UDC 628.3

DOI: 10.15372/CSD2022366

EDN: BZRLHC

Removal of Nickel Ions from Wastewater and Industrial Solutions (a Review)

V. R. KURDIUMOV[1,2], G. I. MALTSEV[1,2], K. L. TIMOFEEV[2,3]

[1]JSC "Uralelektromed", Verkhnyaya Pyshma, Russia

E-mail: vasily.kurdyumov@gmail.com

[2]Ural Mining and Metallurgical Company, Verkhnyaya Pyshma, Russia

[3]UMMC Technical University, Verkhnyaya Pyshma, Russia

(Received 25.03.21; revised 10.06.21)

Abstract

This paper presents conventional and innovative technologies for wastewater and industrial solution purification from Ni^{2+} ions and accompanying non-ferrous metals. Several methods including sorption, extraction, flotation, chemical, electrochemical, membrane and microbiological separation of impurities from the liquid phase are introduced. Chemical methods involve nickel deposition in the form of insoluble compounds (hydroxide, carbonate, bicarbonate, sulphide, dimethylglyoximate), or metal powder by adding certain reagents. Carbon, aluminosilicate and some other inorganic materials in initial and pre-modified forms, as well as weakly acidic, strongly acidic, weakly basic, including chelate ion-exchange resins and fibres are used for sorption. The extraction of nickel ions from the liquid phase is carried out with the derivatives of organophosphorous, carboxylic acids, as well as with materials that combine the properties of solid sorbents and liquid extractants. Nanofiltration and reverse osmosis are the most relevant methods among membrane purification methods. Foam separation of nickel ions during flotation is carried out using anionic and nonionic surfactants. Electrochemical methods include electrocoagulation, electroextraction, electroflotation, and electrodialysis using soluble and insoluble electrodes, as well as galvanic coagulation without connection to external power. Living and non-living biomass of some species of bacteria, fungi, algae, as well as their complex mixture in the form of activated sludge can be deployed for microbial extraction of nickel from aqueous media. The above purification methods are considered on the basis of case studies, both generally applicable and specific ones. Their advantages and disadvantages are briefly described.

Keywords: nickel, removal, water purification, wastewater, industrial solutions

Contents

INTRODUCTION

The problem of access to pure water is one of the most urgent challenges in the modern world: about a billion people are devoid of the access, while more than two billion have to use insufficiently pure water. The problem has been caused not only by depletion in the natural fresh water resources but also by their pollution with wastewaters and solutions formed as a result of human economic activities.

One of the main kinds of pollutants occurring in wastewaters and possessing biological activity with clearly pronounced toxic properties are heavy metal ions, especially Ni^{2+}. Anthropogenic sources from which nickel ions enter water bodies are wastewaters from galvanic plants, nickel concentrating plants, mining industry at the deposits of copper-nickel and iron-nickel sulphide ores, caoutchouc manufacturing plants. The concentrations of Ni^{2+} in anthropogenic sources vary from 1 to 30 mg/dm^3 in mine waters contacting with nickel-containing rocks, from 5 to 100 g/dm^3 in the spent solutions and wastewaters of nickel electroplating plants [1].

As a rule, wastewaters and solutions are purified from Ni^{2+} and other impurities using integrated procedures in several stages. At the first stage, mechanical methods of purification are used (screening, clarification, filtering, centrifuging), allowing separation of coarse mechanical impurities from the liquid phase. After that, chemical, physicochemical, biological methods of water purification are used. Chemical methods are based on the introduction of definite reagents into the liquid phase to decrease acidity or alkalinity, to transform various impurities into insoluble forms. Physicochemical methods include a broad range of procedures (flotation, coagulation, sorption, extraction, baromembrane technologies, *etc*.) that enable the removal of dissolved gases, fine-dispersed liquid and solid particles, heavy metal ions and salts from water. Biological methods involve biological accumulation or oxidation of impurities with the help of specific microorganisms. A compulsory final stage in the case if purified waters are to be discharged into water bodies is decontamination, which is carried out using disinfectants or UV radiation [2].

Traditional and innovative methods of the recovery of Ni^{2+} ions from wastewaters and solutions are considered in the review, with the evaluation of their major advantages and shortcomings.

REAGENT PRECIPITATION

The most widely known method of the purification of wastewaters and solutions from Ni^{2+} ions with the help of reagents is treatment with hydroxides, carbonates of alkaline metals, hydroxides of alkaline earth metals:

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2\downarrow \quad (1)$$

$$2Ni^{2+} + CO_3^{2-} + 2OH^- \rightarrow (NiOH)_2CO_3\downarrow \quad (2)$$

$$Ni^{2+} + CO_3^{2-} \rightarrow NiCO_3\downarrow \quad (3)$$

The solubility product of $Ni(OH)_2$ – $2.0 \cdot 10^{-15}$, $(NiOH)_2CO_3$ – $3.0 \cdot 10^{-16}$, $NiCO_3$ – $1.3 \cdot 10^{-7}$, so it is preferable to use lime containing non-burnt fraction for the most complete recovery of nickel cations from the liquid phase. The use of alkalis, calcium, magnesium and sodium carbonates is less reasonable. For instance, in the case if Ni^{2+} concentration in water to be purified is around 25 mg/dm^3, the optimal dose of lime is 75 to 100 mg/dm^3 per active calcium oxide. The formed suspension can hardly be settled, so it is necessary to use coagulants to achieve settling [2].

In spite of the fact that $Ni(OH)_2$ exhibits definite solubility, the use of alkalis is reasonable for purification of solutions with high nickel content. As a rule, spent solutions from chemical nickel plating, acidic multi-metal solutions from copper refining works are treated with sodium hydroxide at pH from 10 to 11.5 [3, 4].

A method involving multiple contact of the precipitate, obtained after the alkaline treatment of nickel-containing solution, with the subsequent portions of the initial solution may be of interest. The reagent is introduced to achieve pH 9–13, and precipitation and settling are carried out at a temperature within the range from 30 to 100 °C. This allows enhanced nickel recovery in comparison with the standard alkaline treatment [5].

Another method of reagent precipitation of nickel(II) ions from solutions is their transformation into the sulphide form, which possesses even lower solubility product than hydroxide and carbonate forms – $3.2 \cdot 10^{-19}$. To achieve nickel precipitation in the form of NiS, sodium sulphide or hydrogen sulphide is used [6, 7]:

$$Ni^{2+} + S^{2-} \rightarrow NiS\downarrow \quad (4)$$

Nickel is transformed into the sulphide form with the indicated reagents at pH > 10, which is caused by the necessity to remove hydrogen sulphide from the liquid phase (dissolved or formed from sodium sulphide hydrolysis). To carry out precipitation at lower pH, it is recommended to fill the lower layers of granulated charge, which is used to capture nickel sulphide, with the sus-

pension of iron hydroxide. This provides binding hydrogen sulphide into the sulphides of iron(II) and (III) in neutral and alkaline media, respectively [8].

Nickel cations may be precipitated also in the form of NiS_2 by introducing the solution of sodium (or calcium) thiosulphate into the liquid phase in the amount of 110–130 % of the stoichiometric level. The process is carried out at 130–170 °C [9]:

$$4Ni^{2+} + 7S_2O_3^{2-} + 3H_2O \rightarrow 4NiS_2\downarrow + 6SO_4^{2-} + 6H^+ \quad (5)$$

Nickel precipitation in the form of disulphide may also be carried out using elemental sulphur within the same temperature range and at pH < 2, however, it will be necessary to add NiS_2 as the seeding into the solution; the amount of the seeding is 3 to 5 times larger than the amount of precipitating sulphide [10].

From the spent sulphuric acids of nickel plating, Ni^{2+} ions are reduced to metal nickel with the help of hydrogen. Temperatures about 200 °C and pressures of 24 to 31 bar are necessary for the process, so it is carried out in autoclaves [11]. Two-stage treatment with ammonia solution and hydrogen at a temperature of 80–180 °C and pressure 1–20 bar is more efficient [12]:

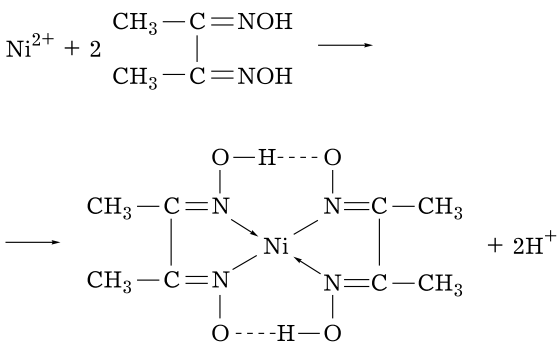
$$NiSO_4 + 2NH_3 \rightarrow Ni(NH_3)_2SO_4 \quad (6)$$

$$Ni(NH_3)_2SO_4 + H_2 \rightarrow Ni\downarrow + (NH_4)_2SO_4 \quad (7)$$

Nickel is recovered from the spent acidic hypophosphite solutions of nickel plating by adding a neutralizing agent, which is dry sodium carbonate, at a temperature of 55 to 65 °C and pH 6–7, and a catalyst – fine nickel powder. The recovered powder with a nickel content of more than 99 % may be used repeatedly as an initiator of precipitation [13, 14]:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Ni\downarrow + 2H_2PO_3^- + H_2\uparrow \quad (8)$$

A method of the purification of wastewaters from the plants of chemical nickel plating and nonferrous metallurgy with the help of alkaline dimethylglyoxime solution at pH 8–9 is known:



(9)

Thus formed nickel dimethylglyoximate is isolated from the aqueous phase using perfluorinated alcohol, and then separated from the latter in the obtained alcohol phase by distillation or flotation. Residual Ni^{2+} concentration is less than several tenths of mg/dm^3 [15]. The solubility product of nickel dimethylglyoximate ($Ni(C_4H_7O_2N_2)_2$) is equal to $2.3 \cdot 10^{-25}$.

A method which is similar in its essence involves the introduction of hydrogen peroxide, formaldehyde or soluble sodium polysulphide into the solution under treatment containing Ni^{2+} up to 1 g/dm^3 at a temperature of 105 °C. Thus, an acidic medium is created, which is suitable for the isolation of nickel oxide. Then dimethylglyoxime is added, at a ratio to Ni^{2+} ions from 2 : 1 to 5 : 1. The formation of nickel dimethylglyoximate is carried out at pH 7–11, so sodium or potassium hydroxide is added to increase the alkalinity of the solution. Unlike for the previous method, separation of reaction product is carried out using mechanical methods. The residual Ni^{2+} content is up to 1 mg/dm^3 [16].

