

SOME WAYS OF PREVENTION OF GETTING HEAVY METAL IONS INTO FOOD CHAINS

Yarema Tevtul¹, Sonia Gutt², Olha Nechiporenko, Sergey Ermolenko

Chernivtsy national university named after Yuriy Fed'covich,

Kocubinsky st., 2, Chernivtsy, 58012, Ukraine.

¹University "Stefan cel mare" of Suceava, Romania.

Abstract

The ways of getting heavy metal ions into food chains are observed. Some results of negative influence of heavy metal ions on organisms are described. The analysis of prevention methods for heavy metal ions presence in the objects of environment is done. The results of researches of prevention of getting heavy metal ions into food chains are given.

Keywords: food chain, ions of heavy metals, prevention of getting.

INTRODUCTION

The anthropogenic period of development of Earth is characterized by active influence of man on the objects of environment. It is evened approximately to 2,5 million years [6]. Although this period is very large, only for the last age negative activity of man especially appeared in relation to nature. We will look at only one problem which touches anthropogenic influence on the food chains. Actuality and ponderability of such questions are predefined by the fact that in every next link of food chain maintenance of some harmful matters is increases approximately in ten times [16]. At the end of any food chain is man. Consequently, it tests the most negative influence. But this influencing is the result of unwise or irresponsible activity of man.

Actual task of the modern stage of anthropogenic period is warning of receipt of toxic matters in the food chains. The first links of food chains are groups of types of plants, animals, mushrooms and microorganisms which are bound by food relations in soils and waters. Among the last are those which are used for irrigation of agricultural lands and growing of organisms. Quite often the amount of links in the food chains does not exceed 4 – 5 [11]. Anthropogenic contamination of primary links of food chains results in migration and accumulation of toxic matters.

Movement of heavy metal ions in food chains is shown on figure 1.

Getting of heavy metal ions into the food chain, as a rule, violates the existent equilibrium of biogeocenosis. Violation of equilibrium in biogeocenosis is not the unique negative consequence of the increased concentration of ions of heavy metals in a reservoir. Other negative influence closely contacts with motion of ions in the food chains: plankton – insects – plants – fishes (animals) – man. This movement takes a place on a molecular exchange level. If plants accumulate surplus of heavy metals as ions, so to the man it reaches as toxic matters, that negatively influence the state of his health, and even can cause death.

We will touch only one question of the outlined problem – prevention of contamination of soils and natural waters by the ions of some heavy metals. In particular, the ions of Fe, Cu and Ni are chosen. Such attention to the ions of this elements is caused by a number of reasons. Firstly, objects made of iron, copper, nickel and their alloys are widely used. In the process of their exploitation and destruction objects of environment are polluted by these metals and compounds of Fe, Cu and Ni.

