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МИРЗО УЛУҒБЕК НОМИДАГИ ЎЗБЕКИСТОН МИЛЛИЙ УНИВЕРСИТЕТИ ИЛМИЙ ЖУРНАЛИ

ЖУРНАЛ 1997 ЙИЛДАН ЧИҚА БОШЛАГАН

2021

3/2/1

Табиий фанлар

ТОШКЕНТ – 2021

Кимё

O‘ZBEKISTON MILLIY UNIVERSITETI XABARLARI, 2021, [3/1/1]
ISSN 2181-7324

KIMYO
www.uzmuxabarlari.uz
Natural sciences

УДК: 541.64:678.745.547.235

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IODINE-CONTAINING ANTIBACTERIAL FIBROUS MATERIALS BASED ON NITRON

Abstract
The iodine complexes based on the ion-changing polyacrylonitrile fibrous materials were obtained and their bactericidal properties were investigated. The kinetics of iodine sorption by anion-changing materials and its desorption from the obtained iodine complexes was investigated. It was shown that desorption of iodine is determined by the nature of the functional groups of the sorbent and iodine content in it. The possibility of using of the obtained iodine complexes of the anion-changing materials as filter-materials for disinfection of water-supply sources was established.
Key words: polyacrylonitrile, sorbent, iodine complexes, filter-materials, microorganisms, disinfection of water.

ЙОДСОДЕРЖАЩИЕ АНТИБАКТЕРИАЛЬНЫЕ ВОЛОКНИСТЫЕ МАТЕРИАЛЫ НА ОСНОВЕ НИТРОНА

Аннотация
Получены комплексы йода на основе ионообменных полиакрилонитрильных волокнистых материалов и исследованы их бактерицидные свойства. Исследована кинетика сорбции йода анионообменными материалами и его десорбции из полученных йодных комплексов. Показано, что десорбция йода определяется природой функциональных групп сорбента и содержанием в нем йода. Установлена возможность использования полученных йодных комплексов анионообменных материалов в качестве фильтрующих материалов для обеззараживания источников водоснабжения.
Ключевые слова: полиакрилонитрил, сорбент, йодные комплексы, фильтрующие материалы, микроорганизмы, обеззараживание воды.

НИТРОН АСОСИДА ЙОДНИ ЎЗ ИЧИГА ОЛГАН АНТИБАКТЕРИАЛ ТОЛАЛИ МАТЕРИАЛЛАР

Аннотация
Ион алмашинувчи полиакрилонитрил толали материаллар асосида йод комплекслари олинди ва уларнинг бактерицид хусусиятлари ўрганилди. Йодни анион алмашинувчи материаллар билан сорбциялаш ва олинган йод комплексларидан унинг десорбцияси кинетикаси ўрганилди. Йоднинг десорбцияси сорбентнинг функционал гуруҳлари ва ундаги йод миқдори билан белгиланади. Олинган анион алмашинувчи материалларнинг йод комплексларидан сув таъминоти манбаларини зарарсизлантириш учун филтр-материал сифатида фойдаланиш имконияти яратилди.
Калит сўзлар: полиакрилонитрил, сорбент, йод комплекслари, филтр-материаллар, микроорганизмлар, сувни зарарсизлантириш.

Introduction. The high degree of biological and chemical contamination of surface water and other sources of centralized water supply leads to the deterioration of the drinking water indicators and makes it unsafe. According to the World Healthcare Organization, a major part of all infectious diseases in the world are due to the usage of polluted water [1]. Untreated water, especially when it is consumed drinking water from natural reservoirs, becomes a carrier of infection, a source of severe massive illness. The water factor is one of the main reasons of the spread of cholera, hepatitis, typhoid fever, and other diseases. In addition, the quality of the of drinking water provided to the population depends on the state of the water supply sources, sanitary condition surface water bodies of underground sources, which are deteriorated as a result of technological pollution. An important problem in water treatment is the disinfection of the water from microorganisms, which cause dangerous diseases. Today various disinfectants such as chlorine, sodium hypochlorite are mainly applied for this purpose. However, most disinfectants while acting with organic substances dissolved in water, can form toxic substances that negatively affect the organism.