The methods of reagent precipitation of Ni^{2+} ions from wastewaters and industrial solutions are rather simple in implementation because they allow obtaining insoluble metal compounds removed during settling and filtration. However, reagent methods do not always provide the necessary purification degree. In addition, their substantial disadvantage is the additional introduction of various chemical compounds into water under treatment, which leads to other problems, for example, those connected with high salt content, alkalinity or hardness.

SORPTION REMOVAL

The practical application of carbon-containing materials for the removal of Ni^{2+} from the liquid phase was not implemented in industry because of the very low sorption capacity of these sorbents with respect to metal ions. It was established in the tests of anthracite, coal, coke, semi-coke, thermally treated phytosorbents (wood chips, bark, lignin) that the capacity of these materials with respect to Ni^{2+} did not exceed 1.2 mg/g [17–19].

The sorption capacity of carbon sorbents with respect to Ni^{2+} may be increased through modification with water-insoluble organic agents interacting selectively with nickel (for example, dimethylglyoxime or acethydrazidine). Modification with the former reagent is carried out from a 10 % solution of sodium hydroxide and 96 % ethanol, while modification with the latter reagent is performed from a 40 % acetone solu-

tion, with subsequent drying of the sorbent to the constant mass. The sorption capacity of modified carbon sorbents in the neutral medium increases to 4 mg/g, and in weakly alkaline medium to 20 mg/g [1, 20].

Methods of nickel removal with aluminosilicate sorbents based on natural minerals and wastes from mining and concentrating plants are also known. The capacity of these sorbents with respect to Ni^{2+} varies within a broad range depending on the mineral composition: the capacity of natural zeolites of the type of clinoptilolite is up to 5 mg/g, aluminosilicate clays composed mainly of montmorillonite – up to 30 mg/g, materials based on glauconite – about 8 mg/g, gaize – about 3 mg/g [21–26].

A promising direction is purification of nickel-containing solutions with the help of modified aluminosilicate sorbents allowing the removal of metals ions within a broad range of pH without changes in the salt composition of the liquid phase. Thus, for instance, the sorption capacity of natural zeolites with respect to Ni^{2+} ions increases to 94 mg/g after treatment with the solution of hexamethyldisilazane in toluene [27]. However, this modifying agent is not easily available, which makes industrial-scale production of sorbents on this basis insufficiently profitable. Chitosan in a more available modifying agent. Clinoptilolite-based sorbent treated with chitosan exhibits sorption capacity up to 250 mg/g [28]. There are examples of the use of polyvinylimidazole and polyvinylpyridine as modifying agents for natural aluminosilicate materials. It is established that the Ni^{2+} sorption capacity of the sorbents treated with these compounds is three times higher than that of the initial materials, however, it is not high in comparison with the previous examples: 15–17 mg/g [29]. It is also known that modification of natural zeolites with phosphoric acid may allow achieving a two-fold increase in their sorption capacity [30].

It was experimentally demonstrated in a number of works that the transformation of natural sorbents from Mg^{2+}- and Ca^{2+}-forms into the Na^{+}-form is accompanied by a substantial increase in their capacity and the degree of Ni^{2+} removal [31–33]. This is due to the fact that the substitution of Na^{+} by Ni^{2+} ions proceeds with lower energy consumption in comparison with similar processes for Mg^{2+} and Ca^{2+}. To transform the sorbent into Na^{+}-form, the sorbent is subjected to acid and alkaline treatment, and then kept in the solution of sodium chloride. The limiting sorption capacity of the sorbents based on montmorillonite and glauconite after this modification reaches 50 mg/g with respect to Ni^{2+}. Further modification of the mineral sorbents in the Na^{+}-form is also possible, for example, through intercalation of sodium aluminate, which promotes an increase in the capacity with respect to nickel to 180 mg/g [34].

Among the wastes from mining and concentrating plants suitable for nickel removal from wastewaters, it is necessary to mention the tailings from copper-nickel ore concentrating, which are composed of 60 % serpentine. These tailings are annealed at 650–700 °C, and then modified with the ethanol solution of dimethylglyoxime by means of noncovalent immobilization, which allows an increase in the capacity of the sorbent with respect to Ni^{2+} ions up to 4 times – to 190 mg/g in the neutral and alkaline media [35].

Nickel forms strong water-insoluble compounds with the ions of sulphur (sulphides) and stable complexes with sulphur-containing ligands, so it is reasonable to introduce sulphur atoms into natural zeolites in order to increase their sorption capacity with respect to metal ions. The following method is used for this purpose: dissolution of sulphur in the system hydrazine hydrate - monoethanolamine; introduction of zeolite into the solution (a 5-fold excess with respect to sulphur); treatment of the mixture with trichloropropane; filtration, washing, and drying of the product. As a result, macro- and mesopores of the network of sulphur-containing polymer are formed on the zeolite surface, and its capacity with respect to Ni^{2+} reaches 500 mg/g [36, 37].

The basis for the deposition of sulphur-containing polymer may be granulated sorbents formed as a result of the interaction of elemental sulphur with sodium hydroxide in the aqueous solution with hydrazine hydrate, followed by polycondensation in the presence of chlorinated lignin and organochlorine wastes from the production of epichlorohydrin. The capacity of the sorbent with respect to Ni^{2+} ions is 330 to 450 mg/g [38].

Among natural minerals for Ni^{2+} removal from liquid media, a promising one is brucite, which is composed mainly of magnesium hydroxide. Under comparable application conditions, the sorption capacity of this mineral is several ten or several hundred times higher than that of other natural mineral and carbon sorbents. Non-equivalent sorption of Ni^{2+} and other heavy metal ions by brucite is due to ion-exchange adsorption and chemisorption, characterized by the substitution of Mg^{2+} ions in mineral structure by metal cations, rupture of chemical bonds on mineral sur-

face and the appearance of hydroxyl groups on side facets, the formation of aqua and hydroxo complexes through metal ion attachment to free OH-groups. The sorption capacity of brucite with respect to Ni^{2+} ions reaches 190 mg/g, but it may be increased by a factor of 3.5–4 by means of thermal modification of the mineral: annealing at 600–700 °C for 1 h. An optimal temperature for nickel sorption on brucite is 20 to 30 °C [39]. Brucite demonstrates the highest efficiency for the recovery of Ni^{2+} ions from chloride solutions rather than sulphate ones. The mineral is known to be more selective to copper and zinc ions, so in the case of their presence in solutions under treatment in significant amounts, nickel removal may be hindered [40, 41].

A method to purify waste and rain waters from Ni^{2+} ions using a suspension of alkylcarboxysiloxanes is known. This mixture is obtained as a result of the interaction of fine silicates in the aqueous medium with the organic modifying agent in the presence of a catalyst. The formed insoluble colloid structure contains carboxylic groups and possesses developed surface due to the small radius of reagent particles [42].

Natural and synthesized magnetic iron oxides may be adsorbents of nickel. To transform the natural iron oxide into its magnetic form, it is to be treated with aniline and sulphuric acid, with subsequent annealing at 800 °C. The synthesized magnetic iron oxide is obtained by precipitation from the solution of iron(II) sulphate and iron(III) chloride with the help of ammonium hydroxide at 100 °C. The maximal capacity of magnetic iron oxides with respect to Ni^{2+} ions reaches 250 mg/g [43].

There are also sorbents with a broad range of action, combining the properties of carbon and mineral materials, however, without additional modification they possess not very high capacity with respect to Ni^{2+} ions. For instance, a carbon-mineral sorbent composed of zeolite, active coal, bentonite clay and thermoreactive synthetic organic material (phenol-formaldehyde resin, resol, aminoplastics, *etc.*) after thermal treatment at 750 °C in carbon dioxide flow exhibits the capacity with respect to Ni^{2+} about 35 mg/g [44]. The sorbent obtained by thermal treatment of sapropel at 350 °C is characterized by the capacity with respect to metal ions up to 50 mg/g [45].

The sorbents that have become most widespread in the sorption removal of nickel are synthetic ion exchange resins possessing an essential advantage over most mineral sorbents: the possibility of multiple regeneration and repeated use.

For a long time, macroporous weakly acidic cation exchange resins with polyacrylic matrix and carboxylic functional groups (SG-1, KB-4P, KM-2P, *etc.*) have been used in homeland practice to remove Ni^{2+} ions from wastewaters and technological solutions. This type of resin exhibits low selectivity to Ni^{2+}, so currently its removal from aqueous media is carried out using other ion exchange resins.

Efficient sorbents for deep removal of Ni^{2+} are chelate ion exchange resins with the functional groups of iminodiacetic acid on the basis of a matrix composed of cross-linked polystyrene (Lewatit MonoPlus TP 207, Purolite S930, Amberlite IRC 748, Chelex 100, ANKB-35). It has been established that these resins demonstrate the highest efficiency within pH 4–5 at 40 °C. For Lewatit MonoPlus TP 207, depending on the conditions of sorption studies, the exchange capacity with respect to Ni^{2+} ions occurs to be within the range from 74 to 157 mg/g; under the optimal conditions, the limiting capacity of Purolite S930 reaches 150 mg/g, Chelex 100 – 126 mg/g, ANKB-35 – 116 mg/g [46–50]. The higher is the percentage of iminodiacetate groups in the cation exchange resin, the higher is its exchange capacity in an acid medium. The ANKB-35 ion exchange resin exhibits the lowest capacity with respect to Ni^{2+} because it contains glycine and amine groups.

It is stated in some studies that cation exchange resins, similar to Lewatit MonoPlus TP 207, are most efficient within pH 4.5–5.5, while in the neutral and weakly alkaline media (pH 7–9) it is reasonable to use macroporous weakly acidic ion exchange resins with the functional groups of carboxylic acids, based on cross-linked polyacrylate, for example, Lewatit CNP 80 with the exchange capacity with respect to Ni^{2+} ions up to 135 mg/g [51].

Strongly acidic macroporous cation exchange resins are less frequently used in the processes of nickel removal than weakly acidic ones, which is explained by their low selectivity to metal ions and a decrease in the capacity under the conditions of increased mineralization. These resins are suitable for the sorption of Ni^{2+} ions from solutions with low salt concentration and pH close to neutral. An example of the sorbents of this kind is a cation exchange resin with the functional groups of sulphonic acid based on the matrix of cross-linked polystyrene – Lewatit MonoPlus SP 112. Its maximal capacity with respect to Ni^{2+} ions is 171 mg/g [52].