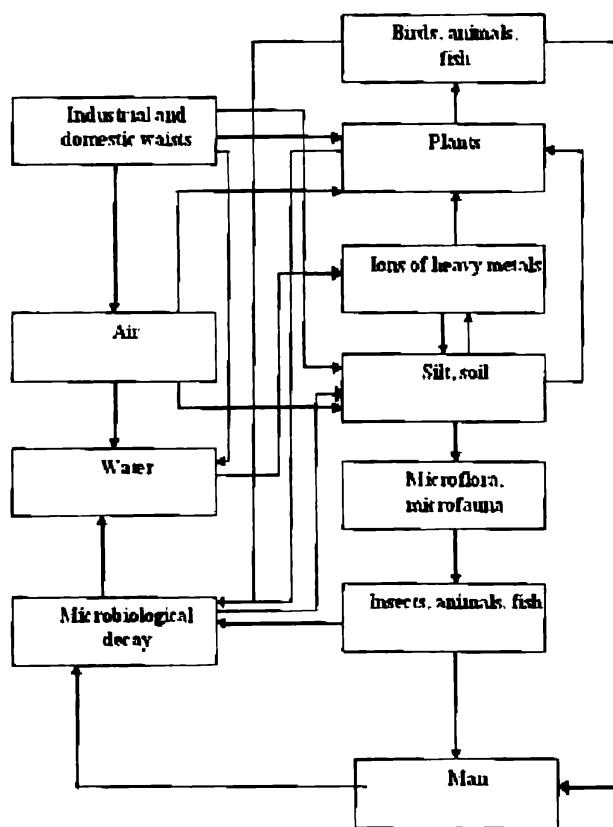


Fig.1: Movement of ions of heavy metals in food chains

Secondly, chemical and electrochemical treatment of wares from iron, copper, nickel and their alloys is accompanied by formation of plenty of liquid and hard wastes which contain toxic ions. The concentration of ions of Fe in the used solutions of steel etching reaches 7 g/l. Thirdly, galvanic processes with the use of solutions which contain the ions of Fe, Cu and Ni also result in formation of toxic wastes. Use of facilities of prevention of plants and poisonous chemicals, corrosion of technological equipment for preparation of food stuffs – it also the way of entering of toxic ions into food chains. This list can be prolonged.

Shortly we will consider influence of connections of the mentioned above heavy metals on organisms.

Ferum compounds are widespread and their entering into food chains is natural. Ferum compounds are vitally needed. The row of component parts of food chains accumulates connections of Ferum intensively. Water flora accumulates them actively, and intensity of absorption depends on time of year – for some plants is on September. Plants accumulate Fe in the form of ions of Fe(II) and Fe(III), and also chelat compounds.

The toxicity of Ferum compounds in water depends on pH [3]. In an alkaline environment the toxicity for fishes grows sharply, ferric hydroxide settle on gills, stops them up and destroy. Water, with the high concentration of Ferum ions is useless for incubation of caviar of fishes, because ferric hydroxide settles on body and gills of young fish; it is the reason of their mass death; very sensible to connections of Ferum are shellfishes.

Extreem amounts of these matters lead to various violations of activity of organisms. The contents of Ferum ions in soil must not exceed 0,42 %, and possible maintenance of Ferum compounds in sewage waters which are utilized for irrigation of soils must not exceed 70 mg/l. Ferum compounds enter organism with food stuffs, water and medications.

Cuprum and Nickel in the form of microelements also are vitally necessary. Migration of Nickel compounds is rather difficult. They migrate from soils into plants, superficial and underground water. The contents of compounds of Nickel in soils constantly recommences as a result of destruction of minerals of soil, decomposition of plants and microorganisms, and also due to activity of man. Migration from soil into plants substantially depends on solubility of compounds of Nickel. In sour soils the compounds of Nickel are less mobile. In poorly alkaline environments Nickel passes to the soluble, mobile and toxic enough forms. A presence in soils of organic acids positively influences the formation of easily soluble compounds. The contents of ions of Nickel in annual silt reaches 0,01 %; its most

maintenance is in the superficial layer of silt. Microorganisms are a component link of food chain and they accumulate the ions of Nickel; their maintenance in ten and hundred times exceeds the concentration of this pollutant in an environment.

The increase of concentration of Nickel ions in a water environment results in the toxicity of organism of plant, weakens photosynthesis, worsens metabolism of some nutritive. The sign of poisoning of plant by Nickel is necrosis of senescent leaves. The harmful action of Nickel compounds on plants shows up, when their maintenance in water for watering is evened to 0,5 mg/l. Absorption of Nickel compounds by plants is increased on 25 – 42 %, if there are ions of Ferum and Cuprum in the soil. Entering of Nickel compounds into organism of man takes a place, mainly, with food stuffs and drinking-water. Hidroflora absorbs Nickel compounds from water, and plants – from soil. Poisoning by Nickel compounds is characterized by general toxic action, formation of dermatitis's, eczemas, poor quality new formations.

Annually 94 thousands t of Cuprum comes into the objects of environment with fertilizers. Sewage waters from manufactures, chemical pharmaceutical enterprises contain up to 500 mg/l of Cuprum [4]. The contents of Cuprum in soils in an amount of 60 mg/kg is considered surplus. If in water for watering of sugar beet, tomatoes and barley maintenance of Cuprum is evened to 0,20 mg/l, it is considered a toxic dose.

