ЭТИЛЕН-ДИАМИДО-ДИИЗОПРОПИЛЕН-О,О'-ДИНАТРИЙ– СРЕДСТВО ДЛЯ ПОВЫШЕНИЯ КАЧЕСТВА ТЕХНИЧЕСКОЙ ВОДЫ, ИСПОЛЬЗУЕМОЙ В СИСТЕМАХ ГОРОДСКОГО ТЕПЛОСНАБЖЕНИЯ

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Проведен анализ воды, которая используется в городских нагревательных системах, и установлено, что проводится неполная очистка от солей различных металлов, как это требуется по методическим рекомендациям по расчету количества и качества принимаемых сточных вод и загрязняющих веществ системы канализации. Для сохранения бойлерной аппаратуры часто используется нитрилотрифосфонат цинка (NTPZn) потому что он был найден как эффективное средство для очистки воды от солей металлов. Также было установлено, что такому веществу необходимо иметь две или три группы P=O и –N=R₂. Есть большая проблема с используемым антинакипином третьего класса опасности, поскольку при высокой температуре, которая имеет место бойлерах, структура этого соединения может разрушаться с выделением таких токсических веществ как цианиды.

Этилен-диамидо-диизопропилен-О,О'-динатрий-дифосфонат (EDDDP), имеющий 4-ый класс опасности согласно биохимическим исследованиям, был впервые синтезирован с хорошим выходом для целей увеличения качества технической дренажной воды. Синтез был проведен через реакцию конденсации между 1-метилакриловой кислотой и 1,2-этилендиамином с последующей реакцией Пудовика полученного промежуточного соединения с динатрийфосфористой кислотой.

Был сделан анализ технической дренажной воды и получены данные жесткости, общей щелочности, токсикологических свойств и эффективности воды в отсутствие и в присутствии EDDDP.

Токсикологический контроль был проведен в соответствии с «Критериями отнесения отходов к классам опасности для окружающей природной среды», Министерства природных ресурсов Российской Федерации от 2001 года и дал заключение, что EDDDP не токсичен по сравнению с бактерией Daphniamagna, которая была взята за стандарт.

Ключевые слова: техническая вода, жесткость воды, щелочность, фосфорное соединение, анти-накипин, эффективность, классопасности.

ETHYLENE-DIAMIDO-DIISOPROPYLEN-O,O′-DINATRIUM-DIPHOSPHONATE IS A MEANS FOR THE RISE OF QUALITY OF TECHNICAL WATER, USEDIN THE SYSTEMS OF A CITY WARM WATER SUPPLY

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The analysis of water used in urban heating systems has been carried out, and it has been found that incomplete purification of salts of various metals is carried out, as required by the methodological recommendations for the calculation of the amount and quality of waste water received and pollutants of the sewerage system. Zinc nitrilotrifosphonate (NTPZn) is often used to preserve boiler equipment because it has been found to be an effective means for purifying water from metal salts. It has also been found that such a substance needs to have two or three groups $P = O$ and $-N = R_2$. There is a big problem with the third class of danger antinacipine used, since at the high temperature that boilers occur, the structure of this compound can break down with the release of toxic substances such as cyanides.

Ethylene diamido-diisopropylene-O,O'-dinatrium diphosphonate (EDDDP), having a 4th hazard class according to biochemical studies, was first synthesized with good yield for the purpose of increasing the quality of technical drainage water. The synthesis was carried out through a condensation reaction between 1-methylacrylic acid and 1,2-ethylenediamine, followed by Pudovik's reaction of the resulting intermediate with disodium phosphorous acid.

Technical drainage water was analyzed and data were obtained on stiffness, general alkalinity, toxicological properties and water efficiency in the absence and presence of EDDDP. Toxicological control was carried out in accordance with the Criteria for Classification of Waste as a Hazard to the Natural Environment, Ministry of Natural Resources of the Russian Federation of 2001year and concluded, that EDDDP was not toxic compared to the bacterium Daphnia magna, which was taken as a standard.

Keywords: technical water, rigidity of water, alkali properties, phosphoric compound, anti-scum, effectivity, class of danger.

Introduction

The organic complex-formation substances are used for the waterpurify after different technological processes [15]. The akin organic compounds as amino acids or substances with phosphor-containing fragments in their structures also often can be used for the extraction of metal ions in liquids to reduce a rigidity of water and doher more potable [6].
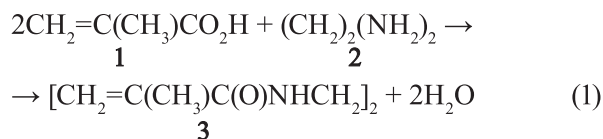
So,nitriletriphosphonate of zinc (NTPZn) was often used as a means against the scum in the systems of a city warm supply [7, 8]. The analysis of such literary data showed, that the substances with the metal-extracting (for example Ca, Mg or Fe) properties must have in the composition from one to three phosphoric groups (=P(O)O) and nitrogen (NHR) containing fragments [911].
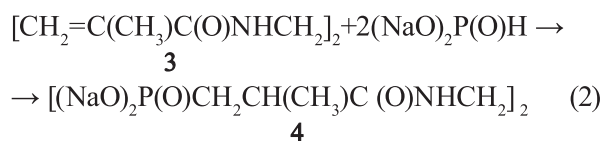
Methods and experiments