Weakly basic ion exchange resins are also sometimes used to remove nickel. One of the rep-

resentatives of this class of resins is Dowex M4195 with bispicolylamine chelate groups grafted to the matrix of cross-linked polystyrene. Its exchange capacity with respect to Ni^{2+} ions is relatively low – about 59 mg/g, however, this sorbent is able to remove the ions from solutions with extremely low pH – about 1 [53]. An analogue of Dowex M4195 is Lewatit MonoPlus TP 220 [54]. Another example of weakly basic cation exchange resins suitable for the sorption of nickel ions is Purolite S950 with the chelate groups of aminophosphonic acid and a capacity of up to 160 mg/g [55].

It follows from the above-described facts that macroporous resins are most frequently used in the processes of sorption removal of nickel. Ion exchange resins of the gel type are less frequently used because they are characterized by the low rate of ion exchange. An example of these resins is Amberlite IR120 – a strongly acidic cation exchange resin with the functional sulphonic groups on the basis of cross-linked polystyrene; its maximal capacity with respect to Ni^{2+} reaches 161 mg/g [56]. Its analogue is Dowex HCR-S resin with the capacity with respect to Ni^{2+} up to 156 mg/g [57]. The optimal pH range for the application of these ion exchange resins is 4–6.

Among ion exchange resins synthesized under laboratory conditions and not yet manufactured on the industrial scale, attention should be paid to the following ones (capacity with respect to Ni^{2+} is indicated in parentheses): 1) based on glycidyl derivatives of aromatic compounds and polyvinylpyridine (60 mg/g); 2) based on hydrolyzed polyacrylonitrile and epichlorohydrin (55 mg/g); 3) based on polyvinyl chloride granules modified with amines and subsequent treatment with phosphoric acid in the presence of formaldehyde (132 mg/g); 4) based on salicylic acid condensed with pyrocatechol in the presence of formaldehyde (96 mg/g); 5) based on cross-linked polyvinylpyridine with the grafted groups of diphenylthiocarbazone (35 mg/g); 6) based on styrene-furfurol polymer with phosphoric acid groups (106 mg/g) [58–64]. In the latter case, its high selectivity to Ni^{2+} ions in the presence of Cu^{2+} and Co^{2+} is of interest.

It is known that nickel removal may be carried out not only by grained sorbents but also with fibrous ion exchange materials. The major advantages of these sorbents in comparison with the former ones are the possibility to work at high flow rates, low hydraulic resistance, more intense sorption kinetics due to the small diameter of elementary fibres, high mechanical stability, diversity of shapes (braid, cloth, yarn, nonwoven materials) [65]. Disadvantages that currently limit their broad application include complicated synthesis, inhomogeneity of the distribution of functional groups over fibres, limitations for application in terms of pH, mineralization, and the content of suspended matter in the solutions.

Among commercial fibrous ion exchange materials, those used to remove nickel include Fiban Kh-1, which is manufactured from polypropylene and nitrone fibres modified with the functional groups of iminodiacetic acid. Its exchange capacity with respect to Ni^{2+} ions is 137 mg/g, which is higher than the values characteristic of the majority of grained ion exchange materials with the same groups [66]. Another example of fibrous ion exchange materials is Vion KN-1 with carboxylic functional groups, with capacity with respect to Ni^{2+} up to 106 mg/g [67].

It is possible to remove nickel from aqueous media using a fibrous complexite based on a copolymer of polycaprolactam and polyglicydylacrylate containing hydrazide groups, and the material based on polyacrylonitrile with amino and carboxylic groups. The exchange capacity of the former with respect to Ni^{2+} ions is 112, while the capacity of the latter is 125 mg/g [68, 69].

The methods of sorption removal of nickel from wastewaters and technological solutions have currently won broad application, which is connected with the possibility to use the filtering material repeatedly after regeneration, and with the high efficiency of ion removal (down to the limiting permissible concentrations). However, there are some limitations connected with their use: the necessity of preliminary treatment of water to be processed (ion exchange materials are sensitive to the presence of oil products, and mineral sorbents conserve their operation ability within rather narrow pH range) and low efficiency in purification of strongly contaminated solutions.

EXTRACTION REMOVAL

In the case of relatively high content of Ni^{2+} ions in industrial wastewaters and technological solutions, an efficient method of purification is extraction. The methods of extraction-based joint removal or separation of nickel and cobalt are most frequently described in publications. This is due to the fact that both these metals are very similar to each other in their properties, and their compounds exhibit similar solubility in liquid media. In the case of the joint removal of nickel and cobalt, it is sufficient to choose

only one type of extractant, while two extractants with different selectivities with respect to these metals are necessary for their separation.

A known extractant used for nickel recovery is Cyanex 272 – bis(2,4,4-trimethylpentyl)hypophosphorous acid. In the case of the joint presence of Cu^{2+}, Co^{2+} and Ni^{2+} ions in the solution under treatment, their fractional selective extraction with gradual variation of pH values is applied: for Cu^{2+} – from 4 to 5, for Co^{2+} – from 5 to 6, and for Ni^{2+} – from 6 to 7. With optimal process conditions maintained, nickel removal reaches 99.8 % within not longer than 30 min [70]. Cyanex 272 and TOPS-99 (the sodium salt of di-2-ethylhexyl-phosphoric acid) in kerosene, with the sequential introduction into a nickel-cobalt solution, allow achieving the degree of nickel recovery into TOPS-99 up to 99.8 % [71]. The data on the efficiency of Cyanex 272 and LIX 84-1 (2-hydroxyl-5-nonyl acetophenone oxime) in synthin for the joint removal of nickel and cobalt at pH ~ 4.5 are reported [72].

The TOPS-99 extractant is a derivative of widely used di-2-ethylhexylphosphoric acid (D2EHPA), which is used mainly in synergic mixtures. Among the mixtures suitable for nickel removal, it is necessary to distinguish D2EHPA and Cyanex 272; D2EHPA and Mextral 84 (an analogue of LIX 84-1); D2EHPA and palm oil in octanol. Nickel removal with the help of the indicated mixtures exceeds 90 % [73–75].

Another organophosphorous reagent suitable for the joint removal of nickel and cobalt is Cyanex 301 based on bis(2,4,4-trimethylpentyl)dithiohypophosphorous acid. A mixture of Cyanex 301 with trialkyl amine and tributyl phosphate allows one to achieve nickel and cobalt removal of more than 98 % within the pH range from 6.2 to 6.8 [76, 77].

Among carboxylic acids, it is necessary to mention 2-ethyl-2,5-dimethylhexanoic (neodecanoic), or Versatic 10. With the help of a synergic mixture of Versatic 10 with alkyl pyridines at the pH ~ 5.8, the joint removal of Ni^{2+} and Co^{2+} exceeds 99 % [78]. It is reasonable to use a mixture of Versatic 10 with Cyanex 272 at pH ~ 5 to extract these impurities from hydrochloric and nitric media [79]. It has been determined that neodecanoic acid forms a synergic mixture with LIX 63 (5,8-diethyl-7-hydroxydodecane-6-oxime) in tributyl phosphate [80]. In comparison with other extractants, a disadvantage of Versatic 10 is its high solubility in water (0.5 g/dm^3).

There are methods of nickel removal from sulphate solutions with high calcium and magnesium content at pH 6.1–6.5 with the help of isocarboxylic acids with not less than 5 carbon atoms per molecule, in a diluter (decane, kerosene, oil paraffins, *etc.*) and in the presence of co-extragent LIX 54 (1-phenyl-1,3-decanedione). The removal of Ni^{2+} was not less than 99.7 % within 1 h for 2–3 steps of extraction [81].

Selective extraction of nickel from acidic solutions containing the ions of other metals may be carried out with the hydrazides of ternary carboxylic acids with 10 to 19 carbon atoms per molecule in organic diluter (kerosene, nonane) with the addition of 2-ethylhexanol. With the use of this mixture, the process takes place rather efficiently and rapidly: Ni^{2+} removal at a level of 99 % is achievable within the first 5–10 min [82].

Among fatty acids, oleic acid is frequently used. A method of Ni^{2+} extraction with a mixture containing the indicated acid, triethanolamine and engine oil at pH ~ 8 for 2 h is known. The limiting nickel removal with the help of this method is 80.6 % [83]. This method takes rather long time and is sensitive to pH variation. Replacement of engine oil by kerosene or petrol allows eliminating these disadvantages: extraction proceeds within 5 min, and the working pH range broadens from 5 to 9. Kerosene is preferable over petrol: Ni^{2+} removal with the help of the former reaches 96.6 %, while it is only 76.2 % when the latter diluent is used [84].

Extraction of Ni^{2+} ions together with other heavy metal ions by a mixture of humic acids and isoamyl alcohol at pH 7–9 is promising. The process takes place within the first 5 min, and the maximal Ni^{2+} removal, equal to 77.8 %, occurs at pH 8.8. The ions of other metals are better removed: Cu^{2+} – up to 95 % (at pH 8.6), Zn^{2+} – up to 93.5 % (at pH 8.2) [85]. The use of humic acids as extractants is attractive due to their safety for human health and for the environment..

Ketones are less frequently used in extraction processes, which is due to their high cost in comparison with traditional extractants. Among the known compositions, an example of a mixture of pentane-2,4-dione (acetylacetone) and 4-phenylbutane-2,4-dione in chloroform may be mentioned. Extraction lasts for 30 min, and Ni^{2+} removal is 98 % [86].

The above-described examples relate to liquid extraction, when the solution under treatment and the extractant are in direct contact with each other. During the recent 15–20 years, attention has been drawn to materials combining the properties of solid sorbents and liquid extra-

gents: impregnates and solid extractants (SOLEX). The former agents are obtained by impregnating a porous sorbent matrix (activated carbon, silica gel, organic and mineral carrier materials) with the extractant, while the latter are prepared by the introduction of the extractant during the synthesis of the polymer matrix. A characteristic feature of impregnates and solid sorbents is the absence of chemical bonding between the extractant and the matrix, which provides the mobility of the liquid phase in the solid one [87, 88].