Especially dangerous for animals are Cuprum ions, which influence the acidity of water and can cause death of whole ecosystem of reservoir. Contents of Cu in water of chlorides and nitrates in the concentrations of 0,01 – 0,02 mg/l are toxic for fishes. The ions of Cuprum and Nickel negatively influence mezofauna reservoirs, which play an important role in its natural cleaning. Plants, as a rule, absorb Cuprum as ions, that is why it surplus in water is especially dangerous. Compounds of Cuprum belong to the high-toxic matters; they are reason of the harmful poisonings with the wide spectrum of action. Poisoning of people by water or by drinks which were in touch with copper wares are described. Taking into account high toxicity of Cuprum compounds, maximum possible concentrations of this element in different food products, garden trucks were found out. The mechanism of toxic action of Cuprum ions is predefined by blocking of SH-groups of albumens, especially enzymes.

Short list of the negative influence of compounds of Ferum, Nickel and Cuprum on organisms, their migration in the food chains is ponderable

foundation for researches for warning of receipt of the indicated elements in the objects of environment.

Existing methods of warning of getting ions of heavy metals into the food chains are often ineffective. They are used for the exception of toxic ions from solutions. More frequently methods of chemical precipitation are used. Hard wastes which contain those toxic ions appear [12, 7]. For example, for the exception of ions of ferum(II) they are oxidated to ferum(III) by oxygen of air, with next formation of $\text{Fe}(\text{OH})_3$. But thus it is not succeeded to withdraw the ions of Ferum from the worked solutions of steel etching, in fact they contain plenty of acids. For the chemical exception of ions of Cuprum and Nickel often CaO is used, which contains CaCO_3 . Thus insoluble connections of $\text{Cu}(\text{OH})_2$, $(\text{CuOH})_2\text{CO}_3$, $\text{Ni}(\text{OH})_2$, $(\text{NiOH})_2\text{CO}_3$, NiCO_3 appear. These methods have a few failings. One of them is a great usage of reagents. The basic failing is a complete loss of valuable matters which form precipitations. This failing can be removed, if to process solutions of different ions of heavy metals separately. But this way processes are not conducted.

Following methods are count to be perspective and effective: regenerations of the worked technological solutions and their multiple-use; an exception of toxic ions, without formation of harmful wastes.

Experimental

By us probed: are conformities to the law of electrochemical regeneration of the worked cuprum-chloride solutions of copper etching; are possibilities of the use of the worked chloride-sulfate solutions of steel etching for coatening of details by iron; features of xray-catalytic method of exception of Nickel ions from the worked solutions of chemical nickel plating. For the study of proceeding in the heavy metals ions the method of voltammety was used. For this purpose potentiostat PI-50-1.1, programator PR-8 and recording device LKD4-003 were used. A working electrode is a immobile platinum mukrodisk; an auxiliary electrode is platinum; electrode of comparison is silver-silver chloride.

For the electrochemical regeneration of the used solutions of copper etching and electrochemical reduction of iron from the used etching solutions membrane elektrolizer was used [14]. Cathode and anodal spaces part the cation-changing membrane of MK-40; in anodal space there are no chloride ions; an anode is insoluble – titanic, covered with RuO_2 . The xray-catalytic method of exception of Nickel ions from the worked solutions of

chemical nickel plating is developed at participation of one of authors of this work [1]. NaH_2PO_2 served as a reductor; a catalyst is a nickel; a working temperature is 363 – 368 K; a method is described in work [15]. Control of maintenance of Nickel ions after their exception was carried out by alcoholic solution of dimetilglioksim.

The used solutions of etching steel SP10, copper and chemical nickel plating were taken for researches. Used chloride-sulphate solutions of etching steel SP10 contained the ions of Ferum (g/l): №1 – 35,06; № 2 - did contain also 35,06 g/l ions of Ferum, but to increase pH till 1,17 NaOH (85,4 g/l); was injected for preparation of the used etching solutions № 1 and № 2 was used solution of chloride (50 g/l) and sulphate (90 g/l) acids. The used etching solution №3 contained Ferum ions of 44,94 g/l, and solution № 4 – 55,98 g/l Ferum ions, after injection of ferum(II) sulphate pH of solution № 4 increased to 2,0, by addition of natrium hydroxide. For preparation of the used etching solutions № 3 and №4 were used chloride (30,2 g/l) and sulphate (233,2 g/l) acids.