Taking into account profitable, cheap and ecological conditions, we undertook the synthesis of the required extract compound for the aims of the warmenergetic systems of the town economy management. The synthesis of ethylene-diamido-diisopropylen-O,O′-dinatrium-diphosphonate (EDDDP) was conducted in some stages. On the first of them the condensation process was carried out between 1-methylacrylic acid (1, 28.7 g, 0.67 mol) and 1,2-ethylenediamine (2, 20.02 g, 0.33 mol) with formation of dimethyl-diacryl-

ethylene-diamide (3, 60.2 g, yield is 92.3 %) at the room temperature in benzene with a trap for the water isolation from the reaction mixture (equation 1).

$$2CH_2=C(CH_3)CO_2H + (CH_2)_2(NH_2)_2 \rightarrow$$
$$\mathbf{1} \qquad\qquad \mathbf{2}$$
$$\rightarrow [CH_2=C(CH_3)C(O)NHCH_2]_2 + 2H_2O \qquad (1)$$
$$\mathbf{3}$$

The next stage consisted in the preparation of 30 % (to volume) base-alcohol-water mixture with industrial phosphoric acid; during of this process the two hydroxyl groups of phosphoric acid were exchanged on NaO-groups of sodium hydroxide and the required substance for next synthesis was Na_2HPO_3.

The last stage of synthesis of required extract means consisted in the use of famous Pudovik-reaction [12]: in the addition reaction of previously received reagent $(NaO)_2P(O)H$ (63.2 g, 0.62 mol) to double bonds of compound (3, 60.2 g, 0.31 mol) at 343348 K during of two hours. After evaporation of the rests of benzene and alcohol the required compound (4) represented yourselves 105.4 g with the yield 91.8 % (equation 2)

$$[CH_2=C(CH_3)C(O)NHCH_2]_2+2(NaO)_2P(O)H \rightarrow$$
$$\mathbf{3}$$
$$\rightarrow [(NaO)_2P(O)CH_2CH(CH_3)C(O)NHCH_2]_2 \qquad (2)$$
$$\mathbf{4}$$

For extract means (4, $C_{10}H_{18}N_2O_8P_2Na_2$) was found C 30.94 %, H 3.86 %; calculated C 29.88 %, H 4.48 %. The signal at 4.6 ppm has been found in NMR ^{31}P spectra, which corresponds to organophosphorus structures with $P(O)CH_2$ groups. There are bands (v) in IR spectrum at 10301100 (P-O-C), 1285 (P=O), 28902980 (C-H), 27502800 (N-H) cm^{-1}, which point on the reality of received structure. There is a patent for the receiving of this compound [13].

Results and discussion

As was mentioned in introduction, such organophosphorus substances are used as effective means against the scum in the city systems. As known, the scum is a product of magnesium and calcium salts in technical waters in large degree. On this reason we undertook the determination of general rigidity and alkaline properties of technical water of Kazan town. The method of the determination of the rigidity of water was described earlier in the works [6, 14].

The determination of general rigidity (R_o) of water (general upkeep of Mg and Ca in it) was conducted by the titration of technical water with ethylene-diamine-tetraacetic acid (EDTA) with the addition of black-eriochrome (erio T) as an indicator in basic medium (pH ~ 10). From general amount of EDTA was excluded the amount of EDTA, which was spent on the titration of equivalent amount of special added magnesium salt. The additional introduction of ammonia buffer blocks the ferric salts in the research technical water and makes the results more correct [14]. The result of such investigation is represented in Table 1.

The general alkali property (A_o) of water was determined as the sum of hydroxyl ions and anions of weak acids [15]. This important parameter was determined through the titration of water test with componentphenolphthalein (PP) in first degree and then with methyl orange (M). Such separation in the titration allow very precisely define the amount of separate components of general alkali of water when: PP is between $0.2 < M$ and pH < 9.5. Moreover, the ions HO^- and HCO_3^- cannot exist together because the reaction (3) take place mixture.

$$HO^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O \qquad (3)$$
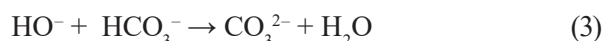
However, not only rigidity and alkali properties characterize the ability of extract means (let's give it a title anti scum) of metals in water. These is an important parameter "effectivity, Z (%)", which can be calculated on equation (4) [16].

$$Z = \frac{[Ca_{last}]}{[Ca_{start}]} \cdot 100 \qquad (4)$$

The data of analysis of technical water (mgr·l^{-1}) in the drainage of Kazan

N of test	Chemical composition of technical water				
	R_o	Ca	Mg	pH	A_o
1	6.26	4.16	2.10	7.32	1.8
2	8.42	4.88	3.54	8.46	2.1
3	7.51	4.36	3.15	7.28	1.6
4	6.48	3.76	2.92	7.93	1.2

Table 2

The components of general alkali properties of technical water

Relation between PP and M	The contain of anions in water	The components of general alkali		
		HCO_3^-	CO_3^{2-}	HO^-
PP = 0	HCO_3^-	M	0	0
2PP < M	HCO_3^- and CO_3^{2-}	M – 2PP	2PP	0
2PP = M	CO_3^{2-}	0	2PP	0
2PP > M	CO_3^{2-} and HO^-	0	2(M – PP)	2PP – M
PP = M	HO^-	0	0	M

In this equation Ca_{last} is the contain of calcium (mgr·l⁻¹) in water after the experiment, Ca_{start} is the contain of calcium (mgr·l⁻¹) before the experiment.