For Ni^{2+} removal from sulphuric solutions, impregnate based on the ion exchange resin Amberlite 200 with D2EHPA is used, with grain surface treated with sodium dodecyl sulphate for hydrophobization [89]. In addition to macroporous resins, this extractant is used to impregnate natural and synthetic fibres; LIX 860 (5-nonylsalicylaldoxime) is added to it to increase the efficiency of Ni^{2+} ions [90]. For the joint removal of Ni^{2+} and Co^{2+}, it is possible to use impregnate based on Lewatit TP 272 with Cyanex 272, which is efficient within pH range from 5.0 to 5.5 [91]. A carrier for Cyanex 272 may also be polystyrene granules [92]. Impregnates based on macroporous resins and Cyanex 301 are in use [93]. An example of the solid sorbent may be a material obtained through the synthesis of styrene-divinylbenzene matrix in the presence of Cyanex 272; this material allows separation of Ni^{2+} and Co^{2+} ions in nitrate and ammonia solutions [94].

The methods of extraction removal of Ni^{2+} from wastewaters and solutions are attractive by their low working temperatures, the possibility of selective removal of metal ions into the extractant phase, simplicity of apparatus arrangement and automation. However, they are efficient and economically reasonable at high Ni^{2+} content (several hundred mg/dm^3 and higher). In addition, many extractants are toxic compounds, and it is difficult to separate them from the aqueous phase.

MEMBRANE SEPARATION

Among the membrane methods for purification of wastewaters and technological solutions, baromembrane methods are in the highest demand: micro-, ultra-, nanofiltration, and reverse osmosis. Because of rather large pores, micro- and ultrafiltration membranes (0.1–100 and 0.01–0.1 μm, respectively) are inefficient for purification of waters and solutions from Ni^{2+} ions without preliminary transformation of the ions into insoluble forms. Nanofiltration and reverse osmosis membranes (with pores 0.001–0.01 and 0.0001–0.001 μm in size, respectively) cope with this problem, however, it is necessary to maintain pH of the aqueous phase within the range from 4 to 9 (the optimal range being 6 to 8), and preliminary treatment of the waters and solutions under treatment is necessary by means of mechanical, sorption purification, the addition of antiscalant and biocide.

Some regularities were established at the Mendeleev University of Chemical Technology of Russia during the development of a combined technology of wastewater purification from heavy metal ions (Ni^{2+}, Cu^{2+}, Co^{2+}), which included the stages of flotation, ultra- and nanofiltration, as well as reverse osmosis. First of all, an essential factor determining the degree of solution purification from metal ions on ultrafiltration membranes is pH. With its increase to the values at which insoluble hydroxides are formed, the degree of metal removal also increases and may reach 90–99 %. Second, the selectivity of nanofiltration membranes grows with an increase in the surface charge. For instance, it was demonstrated by the example of polyamide membranes Vladipor ERN-B-45-300 and Filmtec NF 270-400 that the selectivity of the former membrane to the salts of heavy metals is higher than the selectivity of the latter, as the average surface charge of the former membrane is −3.3, compared to −6.9 mC/m^2 for the latter membrane. The minimum of the selectivity of nanofiltration membranes coincides with the isoelectric point (at pH 5.4 for polyamide membranes). Third, the selectivity of reverse osmosis membranes increases with the introduction of Na^+, K^+, Ca^{2+} ions and divalent cations with larger heat of hydration into the system. The charge-related phenomena on membrane surfaces have a less significant effect on the removal of impurities in reverse osmosis than in nanofiltration [95, 96].

As an alternative to sorption for purification of rinsing waters of galvanic works from the ions of heavy metals, a technology has been developed at the JSC KhK Barnaultransmash (Barnaul), which involves microfiltration, sorption on a carbon sorbent, and a two-step reverse osmosis on acetate cellulose membranes. In the neutral medium, their membranes exhibit an increase in selectivity to Ni^{2+} from 76 to 98 % with an increase in pressure from 0.2 to 1 MPa, while within the range from 2 to 4 MPa a drop to 88 % is observed. In the acid medium, the selectivity of membranes

to Ni^{2+} decreases from 92 to 75 % with an increase in pressure from 0.2 to 1 MPa, while within pressure range 3 to 4 MPa – down to 55 %. This is evidence of ion penetration through the membrane when a definite pressure is reached [97].

At some machine building plants of Russia (SPO Arktika (Severodvinsk), AK Rubin (Balashikha), Orbita (Voronezh), Severniy Press (St. Petersburg), *etc.*), purification of waste and recirculating water from heavy metals is carried out with the help of the technology that combines pH correction, electroflotation, ultrafiltration, and reverse osmosis. For initial Ni^{2+} content in water under treatment from 5 to 30 mg/dm^3, the efficiency of its removal at the stage of electroflotation is 96 to 98 %, which provides a substantial decrease of the load on membranes. At the stage of ultrafiltration, 80 to 94 % of the residual amount of nickel is removed [98].

To purify mine waters from the ions of nonferrous metals, iron, manganese, a technology was tested at ISC Uralelektromed (Verkhnyaya Pyshma) which combined ultrafiltration on the membranes composed of polyvinyldifluoride (Microza UNA 620A) and reverse osmosis on the membranes made of polyamide (Filmtec BW30-4040). At neutral pH, iron is efficiently separated at the stage of ultrafiltration, while complete removal of Ni^{2+}, Mn^{2+} and other metal ions with the efficiency of more than 99 % proceeds at the stage of reverse osmosis. In the case of the addition of $KMnO_4$ before ultrafiltration, oxidation of Mn^{2+} ions with the formation of readily trapped suspension of MnO_2 occurs. Manganese removal with the help of reverse osmosis is favourable for an increase in the selectivity of membranes to Ni^{2+} ions [99].

An interesting practice is the integration of micro- and ultrafiltration membrane modules into flotation chambers, which is a technology developing abroad. In systems of this kind, water is initially treated with a reagent that transforms Ni^{2+} and other metal ions into insoluble forms. Parallel emergence of the suspension on the surface and filtration of its residual amounts from solution volume take place in the flotation membrane chamber. The high degree of purification from metals (>90 %) is observed when pH corresponding to the formation of metal hydroxides occurs. Air bubbles rising upward remove the precipitate from the membrane surface, thus increasing the filtration cycle of the latter [100, 101]. The use of flotation-membrane purification together with electroflotation allows removal of Ni^{2+} ions with the efficiency of more than 95 %, with a decrease in the necessary current from 1.6 to 1.2 A [102].

The main problem with reverse osmosis and nanofiltration is utilization of the concentrate: its yield from the step may vary from 20 to 60 %, depending on the salt content in initial water or solution. To decrease the yield of concentrate to 2–5 %, it is reasonable to perform membrane purification in several stages, and direct the final concentrate to the recovery of valuable impurities (by sorption or precipitation) and evaporation with the removal of salts [99]. A technological decision of this kind was implemented within the integrated technology of the purification of wastewater from nickel plating at the ZAZS plant (Engels), which includes three-step reverse osmosis, reagent treatment and evaporation of the concentrate. After reagent treatment, a precipitate is formed, which is suitable for use as a nickel-containing raw material [103].

Membrane methods for the purification of wastewaters and solutions possess some advantages in comparison with the traditional methods: high efficiency, the absence of secondary pollution, universal nature, and high degree of automation. Shortcomings include the sensitivity of membranes to pH, temperature and the presence of impurities leading to the formation of deposits and films, low rate and high cost of purification, in particular because of the price of membranes and the necessity to utilize the concentrate.

FLOTATION REMOVAL

The reagent that is frequently used as a collecting agent for flotation removal of Ni^{2+} from diluted aqueous solutions is sodium dodecyl sulphate (anionic surfactant), which allows concentrating metal ions into a foamy product with the efficiency not less than 95 % at pH ~ 9. To achieve the largest separation coefficient (170), it is sufficient to carry out flotation for 3 min [104, 105]. In the acid medium (pH ~ 3), sodium dodecyl sulphate may be used in combination with dimethyldioctadecylammonium bromide (collecting agent), Dowfroth 250 (ester of polypropyleneglycolmethyl acid) and methyl isobutyl ketone (both are foam-forming agents). The degree of Ni^{2+} removal from acid solutions reaches 88 % [106].

A known method of flotation purification of solutions from the ions of nickel, other nonferrous metals and iron is carried out in one stage at pH 7.5–8 using a mixture of the hydrazides of

higher carboxylic acids with 6 to 8 carbon atoms in the aliphatic chain as the collecting agent. The flotation reagent of this kind is introduced into solution in the form of a 0.5 % aqueous emulsion prepared with the addition of hydrochloric acid at the equimolar ratio; sufficient flotation time in this case is 5 min [107].

Efficient removal of Ni^{2+} ions, as well as Co^{2+} and Cu^{2+}, from ammonia solutions through flotation with N-(2-hydroxyethyl)alkyl amines (for example, N-(2-hydroxyethyl)dodecyl amine) has been reported; the most complete transition of metal ions into the foamy product occurs within pH 10.6–11.3 [108].

To remove Ni^{2+} from alkaline solutions, Sintamid-5 is used. This non-ionogenic surfactant is a mixture of polyoxyethylated esters of monoethanolamides of fatty acids from coconut oil, with 7 to 17 carbon atoms in the aliphatic chain. The maximal removal of metal ions was achieved at pH ~ 11 for 10 min [109].

The most efficient removal of Ni^{2+} from wastewaters and solutions occurs in the majority of cases within pH range corresponding to the formation of insoluble nickel hydroxide, so, a coagulant (iron or aluminium compounds) and a flocculant are preliminarily added into the liquid phase in order to intensify flotation and decrease the consumption of flotation agent. For example, it is reasonable to introduce coagulating agent in the form of colloid $Fe(OH)_3$ at pH ~ 11 and polyacrylamide flocculant (for example, anionic Praestol 2530) before flotation with sodium oleate and pine oil in Jameson machine to treat wastewaters containing the ions of Ni^{2+} and other nonferrous metals (Cu^{2+}, Zn^{2+}); this method provides ion removal at a level of 98 % [110].

To enhance the degree and rate of the removal of Ni^{2+} and other nonferrous metal ions, purification of wastewaters and solutions is frequently carried out sequentially in coagulating units and in pneumatic column-type flotation devices. It is established that with schemes of this kind the duration of flotation purification decreases to 2–3 min, the consumption of reagents decreases by a factor of 2–3 in comparison with usual ion flotation, and the degree of metal removal is not less than 98 %. Flotation reagents in schemes of this type may be 2–5 % aqueous solutions of a sodium soap of synthetic fatty acids with not less than 21 carbon atoms in the chain (85–95 wt. %), alcohols of pyran and dioxane series (5–15 wt. %) [111, 112].