Composition of the used cuprum-chloride-sour solutions of copper etching is shown in table 1 [8].

Table 1: Compositions of the worked solutions of copper etching

Electrolyte №	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ g/l	Cuprum ions g/l	HCl g/l	KCl g/l
5	186,71	69,88	9,0	250
6	222,44	83,25	21,2	275
7	241,94	90,56	12,0	300

Used solutions of nickel plating № 8 contained Nickel ions ($2,9 \cdot 10^{-2}$ mg/l), that equals 6,8 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

Results and Discussion

Solutions of etching steel, for example, SP10 are considered to be used, if the content of Ferum ions reach 40 g/l. Peculiarity of such solutions – big acidity.

One of the spread ways of getting Fe(II) ions out of used solutions – passing air through them. Thus Fe(II) transforms into Fe(III): $4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^-$; and father into insoluble Fe(III) hydroxide. This method can not be used in our investigations. Great content of acids ceases formation of Fe(III) hydroxide.

For the prognosis of terms of the use of the worked solutions of etching of steel for the electrochemical reduction of iron voltametry research was conducted. On voltametry curves (VAC) two waves which can refer to transitions of $\text{Fe(III)} \rightarrow \text{Fe(II)} \rightarrow \text{Fe}$ were found. Admission of air through solution №1 results in the increase of current density of peak of VAC, displacement of beginning potential and middle point of the second wave to the side of less negative values. Potential of the top of the second wave is displaced to the side of more negative values. Oxidizing of the used etching solution №1, increase of maintenance of ions of ferum(III) and change of parameters of VAC can be predefined by the change of nature of ions; transformation of aqua-complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{Cl}^- \leftrightarrow [\text{FeCl}_4]^- + 6\text{H}_2\text{O}$ is possible.

Research of iron plating out of solutions №1 and №2 led to make such conclusions. Using of solution №1 is inadvisable. Large acidity ($\text{pH} \rightarrow 0$) results in the fact, that speed of chemical dissolution of iron is more than speed of the electrochemical besieging of iron. Using of solution № 2 is more effective. Besieging of iron was conducted within the limits of current density from 0,65 to 20 A/dm^2 . At less current densities (0,5 A/dm^2) speed of chemical dissolution of iron is more then speed of the electrochemical besieging of iron. For a current densities from 0,65 to 5,0 A/dm^2 can be got light, well coupled with basis precipitations. Within the limits of 10 ÷ 20 A/dm^2 appear powder-like precipitations of iron. For research of other direction of application of the used solutions of steel etching solutions № 3 and № 4 were used. It is expedient to use solution № 3 for preparation of the mixed electrolyte of iron plating at small current densities. Using of solution № 4 for iron plating of steel wares is more expedient, so that light precipitations of iron are received at a current density to 10 A/dm^2 . Consequently, used chloride-sulphate solutions of etching of steel SP10 are expedient to use for preparation of the mixed electrolyte of iron plating, getting of powder-like iron. It will allow to decrease getting Ferum compounds into the objects of environment and food chains.

For the prognosis of terms and parameters of electrochemical regeneration of the used solutions of etching of copper the results of voltametry researches are treated. Linear dependence of current peak density (i_p) of voltametry curves (VAC) on speed of potential involute ($v^{1/2}$) (fig.2) in an interval $1 \cdot 10^{-2} \div 5 \cdot 10^{-1}$ V/s was set.

In the indicated interval of speeds of involute of potential, shown on fig. 2 dependence is described by equalization of $i_p = 0,0783 + 0,6325 \cdot v^{1/2}$. According to theoretical presentation it is possible to predict, that the process

of electrochemical renewal is controlled either by speed of diffusion of ions to the electrode or by the speed of transference of charge [5]. According to theoretical presentations, for $v^{1/2} = 0$ value of i_p must equal a zero also. Such dependence between the indicated parameters is executed for small speeds of involutes of potential ($1 \cdot 10^{-2} \div 5 \cdot 10^{-2}$ B/c) : $i_p = 0,9626 \cdot v^{1/2}$. Such dependence allows to talk that for small speeds of involutes of potential the current density of peak is determined by speed of diffusion of ions to the surface of electrode. For intensification of process of electrochemical regeneration of such used solutions of etching copper it is expedient to mix solution. Similar conclusions are made also after the analysis of VAC for solution № 7.

