates of 10-20 l/s and equaled 50-54%

Maximal accumulation of ^{90}Sr by biocenoses occurred over the first 2-2,5 months when water temperature was no less than 13°C.

Discussion

Probably, since fibrous carrier has certain limit of biomass accumulation, after a time activity of "VIYA" samples with previously fixed relatively "pure" hydrobiocenoses in the Nivka River does not increase significantly (Fig.1). "VIYA" samples without previous biofouling accumulate autochtonous biocenoses having been already contaminated. At that, specific activity of biomass increases more intensively.

Although the absolute value of ^{137}Cs sorption on the carrier and in hydrobiocenoses is greater than that of ^{90}Sr, intensity of ^{90}Sr accumulation over the period of August-December was higher. Concentration of ^{90}Sr in water is higher than that of ^{137}Cs. Perhaps, this fact determines greater accumulation of ^{90}Sr in chitin of hydrobionts (also taking into account its bone-seeking features). So, accumulation of ^{90}Sr on the carrier increases as biomass grows and evolves. At the same time ^{137}Cs sorbed by suspended particles (suspension radioactivity is associated mainly with ^{137}Cs) is retained on "VIYA" fringe immediately after its dipping into the watercourse. However, retention of such particles by carrier is of short duration, because it depends more strongly on hydrodynamic conditions than ^{90}Sr sorption from solution by biomass.

Decrease or slowing down of ^{90}Sr and ^{137}Cs accumulation on the carriers at the 3rd row coincides with low intensity of biofouling. This can be explained, on the one hand- by interception of involved hydrobionts by adjacent 2nd row, on the other hand – by unfavorable conditions due to absence of channel coating, which results in increase of mineral suspension in water flow.

Total specific β-activity of biosorbent mainly associated with ^{90}Sr, practically does not depend on changes of water temperature in the range of 13-28°C. However, with coming of autumn cold weather and dropping of temperature below 10°C, significant decrease of biosorption intensity (in the 1st and 2nd row) and even decrease of total β-activity (in the 3rd row) is observed (Fig.1). Change of water discharge rate also doesn't exert any significant effect on the accumulation process. Explained negative correlation coefficients between accumulation and discharge rate (from –0,22 in the 3rd row to –0,52 –in the 2nd row) are somewhat understated because of prevailing tendency of biomass increase without regard to natural factors change.

Probably, maximal intensity of biofouling and radionuclides biosorption is possible at flow rate less than 30 l/s that imposes certain limits on application of given method of deactivation or requires conditions for separation and deceleration of flow. More actual and economically expedient is application of a large amount of "VIYA" carrier rows (up to 20-30) without changing the channel configuration.

For certain flow rates and radionuclides concentrations the necessary number of "VIYA" rows was calculated. For example, to achieve 85-90% deactivation degree of water in the watercourse with discharge rate of 0.06 – 0.12 m^3/s and volumetric activity of 9-15 Bq/dm^3, 20 "VIYA" rows are necessary.

The principle disadvantages of “VIYA” carriers as well as of the most biofilters are their certain dependence on water temperature and deactivation degree as well as concentration of carrier elements in decontaminating waters.

The advantages of described above method of radioactive water decontamination are as follows:

- given method provides rather high degree of water deactivation from ^{137}Cs and ^{90}Sr (up to 90%) due to high density of biofouling by local hydrobionts and high contact with water;
- given method is technologically easy to operate both in sorbent preparation and its further use in the course of water decontamination; moreover it provides for easy extraction of spent biosorbent from water and reuse of carrier after its regeneration if necessary;
- costs of biological sorbent production are rather small.

The above advantages ensure the possibility of effective application of described method for decontamination of radiocontaminated natural watercourses.

References

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