Among the new types of flotation reagents, it is necessary to mention a nanocollector of Ni^{2+}, which is an amino-functionalized graphene oxide (AFGO). In addition to AFGO, 2,6-aminopyridine is introduced to create a negative charge and to improve the recovery of positively charged ions. The formation of coordination bonds between Ni^{2+} and AFGO occurs at pH ~ 9. The declared efficiency of metal removal into foamy product reaches 100 % [113].

A very promising flotation reagent for wastewater purification from Ni^{2+} ions and other nonferrous metals is the agent based on polyethylene waste, which is dissolved in glycerol at a ratio from 1 : 1 to 1 : 3. As a result, polyethylene undergoes destruction with the formation of compounds containing nucleophilic reaction centres: hydroxyl, ester, carboxyl groups, as well as aromatic structures. The molecules of destruction products form chelate complex compounds with Ni^{2+} ions. Technogenic water is subjected to flotation with this mixture for 5 min at pH 7–8 to obtain a foamy product [114].

A definite interest for flotation removal of Ni^{2+} may be represented by mixtures based on mono- or disaccharides (glucose, fructose, saccharose) in the concentration of 25–50 wt. %, amines (methyl amine, ethylene diamine, polyethylene diamine, butane diamine) in the concentration of 15–45 wt. %, ketones (acetophenone, methylacetone, calone) in the concentration of 15–65 wt. %. The introduction of this mixture into water under treatment at a ratio of 1 : 100 to 1 : 1000 allows achieving 99.9 % Ni^{2+} recovery into foamy product [115].

During recent years, studies have been carried out abroad for the purpose of searching for alternative flotation reagents possessing biodegradability, safety for human health and for the environment. These reagents include a surfactant obtained as a result of the reaction of cysteine with octanoyl. The product of this synthesis is well soluble and forms foam within a broad pH range. It allows removal of 97 to 99 % Ni^{2+} and other heavy metal ions, arsenic per one flotation stage [116].

Ion flotation is sometimes combined with liquid extraction, and the combined process is called flotoextraction. The admixture to be removed is thus concentrated within a thin layer of organic solvent on the surface of the aqueous phase, which simplifies its further isolation to obtain a rather pure commercial product. Classical columns and one-chamber flotation machines are used for flotoextraction.

An example of a flotoextraction process may be the treatment of water and solutions with sodium dodecyl sulphate in mixture with heptanoic acid. An optimal pH for this treatment is 9, similarly to the case of ion flotation. The yield of nickel into the final product exceeds 95 % [105].

To remove metal ions from diluted technological solutions (with Ni^{2+} concentration of about 1 g/dm^3), flotoextraction is carried out with the solution of naphthenic acid in kerosene at pH within the range from 8.0 to 8.3. The resulting nickel naphthenate in the foamy product enters the stage at which the aqueous and organic phases are separated: the former is washed with kerosene and directed to crystallization to obtain nickel (II) sulphate; the latter is washed from impurities with sulphuric acid, and then nickel is re-extracted at pH 3.5–4, after which naphthenic acid is regenerated. This kind of combination of flotation with extraction allows obtaining commercial nickel(II) sulphate [117].

Questionless advantages of flotation methods, in particular ion flotation, are simplicity and efficiency, low energy consumption, low residual concentrations of metal ions, high process rate, small size of the apparatuses, the formation of a small volume of precipitate, and good compatibility with other purification methods. However, it is unreasonable to use flotation methods in the case of high Ni^{2+} ion content in the medium under treatment. In addition, many flotation reagents are toxic substances. One of the major problems with flotation purification is regeneration of the collecting agent because it may form strong complex compounds with the metal to be removed.

ELECTROCHEMICAL PURIFICATION

Electrochemical methods for the purification of industrial solutions and wastewaters from nonferrous metals are actually among the most widespread physicochemical methods. Electrochemical methods include electrocoagulation, galvanocoagulation electroextraction, electroflotation, electrodialysis.

Electrocoagulation purification of water and solutions form nickel is carried out using aluminium or iron electrodes at ion concentration not less than 0.15 mg/dm^3. For instance, in the tests of the method with solutions containing 10–50 mg/dm^3 Ni^{2+}, the highest removal (>96.5 %) is achieved at pH 7.6, and current density 6–9 A/m^2 for 10 min. The adsorption capacity of the formed flakes of aluminium hydroxide with respect to metal ions is 310 mg/g [118, 119].

Using a pair of electrodes made of iron and aluminium, with monopolar configuration, for the purification of wastewaters from electrochemical nickel plating, one may achieve the efficiency of Ni^{2+} removal about 98 %, and the ions of other nonferrous metals (copper, chromium) – about 99 %, at lower pH (~3). The current density necessary to achieve these parameters increases to 100 A/m^2, while the sufficient electrocoagulation time is 20 min. The standard energy consumption for the purification of this kind of wastewater is 10.1 (kW · h)/m^3, and electrode metal consumption is 1.08 kg/m^3 [120].

Within the alkaline pH region (8–10), for instance, in cyanide wastewater from galvanic works, with iron electrodes at the current density of 10 A/m^2, one may achieve Ni^{2+} removal about 90 % within 60 min; with an increase in the parameter to 60 A/m^2 the efficiency of cation removal is 99.1 % within 80 min. in the latter case, the most complete purification of wastewater occurs also with respect to cyanides: by 99.7 %. It was established that the need for longer purification of nickel cyanide solutions at high current density is connected with practically 10-fold deceleration of nickel deposition due to the formation of its complex with cyanides. This also affects specific energy consumption. Thus, for Ni^{2+} ion content in solution of about 20 mg/dm^3 in the case of the absence of cyanides, the parameter is equal to 1.36 (kW · h)/m^3, and in the case of cyanide presence it is 4.8 (kW · h)/m^3 [121, 122].

Within the neutral pH range, nickel removal up to 99.9 % may be achieved with the help of iron electrodes in mono- and bipolar configurations, at initial metal ion concentration in solution 250–500 mg/dm^3. The optimal duration of electrocoagulation under these conditions is 25 min. An increase in contact time leads to voltage drop because of the formation of deposits on cathodes [123].

Unlike electrocoagulation, galvanocoagulation is carried out without applying an external electric power source, just due to the formation of a short-circuited galvanic couple by introducing current-conducting materials into the solution to be purified. The mixtures that are mainly used for nickel deposition are: iron–coal, aluminium–coal. The process is carried out in galvanic coagulators of column, cylindrical and oscillatory types. The latter is considered to be the most efficient apparatus because no passivation of the galvanic couple elements and no cementation occur during its operation [39]. The degree of solution purification from nickel increases in the

case if the ions of other heavy metals are present, as well as with an increase in pH and the temperature of the liquid phase. Galvanocoagulation is most efficient for Ni^{2+} content up to 100 mg/dm^3 [124].

The possibility to deposit up to 99.7 % nickel in the form of compound $NiO \cdot Fe_2O_3$ within 20 min at the initial metal ion content of about 30 mg/dm^3 was demonstrated for the use of a mixture of iron chips and graphite at a mass ratio of 4 : 1 with air bubbling. The efficiency of solution –purification from the ions of other metals (copper, zinc, cadmium, cobalt, chromium) reaches 99.9 % if their initial concentrations are within the range from 80 to 130 mg/dm^3 [125]. It was determined experimentally that in the case if an iron–coal mixture at a ratio of 4 : 1 is used, it is reasonable to recirculate the formed precipitate in the amount of 5–7 % of the volume of wastewater entering the process, which allows a two-fold decrease in purification time due to the formation of larger flakes of iron metahydroxide [126].

Galvanocoagulation is suitable for nickel removal in the case of substantially lower initial concentrations: several tenths of mg/dm^3. This may be relevant for the purification of wastewaters with low pollution degree, for example, before the stage of sorption purification, for the purpose of increasing the filter cycle of the load. Thus, for Ni^{2+} content of about 0.5 mg/dm^3 and total content of nonferrous metals about 8 mg/dm^3, the efficiency of nickel deposition with the help of a mixture of aluminium chips with activated carbon at a mass ratio of 3 : 1 reaches 80 % within 30 min [127, 128].

In schemes with the flow-through purification of water (solution) from heavy metal ions in a galvanocoagulator, an optimal range of the linear flow rate through the iron–coal and aluminium–coal loads is 0.5 to 1.5 m/h [127].

In some technological flowcharts, a galvanocoagulator is used to prepare the pulp, to be directed to a separate reactor into which water under treatment is also supplied. Direct contact of water with scrap is excluded in these flowcharts, which is reasonable in the case of high flow rates. In this case, it is advisable to provide ultrasonic treatment of the pulp at the outlet of the galvanocoagulator at about 25 kHz with the intensity of 30–40 V/cm^2. As a result, particle size in the pulp decreases from 8.5 to 5 μm. This causes an increase in the specific surface of the solid phase and, as a consequence, an increase in sorption capacity, which allows a decrease in the duration of water (solution) purification in the reactor by 20–25 % and increase in the efficiency of impurity removal by 10–15 % [129].

Electroextraction of Ni^{2+} from aqueous media is possible with the use of cathodes made of activated carbon and lead anodes with the addition of sodium sulphate at 10–20 g/dm^3 (calculated for decahydrate of the salt). Metal removal process is performed at pH 6–8 and current density about 500 A/m^2. A shell is formed on the cathode surface, and more than 99 % of the nickel present in the initial solution pass into this shell. After electroextraction, the cathodes are transferred into a solution of mineral acid (hydrochloric, sulphuric, nitric) to obtain a solution of the corresponding nickel salt, which is then subjected to additional purification, evaporation and crystallization [130].

Chemical and galvanic nickel plating involves the method of Ni^{2+} removal from the spent technological solutions by the treatment with alkali, resulting in the formation of nickel(II) hydroxide, followed by electroextraction of the metal. An installation for electroextraction is a bath separated into three sections by a diaphragm: the first (anode) section contains $NiSO_4$, H_3BO_3 and Na_2SO_4 solutions; the second one (middle) contains the same reagents as in the first one, but additionally $Ni(OH)_2$; the third (cathode) section contains the same solutions, but additionally H_2SO_4 solution. The solutions are maintained at a temperature within 20–60 °C, pH in the anode section is 4 to 5, in the middle section 8 to 9, and in the cathode section 1 to 2. Nickel electroextraction is carried out with titanium cathodes and lead anodes, with current density 2 to 6 A/m^2 at the former and 3 to 9 A/m^2 at the latter. Nickel yield as a function of current reaches nearly 97 % within 5 h under these conditions [131].