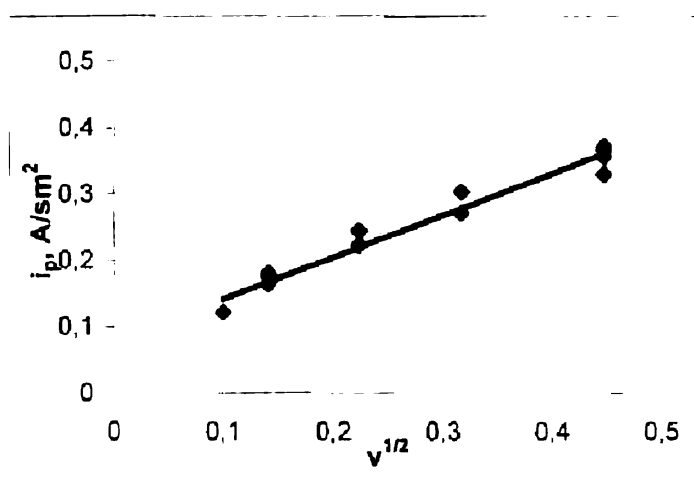


Fig. 2: Dependence of current density peak of VAC on $v^{1/2}$ (speed of potential involute) for an electrolyte № 6

The regeneration of the used solutions of copper etching takes a place by reduction of the ions of Cuprum from their complex compounds. In the freshly prepared cuprum-chloride-sour solutions of etching most probably is the existence of mixture of aqua-chloride cuprum(II) complexes: $[\text{CuCl}_3(\text{H}_2\text{O})_3]^-$, $[\text{CuCl}_2(\text{H}_2\text{O})_4]^0$ i $[\text{CuCl}(\text{H}_2\text{O})_5]^+$ [10]. In the used etching solutions the existence of complex ions of cuprum(I) is also possible. As electrochemical renewal – one of the stages of row of series processes, dissociation of complex ion can be the limiting stage. For description of electrode process additional treatment of VAC of reduction of Cuprum ions from their complex compounds was conducted. On VAC two waves which usually explain two stages of reduction of cuprum(II) ion were fixed. Description of the second stage of reduction in Cu^+ to Cu^0 is given here. Graphs are built and the coefficients of equalizations of dependences $\varphi = C +$

$D \cdot \ln(i_p - i)$ and $\varphi = A + B \cdot \ln(i / i_p - i)$ are calculated. One example of such dependences is with the use of solution № 7 it is shown on fig. 3; they are described by equalizations $\varphi = -0,1672 + 0,0368 \cdot \ln(i_p - i)$, ($R^2 = 0,901$)
 $i \varphi = -0,2132 - 0,0199 \cdot \ln(i / i_p - i)$, ($R^2 = 0,987$).

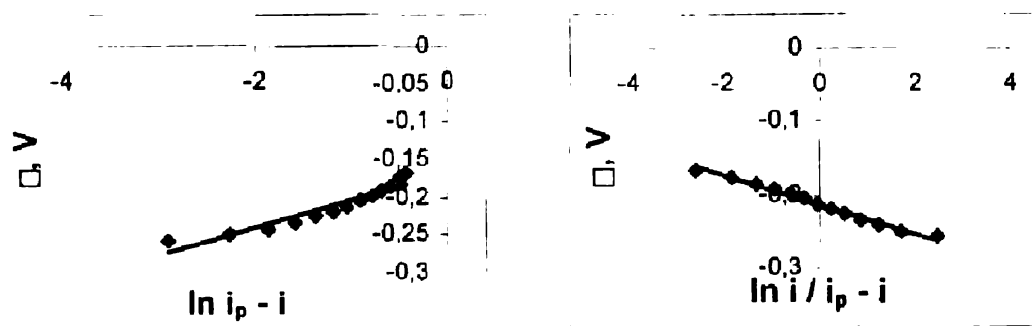


Fig. 3: Dependences $\varphi - \ln(i_p - i)$ i $\varphi - \ln(i/i_p - i)$: used solution of etching copper № 6; speed of potential involute 0.2 V/s