At the same time, it is known that linking bactericidal agents to polymers elongates the period of their actions and reduces their toxic properties. Complexes of iodine with polyvinylpyrrolidone (PVP) and polyvinyl alcohol are all-known antiseptic drugs. These complexes are water-soluble and are used like aqueous solutions or ointments in the medicine as antimicrobial disinfectants. Of particular interest is that strongly basic iodine-containing anion exchangers can be used as new polymeric bactericide materials intended for disinfection drinking water from microorganisms in portable stand-alone water purifiers [2]. For this purpose, iodine complexes were obtained by the reaction of the strongly basic anion exchanger AB-17-8 in chloride form with iodine solution in KI [3].

However, iodine-containing granular sorbents have several disadvantages, such as low specific surface, different pore volume and long-term diffusion of ions. Therefore, fibrous materials formed from the mixtures of fine-grained ion exchangers and polyacrylonitrile (PAN) are used for anion exchange [4]. Bactericidal activity of such materials is in the release of biologically active substances (BAS) from the polymer by the following scheme: $(BAS)_n \rightleftharpoons (BAS)_{n-1} + BAS$ where $(BAS)_n$ is an oligomeric bactericidal substrate; n is the number of its units.

One of the main properties of this system is the gradual release of BAS what gives a perspective for the design of the controlled release system where the BAS is slowly released over time so that concentration oscillations are negligible.

This work is aimed at the solving of rational usage of water issue, which is achieved in the application of new fibrous filter materials based on chemical resistant synthetic fibers. These fibrous sorbents have high porosity, sorption capacity and selectivity with respect to reagents. Obtained fibrous sorbents based on the polyacrylonitrile polymers have cation exchange, anion exchange and complexing abilities [5],[6]. The formation of complexes by the obtained sorbents with halogens [7] also will allow the development of bactericidal filter materials for the disinfection of drinking water from microorganisms which cause especially dangerous diseases in humans.

In this regard, we have studied the complex formation of synthesized sorbents with iodine. These sorbents were obtained by modification of the PAN with hexamethylenediamine (SMA-1), hydroxylamine (SMA-2) and hydrazine (SMA-3).

Experiment. Complexation of iodine with modified PAN was studied by the static method. Therefor the polymer material, which was preliminarily swollen in the KI solution, was placed in the iodine solution in 4% KI and the iodine concentration in the solution was measured after certain time intervals. The iodine concentration was determined by the photocolorimetric method at λ = 440 nm. Experimental studies were carried out to clarify the bactericidal properties of the fibers passing artificially infected microbes in the tap water through them. As microbes used E. coli, murine typhus salmonella and causative agent paratyphoid. Experimental studies of antimicrobial activity of the samples were performed at the Institute of Sanitation, Hygiene, and occupational diseases under MH RUz.

Results and discussion. Kinetic curves of the complex formation of iodine with the sorbents SMA-1, SMA-2 and SMA-3 are shown on the Figure 1, 2. Fig. 1 shows that the saturation of the sorbent with iodine in the initial steps is achieved very fast, then the process slows down and an asymptote is observed. Moreover, the capacity of sorbents for I2 does not depend only on the time of contact, but also on the nature of functional groups in the sorbent, as well as on the temperature of the process (Fig. 2). Iodine binding mechanism as shown in works [8],[9], proceeds due to ion exchange, I- to I3-. Iodine-containing fiber SMA-2 (23% of iodine) was used as a bactericidal fiber.

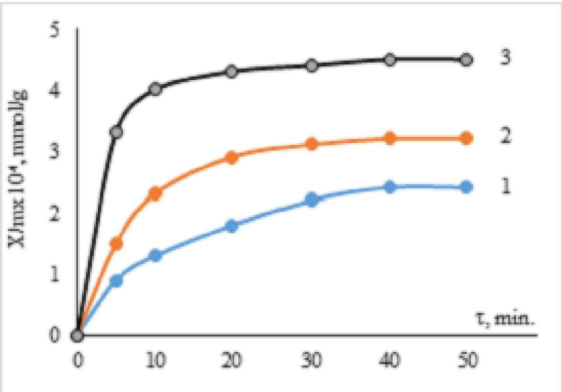

Fig. 1. Kinetic curves of the iodine sorption by the fibrous sorbents SMA-3 (1), SMA-1 (2) and SMA-2 (3) at the temperature 400C. [J2]=25 mg-equiv/l.