The method of nickel electroextraction from sulphate and chloride-sulphate spent solutions containing also Mn^{2+} ions is known. In this process, nickel is selectively deposited on the nickel cathode, and manganese is removed with the slime formed at the lead anode. The method is efficient for high Ni^{2+} content in solution (10–50 g/dm^3). The best results on the yield of cathode metal with purity up to 95 % were obtained for current density of about 70 A/m^2 and temperature 50–60 °C [132].

Electroflotation purification of wastewater and solutions from Ni^{2+} ions often involves a surfactant and/or flocculant. It was established in some experiments that the introduction of anionic surfactants promotes an increase in the size of the formed nickel (II) hydroxide particles from 50

to 110 μm, non-ionic surfactants – up to 125 μm, while the addition of cationic surfactants causes a decrease in particle size to 35 μm. With the introduction of flocculants with any charge, the size of $Ni(OH)_2$ particles increases from 50 to 80 μm. So, the most efficient and rapid nickel removal from solutions during electroflotation occurs in the presence of a surfactant of the anionic type. It was established that nickel removal in the presence of these substances was 74 % after 5 min, 95 % after 30 min; without surfactants: 45 % after 5 min, 92 % after 30 min [133].

To purify waters and solutions from Ni^{2+} by means of electroflotation, it is recommended to add preliminarily sodium or potassium chloride, fluoride, phosphate, nitrate at the mass ratio of Ni^{2+}/anion = 1 : (0.3–1.5). Alkali is added to the solution to achieve pH 9–10 to obtain $Ni(OH)_2$. After that, a surfactant is introduced at a ratio of Ni^{2+}/surfactant = 1 : (0.002–0.003), or a flocculant of polyacrylamide class at a ratio of Ni^{2+}/flocculant = 1 : (0.005–0.008). With a surfactant, electroflotation is carried out for 7 min at the current density of 10 A/m^2, and in the case of flocculant – for 4 min at the current density of 8 A/m^2. The process is carried out with insoluble electrodes, for example, cathodes made of stainless steel and ruthenium-titanium oxide anodes. The degree of solution purification from Ni^{2+} is up to 99 % [134, 135].

As the practice shows, the presence of petroleum products in the solutions under treatment to a definite extent promotes an increase in nickel removal. For instance, Ni^{2+} removal by means of electroflotation from phosphate solutions containing oil products, with the use of anionic surfactant (sodium dodecylbenzene sulphonate) increases by 5–7 % (up to 98 % within 5 min) [136].

Purification of nickel-containing solutions (rinsing waters from electrochemical nickel plating) by means of electrodialysis is carried out with titanium electrodes, cation-exchange (*i.e.* Ionac MC-3470) and anion-exchange (*i.e.* Ionac MA-3475) membranes at the quantitative ratio of 1 : 3. Thus, for nickel chloride content of about 0.7 g/dm^3 and nickel sulphate about 2.8 g/dm^3 in rinsing waters, electrodialysis is carried out in a 5-chamber apparatus at the current density of 18 A/m^2 at pH 2–4. The process is characterized by the low specific rate of metal removal – 90 mg/($A \cdot h \cdot cm^2$); the 95 % degree of Ni^{2+} removal is achieved only through electrodialysis for 40 h [137].

Electrodeionization is frequently used to remove nickel from aqueous media. Ion exchange membranes are used in installations for electrodeionization, similarly to electrodialysis installations. The space between the membranes is filled with ion exchange resin (as a rule, it is a mixture of cation- and anion-exchange resins), which provides the transfer of similarly charged ions through the membrane and then into cathode or anode chambers. A mixture of KU-2-8 and AV-17 with the dynamic exchange capacities 450 and 700 $mmol/dm^3$, respectively, at a mass ratio of 1 : 1.4 may be mentioned as an example. In parallel to sorption and membrane transfer, regeneration of ion exchange resins proceeds due to water dissociated under the action of electric current [138].

Using foreign strongly acidic cation exchange resins and strongly basic anion exchange resins with the dynamic exchange capacities about 1500 and 1000 $mmol/dm^3$, respectively, at a ratio of 1.5 : 1, and ion exchange membranes with poor permeability for water, at a voltage of 12 V, nickel removal about 99.8 % from sulphate (chloride) solutions containing several ten milligrams of Ni^{2+} ions may be achieved within 7 min. Before loading the resins, to accelerate the process, it is recommended to transform the cation exchange resin into the nickel form, and anion exchange resin into the sulphate (chloride) form by treating with the solution of nickel sulphate (chloride) [139].

Cementation is worth mentioning separately. In its essence, this is a precipitation method based on the difference of electrochemical potentials of the precipitator metal and the precipitating metal. Iron in the form of plates, chips or powder is often used as the precipitator. For efficient cementation of a metal by iron, it is necessary that the potential difference between it and the metal to be precipitated will exceed 0.3 V. The potential difference between nickel (–0.25 V) and iron (–0.44 V) is only 0.19 V, so the technological yield of the process with respect to nickel is not high [140]. Efficient nickel cementation on the basis of iron is possible under the action of UHF radiation with the frequency of 7.5–10.5 GHz at a temperature of 20–30 °C on the reaction mixture. Thus, after a single pass of the solution with Ni^{2+} concentration about 6 g/dm^3, nickel removal into the deposit may reach 58 %, after two passes 75 %, and after three passes 85 %. For comparison: without the action of UHF radiation, nickel removal from the same solution does not exceed 26 % after many passes through the iron base [141].

Electrochemical purification methods allow the maximal degree of nickel concentrating and removal from solutions. These methods are ecologi-

cally safe, excluding secondary pollution of water with cationic and anionic residues. Installations for electrochemical purification are distinguished by compactness, simplicity of handling and automation. In spite of the indicated advantages, these methods are characterized by substantial energy consumption and the use (in some cases) of insoluble anodes, which causes significant metal consumption for the removal process.

MICROBIOLOGICAL PURIFICAITON

Among microbiological methods of wastewater purification from Ni^{2+} ions, the most widespread one in industry is anaerobic deposition with the help of sulphate-reducing bacteria (SRB). This bacterial species reduces sulphate ions into hydrogen sulphide

$$SO_4^{2-} + 8H^+ \rightarrow H_2S\uparrow + 2H_2O + 2OH^- \quad (10)$$

which in its turn, interacts with nickel ions forming insoluble sulphides [142]:

$$H_2S + Ni^{2+} \rightarrow NiS\downarrow + 2H^+ \quad (11)$$

Bacterial species *Desulfobulbus* sp., *Desulfovibrio desulfuricans, Desulfomonas pigra* are used as SRB. The rate of nickel deposition in the form of NiS depends on the instrumentation of the purification process. Thus, under static conditions, *Desulfobulbus* sp. bacteria provide nickel deposition: for its initial concentration within the range 5 to 30 mg/dm^3, removal degree is 99 % within 30 days, and in a bioreactor for initial concentration 100 mg/dm^3 – 5 times faster. The yield of metal into the deposit after the first 2 days is 60 %, while after 4 days it is 85 % [142]. The highest efficiency of sulphate reduction and therefore nickel removal to NiS is achieved at the ratio of COD (chemical oxygen demand) to sulphates equal to 2 : 1 [143].

The majority of SRB remain vital within a narrow pH range from 6.5 to 8.5, and exhibit sensitivity to the high concentrations of heavy metal ions. There are cultivated bacterial strains resistant to more rigid conditions. For instance, the strain *Desulfovibrio* sp. VK-9 is able to grow at 2.7–7.5 and Ni^{2+} concentrations up to 250 mg/dm^3, Cu^{2+} – 125 mg/dm^3, Co^{2+} – 350 mg/dm^3, Cd^{2+} – 60 mg/dm^3 [144].

Some foreign researchers assert that preliminary passing of water under treatment through the filter with zero-valence iron promotes a change in its oxidation-reduction potential and pH, which ensures favourable anaerobic conditions for the growth of SRB. For example, for nickel-containing solution (150 mg/dm^3) in contact with the biofilm of SRB, after its preliminary admission through iron, the efficiency of nickel deposition increases by 15.1 % after 6 h (up to 96.5 %) [145].

Many microorganisms are prone to bioconcentrating (adsorption or accumulation) of metal ions. Biosorption (passive sorption) is due to the presence of specific functional groups (for example, –COOH, –SH, –OH, –C=O, –C–NH_2) in the cell walls of microorganisms; it proceeds either in living or in dead individuals. Bioaccumulation (active sorption) is a more complicated process of impurity sorption involving metabolic processes in living microorganisms [146].

Since the cell membrane is involved in bioconcentrating, it is evident that membrane modification may allow increased removal of impurities from the liquid phase. The simplest modification methods are heating, drying, freezing, autoclave treatment, lyophilization. Chemical treatment may be carried out for the purpose of changing the cell membrane surface and providing access to functional groups responsible for biosorption: specific washing (with deionized water, alcohols, detergents), cross-linking (with aldehydes), alkaline or acid hydrolysis. Mechanical strength is rendered to an amorphous biosorbent through immobilization of microorganisms in an inert water-insoluble matrix, which provides the possibility of its use in intense hydrodynamic regimes [146].

Investigation of microbiological purification of waters and solutions from nickel with the help of bacteria has been carried out rather actively during the recent 10–15 years. Different bacterial species demonstrate different sorption properties with respect to metal ions in the liquid phase: the sorption capacity of *Rhodococcus opacus* reaches 7.6 mg/g, *Acinetobacter baumannii* (UCR-2971 strain) – 8.8 mg/g, *Pseudomonas aeruginosa* (UCR-2957 strain) – 5.7 mg/g, *Bacillus* sp. – 2.5 mg/g, *Serratia marcescens* (C-1, C4, 16 strains) – 12.9 mg/g, *Kluyvera* sp. (Nic3 strain) – 6.5 mg/g [147–150]. It is established that the optimal acidity range for the majority of bacterial species is pH 4–6, and their application is reasonable for initial Ni^{2+} concentrations at a level of several ten mg/dm^3. Cyanobacteria (blue-green algae) are also of definite interest, namely *Phormidium ambiguum, Phormidium boryanum, Leptolyngbya foveolarum and Plectonema boryanum*, to be added into water under treatment in the form of suspension at about 0.2 g/dm^3. The sorption capacity of these bacteria with respect to Ni^{2+} reaches 42.1 mg/g [151, 152].