Comparing the coefficients of R^2 of the given equalizations and numerical values of coefficients A and C with the value of potential of middle of VAC ($\varphi_{1/2} = -0,2125$ V) a conclusion is done, that linear area $i - \varphi$ is described by dependence $\varphi = A + B \cdot \ln(i / i_p - i)$. Using a numerical value B the coefficient of transfer $\alpha = 0,63$ was calculated. Consequently, the linear areas of VAC show an irreversible electrode process, when speed of electrochemical reaction is not very high and practically ripened measured with speed of diffusion.

The electrochemical regeneration of the used solutions of etching of copper was done in membrane electrolyzer at current density from 6 to 25 A/dm^2 . At less current density speed of chemical dissolving of copper was more than the speed of the electrochemical precipitation of this metal. Dissolutions of copper are described by the reaction of disproportion with formation of cuprum(I) chloride [8, 9]. Cuprum(I) chloride which appears is insoluble, however in presence of chlorine ions soluble complexes appear. Partly cuprum(I) chloride is oxydated by oxygen of air in a sour environment [8] $4CuCl + O_2 + 4HCl \rightarrow 4CuCl_2 + 2H_2O$.

Some authors describe the process of dissolution of copper in cuprum-chloride solutions by equation of reaction $Cu + CuCl_2 + 4KCl \rightarrow 2K_2CuCl_3$. Ions of $CuCl_3^{2-}$ gradually oxide to complex ions compounds of Cu(II) [2]. Consequently, in solution, that is regenerated, there are complex ions, formed by cuprum(I) and cuprum(II). Speed of regeneration of solution № 6 is proportional to the current density (i) within the limits of 5 ÷ 11

A/dm^2 : $V = 0,0184 \cdot i - 0,0758$. In the indicated interval of current density on current exit (CE) increases from 32,26 % to 80,47 %. Regenerated solution of copper etching is used for etching of copper. Speed of etching of copper in the regenerated solution is $0,0048 \text{ g/min}\cdot\text{sm}^2$, and in fresh-made – $0,0049 \text{ g/min}\cdot\text{sm}^2$. These values are of one order and used solution of copper etching, after the electrochemical exception of Cuprum ions is suitable for usage in future. Introduction of regeneration of etching solution allows to create ecologically safe process of copper etching in copper–chloride–sour solution, to warn the getting of Cuprum ions in to objects of environment and food chains.

For the exception of Nickel ions from used solutions of chemical nickel plating membrane electrolyzer can be used as well. Exception of Nickel ions out of solution № 9 has been studied; cathodes – nickel, anodes – titan, covered with a mangan(IV) oxide. At the current density 15 A/dm^2 in 2 hours of electrolysis concentration of nickel ions diminished a to 1 g/l. After the first hour of electrolysis current exit (CE) of nickel equaled 26,0 % at the current 15 A/dm^2 ; after continuation of electrolysis at the same current density of CE diminished to 10,3 %. The subsequent electrochemical exception of Nickel ions is inadvisable.

The Nickel ions can be withdrawn from the used solutions of chemical nickel plating to the maximum possible concentration without formation of Nickel compounds. A xray-catalytic method is applied for this purpose. For its realization it is necessary to create such terms for which used solution of chemical nickel plating becomes unsteady. It is foremost necessary to change pH of the solution. Value of pH of the used solution № 8 evened 5,0. With the saturated solution of NaOH acidity of electrolyte was led to 7,0. Then solution № 8 was heated to 343 K, a reducer ($\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$) and catalyst powder of nickel were entered. Reducer was taken from the calculation of 30 g on a 1 litre of the used solution of chemical nickel plating. Approximately in 30 min solution becomes colourless and turbid as a result of formation of powder of nickel. Selfarbitrary acidification of solution, as a result of flowing of reaction of $\text{Ni}^{2+} + 2\text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{PO}_3^- + \text{H}_2 + 2\text{H}^+ + \text{Ni}$ will hinder the exception of ions of Nickel to the maximum possible concentration. That is why during conducting of this process it is necessary to support the set value of pH. To control the exception of Nickel ions from solution alcoholic of dimetilglioksim is used. The sensitiveness of qualitative reaction to the ions of Nickel equals 0,01 mg/l. It refers to maximum permissible concentration (MPC) of ions of Nickel in waters for growing of fish [13]. Consequently,