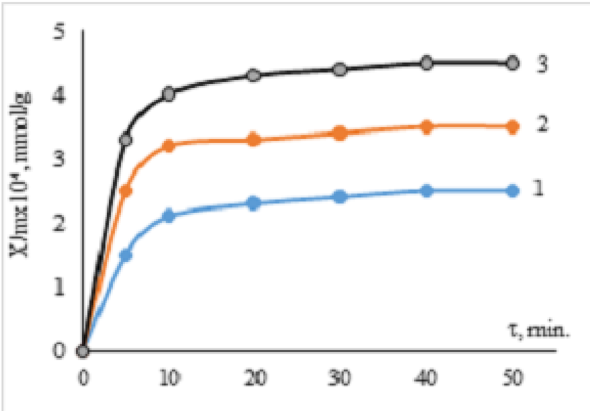

Fig. 2. Iodine sorption by SMA-2 sorbent at temperatures 200C (1), 300C (2) and 400C (3). [J2]=25 mg-equiv/l.

It is known that for the manifestation of bactericidal properties of iodine-containing materials are necessary gradual release of iodine into the disinfected object [10],[11],[12]. Therefore, to clarify the possibilities of using fibrous materials to create bactericidal medical dressings, the desorption of iodine from obtained polymer complexes was studied with distilled water under dynamic conditions. The iodine content in the solution was analyzed by the spectrophotometric method. Fig. 3 shows the dependence of the concentration of leached iodine from the volume of the passed eluate from iodine sorbent complexes. The transmission speed of water through the sorbent was 25-30 ml per minute.

As it is seen in the Fig. 3, with continuous transmission of the distilled water through the layer of iodine-containing fibrous materials SMA-1 and SMA-2 a gradual decrease in the iodine concentration until its remaining constant in water is observed and after passing 40 liters of water. In the case of iodine desorption from the SMA-3 destruction of unstable polyiodide anions is observed accompanied by the release of the increased amount of iodine.

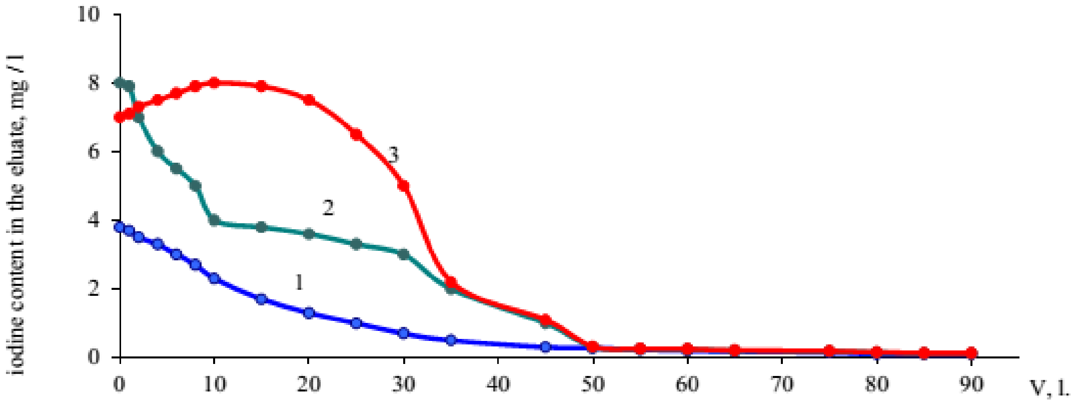

Fig. 3. Iodine concentration in distilled water vs volume of the water passed through the layer of sorbents SMA-1 (1), SMA-2 (2) and SMA-3 (3). Iodine content in the sorbents is 3 mg-equiv/g, diameter of the layer 2 cm, fiber mass 5 g, layer height 15 cm, T=250C.

A characteristic feature of the release of iodine from materials is a jump in iodine concentration after a break in water supply (fig. 4).