Another group of microorganisms used for biochemical purification of waters and solutions form metal ions are fungi: filamentous (with the developed vegetative body) and yeast (single-celled).

Bioconcentration of Ni^{2+} ions by filamentous fungi has been studied most thoroughly, which is due to their species diversity. Sorption capacities with respect to Ni^{2+} have been determined for the biomasses of the following fungi: *Aspergillus terreus* – 3.9 mg/g, *Aspergillus niger* – 2 mg/g, *Rhizopus* sp. – from 22.2 to 45 mg/g (depending on specific strains), *Trichoderma viride* – 47.6 mg/g, *Eupenicillium ludwigii* – 5.2 mg/g [149, 153–156]. Cultivation of filamentous fungi with initially low biosorption capacity with respect to Ni^{2+} on soils subjected to long-term action of nickel-containing wastewaters may result in the formation of especially resistant strains with high sorption capacity: for instance, for *A. niger* – up to 25.1 mg/g, and for *Penicillium* sp. – up to 17.9 mg/g [157]. Preliminary treatment of fungal biomass with an alkaline solution may cause an increase in its biosorption capacity by a factor of 2 and more, which may be due to the activation of hydroxyl groups in the mycelium [156].

For the majority of filamentous fungal species, an optimal pH range for bioconcentration of Ni^{2+} ions is 4–7. It is stressed that the effect of temperature within the range of 5 to 40 °C on the sorption of these ions is insignificant.

Among yeast fungi, attention of researchers in connection with nickel removal from waters and solutions was attracted to widespread species *Saccharomyces cerevisiae* and *Schizosaccharomyces pombe*. The maximal sorption capacity of the former with respect to Ni^{2+} reaches 9.8 mg/g at pH ~ 7, and the latter – 33.8 mg/g at pH ~ 5. For both yeast species, the optimal temperature is 25 °C [158, 159]. It is possible to achieve an increase in the sorption capacity of the yeast biomass to 46.3 mg/g through its chemical modification [160]. Non-pathogenic yeast-like fungi of *Candida* sp. genus deserve attention: their sorption capacity with respect to Ni^{2+} ions is 30.8 to 46.8 mg/g depending on strain type (adapted or non-adapted to the high content of nonferrous metals). These microorganisms may be used for nickel (II) content in the liquid medium up to 500 mg/dm^3, but for higher values inhibition of their growth and development is observed. An optimal pH for Ni^{2+} removal by the fungi of *Candida* sp. genus is 4 [161].

After several cycles of fungal biomass usage in water purification from nickel ions, it may be treated with limewater at a ratio of nickel ions to limewater 1 : (5–8). The mixture is then subjected to wet treatment at 90 °C and isolated in the lime paste [162].

In coastal regions, much attention is attracted to the possibility to purify wastewaters and solutions form nickel ions using local algae. The sorption capacities with respect to Ni^{2+} are determined for the following species, mg/g: *Chlorella kessleri* 29.3; *Durvillaea antarctica* 32.9; *Dunaliella salina* 76.3; *Oocystis* sp. 35.3; *Porphyridium cruentum* 47; *Scenedesmus protuberans* 35.3; *Padina pavonia* 41.1; *Sargassum vulgaris* 49.9; *Sargassum angustifolium* 45.8; *Sargassum fluitans* 44; *Sargassum natans* 24.1; *Sargassum wightii* 18.8; *Sargassum glaucescens* 56; *Cystoseria indica* 50; *Nizmuddinia zanardini* 56; *Padina australis* 27 [163–169]. For the majority of micro-algae, the optimal pH range is 4–6. It is stated in some studies that, since algae contain carbohydrates, lipids, proteins and pigments in large amounts, during metal ion sorption, some organic substances may pass into the solution thus causing a decrease in the sorption capacity of the biomass. To prevent this decrease, preliminary treatment of algae with a solution of hydrochloric acid at pH ~ 5 is recommended [168].

Sorption of Ni^{2+} ions by bacterial, fungi and algae worsens frequently if competing ions of other heavy metals are present in solutions. The series of the selectivity of microorganisms to these metals may be represented as $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Cr^{6+}$ [153, 170].

To isolate nickel from the spent biomass of dead bacterial, fungi and algae, 10 % solutions of hydrochloric or nitric acids are often used. Nickel isolation from the biomass of living microorganisms is performed using gentler reagents, such as EDTA, sodium citrate, *etc.*

A special method of wastewater purification from impurities is its treatment with active sludge, which is an artificially collected complicated combination of microorganisms, the products of their vital functions, and inert particles. To remove Ni^{2+} ions, mainly anaerobic active sludge is used, which is mainly a community of anaerobic bacteria. The maximal sorption capacity of active sludge with respect to Ni^{2+} ions reaches 26 mg/g. One of the methods to prepare anaerobic biomass for use includes centrifuging at 2000 min^{-1} for 20 min and drying in the form of pellets for 6 days at 50 °C [171].

Biological purification of solutions from Ni^{2+} ions with the help of active sludge may be intensified with a polyfunctional catalyst operating under aerobic and anaerobic conditions. This catalyst con-

tains transition metal oxides (23–25 % MnO_2, 3–5 % CrO_3, 5–7 % MoO_3, 3–5 % NiO) and high-pressure polyethylene [172].

Pyrolysis of the biomass of excess active sludge from purification facilities may be used to obtain biogas suitable for combustion for energy-related purposes, and biocoal – efficient sorbent for heavy metals. The biomass is burnt at a temperature of 200–330 °C without oxygen access. The sorption characteristics of biocoal with respect to Ni^{2+} ions may be improved through its modification with α-oxide of iron (III) and α-metahydroxide of iron(III). The capacity of modified biocoal with respect to Ni^{2+} reaches 35.5 mg/g [173].

Biopolymer compounds that are the products of vital functions of bacterial microflora of the sludge may be isolated from it. Due to flocculation, these compounds form polymer-organometallic agglomerates with nonferrous metals. These agglomerates can be readily precipitated from wastewaters and solutions [174]. Biopolymer compounds may be isolated by centrifuging active sludge at 20 000 min^{-1} for 30 min. Specific yield of biopolymer compounds (with 1 g of dry active sludge) at 25 °C is about 7 mg/g, and at 80 °C it increases to 58 mg/g [175].

Microbiological methods of wastewater and solution purification from nickel ions are attractive due to their environmental safety. However, these methods are characterized by high investment expenses, the necessity to strictly adhere to the technological mode of purification (definite ranges of temperature, acidity, concentrations of other impurities), as well as low purification rates. Definite complications are connected with the choice of nutrition medium suitable for microorganisms, as well as with the maintenance of a relatively constant amount of the biomass. Desorption of valuable admixtures from living microorganisms has some limitations connected with the necessity to maintain also the conditions to provide their vitality.

CONCLUSION

The choice of a specific method of the purification of wastewaters and industrial solutions from nickel ions depends on their concentration, the presence of the ions of other nonferrous metals, the flow rate of water or solution, standard requirements to purified water, technical and economical parameters, and other factors. In view of the current lack and high cost of metal nickel and nickel salts in the world, during the recent years, the methods of selective removal of this element from liquid media gain high relevance: sorption on synthetic ion exchange resins, removal with the help of low-toxic extractants and flotation agents, electrochemical deposition. Definite outlooks are also open for microbiological methods, especially under the conditions of tightening the legislation in environmental protection.

REFERENCES

1 Dudareva G. N., Vezentsev A. I., Carbon sorbents for selective extraction of nickel (II) ions from aqueous solutions, *Nauchn. Ved. BelGU. Ser.: Estestv. Nauki*, 2013, No. 10, P. 125–129. (In Russ.).
2 Milovanov L. V., Treatment and Use of Wastewaters of Non-Ferrous Metallurgy Enterprises, Metallurgiya, Moscow, 1971. (In Russ.).
3 RU Pat. 2066707 C1, 1996.
4 Giannopoulou I., Panias D., Differential precipitation of copper and nickel from acidic polymetallic aqueous solutions, *Hydrometallurgy*, 2008, Vol. 90, No. 2–4, P. 137–146.
5 RU Pat. 2221883 C2, 2004.
6 Kochergin A. S., Intensification of the work of local treatment facilities of galvanic wastewaters using precipitating reagents (Thesis for Cand. Sci. in Technology), Penza, 2010. (In Russ.).
7 Rozov D. E., Precipitation of sulfides of non-ferrous metals from solutions with mattes of copper-nickel production (Thesis for Cand. Sci. in Technology), Saint Petersburg, 1999. (In Russ.).
8 Girikov O. G., Improvement of the new technology for deep purification of wastewater from heavy metal ions, *Izv. Vuzov. Stroitelstvo*, 2018, No. 1, P. 57–68. (In Russ.).
9 RU Pat. 2328537 C2, 2008.
10 US Pat. 5178842 A, 1993.
11 Benson B., Calvin H., Nickel receiving technology in plants by hydrogen reduction, Int. Symp. "Hardware Processes in Hydrometallurgy", 1964, P. 752–753.
12 RU Pat. 2237737 C2, 2004.
13 RU Pat. 2166552 C2, 2000.
14 Shemel I. G., Ostanin A. N., Physicochemical foundations of autocatalytic sedimentation of nickel from the processed solutions of chemical nickel-plating, *Mezhdunar. Nauch.-Issled. Zhurn.*, 2017, No. 11/4, P. 87–91. (In Russ.).
15 RU Pat.2010012 C1, 1994.
16 EP Pat. 0190478 B1, 1989.
17 Lykova O. V., Research and development of technology for local sorption treatment of metal-containing wastewater (Thesis for Cand. Sci. in Technology), Irkutsk, 1998. (In Russ.).
18 Syrykh Yu. S., Dudarev V. I., Afonina T. Y., Moskaeva N. Y., The adsorption extraction of nickel(II) ions from aqueous solutions, *Russ. J. Non-Ferr. Met.*, 2009, Vol. 50, No. 1, P. 9–12.
19 Berrima B., Maatar W., Mortha G., Boufi S., El Aloui L., Belgacem M. N., Adsorption of heavy metals on charcoal from lignin, *Cellulose Chem. Technol.*, 2016, Vol. 50, No. 5–6, P. 701–709.
20 Dudareva G. N., Irinchinova N. V., Dudarev V. I., Adsorption extraction of nickel(II) from industrial solutions, *Izvestiya Vuzov. Priklad. Khimiya i Biotekhnologiya*, 2020, Vol. 10, No. 1, P. 133–139. (In Russ.).
21 Pomazkina O. I., Filatova E. G., Pozhidaev Y. N., Adsorption of nickel (II) cations by natural zeolites, *Prot. Met. Phys.*