using this method it is succeeded to decrease maintenance of ions of Nickel in solution to the concentration, less MPC.

Conclusion

Usage of results of the researches mentioned above allows: – to create ecologically safe technologies; – to utilize the valuable components of the used technological solutions; – to warn the getting of ions of heavy metals into the objects of environment and food chains.

References

- Tevtul' Ya.Yu., Pahomova E.P. (1991). *Sposob vydeleniya nikelya iz otrabotannykh rastvorov himicheskogo nikelirovaniya*. A.s. №1673616 (SSSR) B.i. №32, 30.08.1991.
- Byalozor S.G. (1968). K voprosu o vliyaniy hloridnykh ionov na elektroydelenie medi na tverdykh elektrodah. *Elektrohimiya*, 6 (5), 581-583.
- Vrednye himicheskie veschestva. Neorganicheskie soedineniya elementov V-VIII grupp.* (1989). /Pod red. V.A.Filova. Leningrad:Himiya.
- Vrednye himicheskie veschestva. Neorganicheskie soedineniya elementov I-IV grupp.* (1988). /Pod red. V.A.Filova. Leningrad:Himiya.
- Galyus Z. (1974). *Teoreticheskie osnovy elektrohimicheskogo analiza*. Moskva:Mir.
- Dedyu I.I. (1990). *Ecologicheskii encyklopedicheskii slovar'*. Kishiev: Glavnaya redakciya moldavskoi sovetskoi enciklopedii.
- Zapol's'kyi A.K., Mishkova-Klymenko N.A., Astrelin I.M. (2000). *Fizyko-himichni osnovy tehnologii ochyschennyya stichnykh vod*. Kiev:Libra.
- Il'in V.A. (1984). *Tehnologiya izgotovleniya pechatnykh platt*. Leningrad:Mashinostroenie.
- Kozin L.F., Omel'chuk A.A., Buryak N.I. (2004). Obrazovanie hloridnykh kompleksov odnovalentnoi medi. *Ukrains'kyi himichnyi jurnal*, 70 (1), 12-16.
- Larin G.M., Minin V.V., Levin B.V., Buslaev Yu.A. (1989). Kompleksoobrazovanie v sisteme $CuCl_2-HCl-H_2O$. *Izvestiya Akademii nauk SSSR. Seriya himicheskaya*, (60), 1223-1228.
- Musienko M.M., Serebryakov V.V., Braion O.V. (2002). *Ekologiya. Ohorona pryrody*. Kyev:Tovarystvo «Znannya».
- Radionov A.I., Klushin V.N., Torocheshnikov N.S. (1989). *Tehnika zaschity okrujayuschei sredy*. Moskva:Himiya.
- Sahaev V.G., Scherbyc'kyi B.V. (1986). *Spravochnik po ohrane okrujayuschei sredy*. Kiev:Budivel'nyk.
- Tevtul' Ya.Yu., Hrab O.V. (2006). Prystrij dlya elektrohimichnogo vylechennyya ioniv Kuprum(II) z vidprac'ovanykh rozchyniv travlennyya midi. Deklaraciyniy patent na korysnu model' №11856.
- Tevtul' Ya.Yu., Markovskii B.I., Pahomova E.P., Lavrenchuk L.N. (1995). Izvlechenie nikelya iz otrabotannykh rasvorov himicheskogo nikelirovaniya. *Ukrains'kyi himichnyi jurnal*, 61 (5), 35-40.
- Eihler V. (1993). *Yady v nashei pische*. Moskva:Mir.