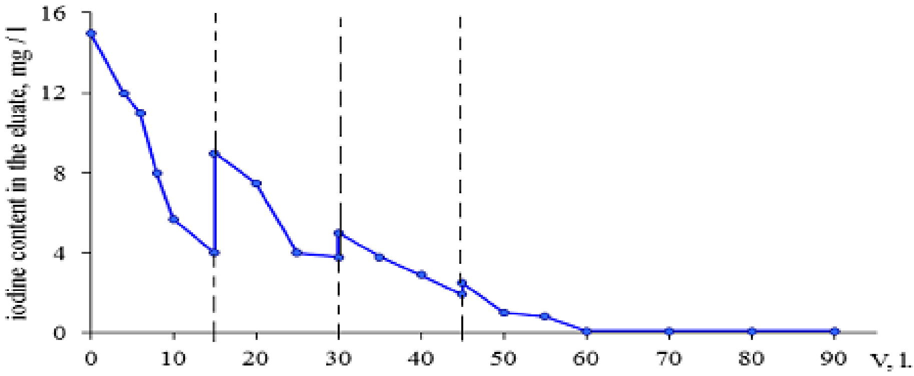

Fig. 4. Iodine concentration in distilled water vs volume of the water passed through the layer of the SMA-3 iodine-containing sorbent with 10-12 h elution breaks.

The maxima on the curves correspond to the samples taken after a 12-hour elution break. Apparently, the water in the column, when the elution is stopped for 12 hours, continues to desorb iodine in static conditions, which leads to an increase in the concentration of iodine in the eluate taken for the sample immediately after elution.

In the UV spectra of the eluates obtained after passing water through the iodide complex with high content of iodine (3 mg-eq/g) two peaks at 360 and 208 nm were observed corresponding to molecular iodine and iodide-ions, and at low iodine content (1mEq/g) one maximum at 208 nm was observed, which indicates the presence of iodide-ions, apparently formed during the hydrolysis of leached molecular iodine.

From the data shown in Fig. 4 and 5 it is seen that the amount of desorbed iodine and the rate of the iodine release highly depends on the nature of functional groups of the initial anion exchangers used for complexation. In the case of SMA-1, which is strongly basic sorbent, release of the iodine occurs more evenly and in the smaller quantities, rather than when slightly alkaline sorbents SMA-2 and SMA-3 are used. The reason of the observed effect is the different iodine binding strength by the sorbents.

Moreover, the sanitary-hygienic properties of the sorbents and their complexes with iodine were studied to identify the possibility of creating water purification systems from the microorganisms. For this purpose, the samples were placed into a glass column and dechlorinated tap water of Tashkent city was passed with the rate 1 ml / min. The quality of the original dechlorinated tap water was taken as a reference. Filtration of the contaminated water through the fiber provides an improvement in its sanitary bacteriological quality, which is indicated from the total viable count (TVC) in 1 ml of water and coli-index. The data represented in the Table 1 shows good bactericidal properties of the fibers.

Table 1

Results of an experiment on studying bactericidal properties.

Research objects	Total microbe number per 1 ml	Coliform index	Salmonella
Tap water. Infection dose 1000 cells/1 l	17	920	-
After filtration through fiber	4	3	-
Infection dose 10000 cells/1 l	24	13000	-
After filtration through fiber	2	4	0
Salmonella contaminated water 50 cells/1 ml	-	-	40
After filtration through fiber	-	-	no growth observed

In the tables 2, 3 it is shown that organoleptic and sanitary chemical indicators of the water, passed through sorbents, do not exceed the established standards, and have no difference with the reference indicators. At the same time, it is noticeable that after the sorption of iodine by the sorbents (here iodine content reached 68%) in the filtrate there is a taste and an odor of the iodine with the 3 points intensity and its yellow color. Although, it should be noted that the complexes of iodine with the sorbents negatively affect some sanitary chemical indicators of water quality. In particular, its ability to oxidation (AO) increases to 9,8-14 mg O2/l.

Table 2

Organoleptic indicators of the quality of the filtrate after passing through the original sorbents and their complexes with iodine

Sorbent, complex	color	Odor, intensity	Transparency, cm	Taste of the water, points
SMA-2	Colorless	0	30	2
SMA-3	Colorless	0	30	2
SMA-1	Colorless	0	30	2
[SMA-2]I2	Yellow	3	30	3
[SMA-3]I2	Yellow	3	30	3
[SMA-1]I2	Light-yellow	3	30	3
Layout-1	Colorless	0	30	0
Layout -2	Colorless	0	30	0
Reference point	Colorless	0	30	1

Table 3

Sanitary and chemical indicators of the quality of the filtrate after passing through sorbents and their complexes with iodine.