Taking into account the all mentioned above, the research of the properties, applicability and effectivity of already synthesized EDDDP was followed on such way at the same conditions, which are pointed in Table 1(concentration of Ca, Mg, general rigidity and alkali properties):

– the synthesized anti scum was added in the analyzing waters in the amounts 2–10 mgr·l⁻¹ as it is recommended in literature [1719], because the amount of this agent must be proportional to the formed scum in water,

Table 3

The results of analysis (mgr·l⁻¹) of the effectivity of EDDDP in testing water

No of test	Concentration (mgr·l⁻¹)	Reagent	Z*
1	3	EDDDP	97
	3	NTPZn	73
2	5	EDDDP	91
	5	NTPZn	56
3	3	EDDDP	99
	5	NTPZn	59
4	3	EDDDP	92
	3	NTPZn	65

*Z-Effectivity was determined as the relation of calcium and magnesium ions in water before and after experiments (eq. 4).

– four tests were heated at 363 K during of 3 hours and after this actions were exposed to analysis; for comparison NTPZn was used.

The results of these experiments are in Table 3.

As can be seen from the data of Table 3, the synthesized EDDDP is more effective in different concentrations then often used in a city thermal supply nitriletriphosphonate of zinc (3-rd class of the danger) for the cleaning of drainage water.

The theoretical calculation of the estimation of ecological danger for the environment was made for the suggested ethylene-diamido-diisopropyliden-O,O'-dinatriumdiphosphonate (EDDDP) and have been found that this anti scum corresponds to 4-th class of the danger for the natural water reservoirs (Table 4).

The indicator K_i of the degree of the scrap danger can be calculated on Eq. (5),

$$K_i = C_i/W_i \tag{5}$$

where C_i– a concentration of i-th component in the danger scrap, W_i– a coefficient of the degree of danger of i-th component, i.e. a conditional indicator, equal to the amount of the scrap component, lower of the magnitude of which it cannot in no way do a negative interaction on the environment.

The indicator K of the degree of the scrap danger can be calculated as a sum of Ki of the separate components of the scrap (eq. 6),

$$K = K_1 + K_2 + ... + K_i \tag{6}$$

Table 4

The results of the calculation of the danger class on the componentsof thescrap

Component	Compound, %	C_i(mgr/kgr)	W_i (mgr/kgr)	K_i
Phosphoric acid	3.87	38700	16785.463	2.201
EDDDP and his metabolite (in the sum)	0.03	300	132.591	0.858
Water /p.13 from"Criteria"/	96.10	961000	1000000.00 (standard)	0.961

in which K_i – indicators of the degree of the danger of the number (i) of the amount of the scrap. The indicator K for EDDDP of degree of scrap consists 4.02, on this reason this anti scum is the 4-th degree of the danger [20].

The installation of the class of danger has been done accordingly with "Criteria of reference of waste to classes of danger to a surrounding environment", which have been confirmed by the ministry of natural resources of Russian Federation from 2001 year [20].

The results of toxicological control of EDDDP are the next:
– form of the test-object: solution of EDDDP (gr·dm³);
– title of the test-object: Paramecium caudatum Evidence No 01.19.229/2000;
– nature of experiment (sharp, chronical): Paramecium caudatum is sharp: *Daphnia magna* PhR 1.39.200100282 – 14.1:1:2:3:4.5-99 is sharp;
– toxicological index: for solution of EDDDP is $LD_{(50)} = 0$ (nontoxic),
for *Daphnia magna* PhR is $LD_{(50)} = 2.0$ (toxic).

Conclusion

The compound ethylene-diamido-diisopropylen-O,O′-dinatrium-diphosphonate (EDDDP) was synthetized with good yield in the first time for the aim of the rise of quality of technical drainage water. The synthesis was conducted through the condensation between 1-methylacrylic acid and 1,2-ethylenediamine and the Pudovik-reaction of the received substance and dinatriumphosphosphoric acid.

The analysis of technical drainage water was conducted and was received the data of rigidity, general alkali and toxicalproperties, effectivity of water in the absence and presence of EDDDP. Such substance has a fourth class of the danger.

The toxicological control in the accordance with "Criteria of reference of waste to classes of danger to a surrounding environment" of russianministry of natural resources from 2000 year gave the conclusion that EDDDP is nontoxic in the compassion with bacterium *Daphnia magna*, which was taken as the standard.

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