Sorbent, complex	Ammonia, mg/l	Nitrites, mg/l	Nitrates, mg/l	Alkalinity, mg-eq/l	Total hardness, mg-eq/l	Oxidizability, mg O2/l
SMA-2	0.01	0.002	0	1.7	4.0	0.52
SMA-3	0	0.001	0	1.9	5,0	0.44
SMA-1	0	0.002	0	1.7	4.8	0.48
[SMA-2]I2	0	0.002	0	1.6	4.0	10.0
[SMA-3]I2	0.05	0.006	0	1.7	4.8	14.0
[SMA-1]I2	0	0.003	1.8	1.6	4.0	9,8
Layout-1	0.04	0.001	1.2	1.8	3.7	2.0–5.0
Layout-2	0.03	0.001	1.3	2.0	4.0	0.36
Reference point	0	0.001	2.0	2	4.2	0.56

Table 4

Results of bacteriological studies of the quality of water artificially contaminated with E. coli culture after filtering it through models

Layout	E.coli		S. Paratyphi B	
	10 u*	100 u.	10 u.	100 u.
1	<3	<3	<3	<3
2	<3	<3	0	0
Reference point	10	96	11	102

(*"u" means the units of concentration of cells)

As it was already noted above, the reason of the appearance of AO in water is the existence of the excess of the iodine-ions in the filtrate. Considering the above information, complexes with low iodine content, (iodine content was reduced from 68 to 23%) were prepared for further experiments. Furthermore, columns were equipped with the special protection, which consists of the original sorbents and activated carbon (AC). This protection allows to reduce the iodine concentration in filtrate (Fig. 5, a). The layout is a glass column, which is filled with the fibrous iodine-containing sorbent. The original sorbent and AC were used as a sorbent for the iodine absorption. Today many types of stand-alone water purifiers (SWAPs) are known

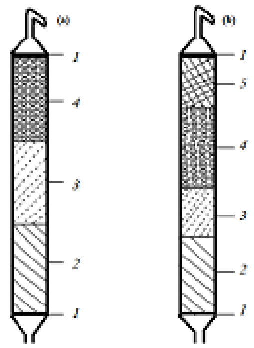

Fig. 5. Scheme of columns for water disinfection. (a) layout-1; (b) layout-2. (1) purified nitron4 (2) SMA-2 ionite - iodine complex; (3) SMA-2 ionite; (4) BAS; (5) silver-containing ionite.

[13],[14],[15],[16],[17],[18]. For instance, there are reagent-free, reagent- needed, and combined type SWAPs, but latter type devices found to be the most efficient. Firstly, water is disinfected by the iodine, chemical disinfectant. Then the sorption of the iodine excess amount, which did not react with the microorganisms, occurs up to the safe norms of iodine. In this stage, the sorption of other dangerous chemical impurities takes place as well.

Sanitary-hygienic research with the layout-1 showed that after the filtrate was passed through these complexes, its AO decreased from 9-14 to 2-5 mg O2/l. The most effective ones are the complexes based on the sorbents SMA-1 and SMA-2; complexes based on the sorbent SMA-3 showed lower bactericidal activity. However, the supplying of the system with the special protection could not completely remove AO filtrate. Therefore, as a protection to reduce the concentration of the iodine in the filtrate to the required value and thus creating conditions for the functioning of the water disinfection system a silver-containing cation exchanger based on the polyacrylonitrile fiber with carboxylic strong and amine groups was developed (layout-2), which has the capacity to silver ions 70 mg/g.

It turned out that there is no notable difference between sanitary-hygienic properties of the layout-2 and the reference and that the AO of the filtrate is only 0,36 mg O2/l.

Additionally, results of the bacteriological studies of the quality of the water, which was artificially polluted with the E. coli cultures, after filtration it through layouts became very successful, what is observed in the negligible difference of the sample with the reference.

Thus, from the above, it can be seen that sanitary, hygienic and bactericidal properties of water passed through the layout-2 fully match with the criteria “Drinking water”.

The layout-2 belongs to the category of the daily combined SWAPs. Disinfection process of the drinking water is represented as a chemical process of the interaction of the iodine molecules or iodide-ions with subcellular molecular structures with the next inactivation of microorganisms. To solve the issues of introduction of the daily SWAPs to the exploitation it is necessary to determine the validity of the layout, to realize structural and technical work, establish fields of application of the device (tap water, groundwater, surface water or other water reservoirs.

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