Chem. Surf., 2014, Vol. 50, No. 3, P. 262–268. (In Russ.).
22 Ivanova E. S., Gavronskaya Yu. Yu., Pak V. N., Structure and sorption properties of H-form clay from the Lukovskoe field of the Pskov region, *Sorb. i Khromatogr. Protsessy*, 2014, Vol. 14, No. 2, P. 254–259. (In Russ.).
23 Belenova S. V., Vigdorovich V. I., Tsygankova L. E., Sorption of Ni (II) cations from chloride solutions by glauconite concentrate, *Vestn. Tambov. Un-ta. Ser.: Estestv. i Tekhn. Nauki*, 2015, Vol. 20, No. 2, P. 397–403.
24 Klimov E. S., Buzaeva M. V., Natural Sorbents and Complexones in Wastewater Treatment, UlGTU, Ulyanovsk, 2011. (In Russ.).
25 Fominyh I. M., Galkin Yu. A., Nikiforov A. F., Anikin Yu. V., Balakina O. S., Sorption of nickel by materials based on opal-cristobalite rocks, *Izv. Chelyabinsk. Nauch. Tsentra UrB RAS*, 2006, No. 1, P. 67–70. (In Russ.).
26 Rajic N., Stojakovic D., Jovanovic M., Zabukovec Logar N., Removal of nickel(II) ions from aqueous solutions using the natural clinoptilolite and preparation of nano-NiO on the exhausted clinoptilolite, *Appl. Surf. Sci.*, 2010, Vol. 257, No. 5, P. 1524–1532.
27 RU Pat. 2524111 C2, 2014.
28 Dinu M. V., Dragan E. S., Evaluation of Cu^{2+}, Co^{2+} and Ni^{2+} ions removal from aqueous solution using a novel chitosan/clinoptilolite composite: Kinetics and isotherms, *Chem. Eng. J.*, 2010, Vol. 160, No. 1, P. 157–163.
29 RU Pat. 2632844 C1, 2017.
30 Panneerselvam P., Sathya Selva Bala V., Thinakaran N., Baskaralingam P., Palanichamy M., Sivanesan S., Removal of nickel(II) from aqueous solutions by adsorption with modified ZSM-5 zeolites, *E-Journal of Chemistry*, 2009, Vol. 6, No. 3, P. 729–736.
31 Pomazkina O. I., Filatova E. G., Lebedeva O. V., Pozhidaev Yu. N., Deep purification of technogenic solutions from nickel ions (II) by the modified aluminosilicates, *J. Siberian Fed. Univ. Eng. Technol.*, 2017, Vol. 10, No. 3, P. 327–336.
32 Ganebnykh E. V., Sviridov A. V., Maltsev G. I., Extraction of nickel from solutions with highly dispersed modified aluminosilicates, *Izv. Vyssh. Uchebn. Zaved. Khimiya i Khim. Tekhnologiya*, 2015, Vol. 58, No. 1, P. 45–50. (In Russ.).
33 Kormosh E. V., Modification of montmorillonite-containing clays for integrated sorption wastewater treatment, Abstract of Thesis for Cand. Sci. in Chemistry, Belgorod, 2009. (In. Russ.).
34 Sviridov A. C., Yurchenko V. V., Sviridov V. V., Ganebnykh E. V., Sorption of copper and nickel cations in the layered aluminosilicates, *Sorbts. Khromatogr. Protsessy*, 2016, Vol. 16, No. 1, P. 78–86. (In Russ.).
35 RU Pat. 2656451 C2, 2017.
36 Deryagina E. N., Levanova E. P., Grabel'nykh V. A., Sukhomazova E. N., Russavskaya N. V., Korchevin N. A., Thiylation of polyelectrophiles with sulfur in hydrazine hydrate-amine systems, *Russ. J. Gen. Chem.*, 2005, Vol. 75, No. 2, P. 194–199.
37 RU Pat. 2624319 C1, 2017.
38 RU Pat. 2558896 C1, 2015.
39 Bobyleva S. A., Sorption treatment of wastewater from heavy metal ions using brucite, Thesis for Cand. Sci. Degree in Technology, Novosibirsk, 2005. (In. Russ.).
40 Sklyarova G. F., Prospects for the integrated use of magnesite raw materials from Russian Far East deposits, *Gornyi Inform.-Analit. Byulleten (Nauch.-Techn. Zhurn.)*, 2012, No. 1, P. 302–309. (In Russ.).
41 Korolev V. A., Samarin E. N., Panfilov V. A., Romanova I. V., Sorption properties of brucite and brucite-based clay mixtures and their use in barrier technologies, *Ecologiya i Promyshlennost Rossii*, 2016, Vol. 20, No. 1, P. 18–24. (In Russ).
42 RU Pat. 2118296 C1, 1998.
43 Kouh Sone P.-M. A., Tagne G. M., Lekene Ngouateu R. B., Belibi Belibi P. D., NdiNsami J., Kouotou D., Chogomu Numbonui J., Anagho Gabche S., Ketcha Mbadcam J., Kinetics and equilibrium studies of the adsorption of nickel(II) ions from aqueous solution onto modified natural and synthetic iron oxide, *Int. J. Basic Appl. Sci.*, 2015, Vol. 4, No. 3, P. 277–287.
44 RU Pat. 2122894 C1, 1998.
45 RU Pat. 2523476 C1, 2012.
46 Kurdiumov V. R., Timofeev K. L., Maltsev G. I., Lebed A. B., Sorption of nickel (II) and manganese (II) ions from aqueous solutions, *Zapiski Gornogo Instituta*, 2020, Vol. 242, P. 209–217. (In Russ).
47 Makovskaya O. Y., Kolmachikhina O. B., Lobanov V. G., Polygalov S. E., Nickel sorption from solutions with high salt concentration, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2020, Vol. 966, Art. 012007.
48 Seggiani M., Vitolo S., D'Antone S., Recovery of nickel from Orimulsion fly ash by iminodiacetic acid chelating resin, *Hydrometallurgy*, 2006, Vol. 81, No. 1, P. 9–14.
49 Leinonen H., Lehto J., Ion-exchange of nickel by iminodiacetic acid chelating resin Chelex 100, *React. Funct. Polym.*, 2000, Vol. 43, No. 1–2, P. 1–6.
50 Umanskii A. B., Klyushnikov A. M., Recovery of nickel from hydrate pulps at amino carboxylic cationites, *Russ. J. Non-Ferr. Met.*, 2013, Vol. 54, No. 2, P. 148–150.
51 Pehlivan E., Altun T., Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution by Lewatit CNP 80, *J. Hazard. Mater.*, 2007, Vol. 140, No. 1–2, P. 299–307.
52 Dizge N., Keskinler B., Barlas H., Sorption of Ni(II) ions from aqueous solution by Lewatit cation-exchange resin, *J. Hazard. Mater.*, 2009, Vol. 167, No. 1–3, P. 915–926.
53 Mendes F. D., Martins A. H., Selective sorption of nickel and cobalt from sulphate solutions using chelating resins, *Int. J. Miner. Process.*, 2004, Vol. 74, No. 1, P. 359–371.
54 Kang N.-H., Park K.-H., Parhi P. K., Recovery of nickel from sulfuric acid solution using Lewatit TP 220 ion exchange resin, *J. Korean Inst. Resour. Recycl.*, 2011, Vol. 20, No. 6, P. 28–36.
55 Deepatana A., Tang J. A., Valix M., Comparative study of chelating ion exchange resins for metal recovery from bio-leaching of nickel laterite ores, *Miner. Eng.*, 2006, Vol. 19, No. 12, P. 1280–1289.
56 Zaidi S., Musarrat J., Characterization and nickel sorption kinetics of a new material hyper-accumulator *Bacillus* sp., *J. Environ. Sci. Health A: Tox. Hazard. Subst. Environ. Eng.*, 2004, Vol. 39, No. 3, P. 681–691.
57 Alyüz B., Veli S., Kinetics and equilibrium studies for the removal of nickel and zinc from aqueous solutions by ion exchange resins, *J. Hazard. Mater.*, 2009, Vol. 167, No. 1–3, P. 482–488.
58 Ergozhin E. E., Begenova B. E., Chalov T. K., Pyridine-containing sorbents for the extraction of non-ferrous metals, *Tsvet. Metally*, 2008, No. 5, P. 31–32. (In Russ.).
59 Eeshkurbonov F. B., Djalilov A. T., Research in sorption properties obtained ion exchanger of hydrolysed polyacrylonitrile, *Universum: Khimiya i Biologiya*, 2014, No. 3. (In Russ.).
60 Bekchanov D. J., Sagdiev N. J., Mukhamediev M. G., Study of sorption of heavy metals on nitrogen and phosphorous containing polyampholytes, *Am. J. Polym. Sci.*, 2016, Vol. 6, No. 2, P. 46–49.
61 Bhatt R. R., Shah B. A., Sorption studies of heavy metal ions by salicylic acid–formaldehyde–catechol terpolymeric resin: Isotherm, kinetic and thermodynamics, *Arabian J. Chem.*, 2015, Vol. 8, No. 3, P. 414–426.
62 Azarudeen R. S., Ahamed M. A. R., Burkanudeen A. R., Chelating terpolymer: Synthesis, characterization and

its ion-exchange properties, *Desalination*, 2011, Vol. 268, No. 1–3, P. 90–96.
63 Shah R., Devi S., Chelating resin containing s-bonded dithizone for the separation of copper (II), nickel (II) and zinc (II), *Talanta*, 1998, Vol. 45, No. 6, P. 1089–1096.
64 Pulatov Kh. L., Turabzhanov S. M., Igitov F. B., Hamdamova O. B., Polycondensation phosphate cation exchangers for wastewater treatment from heavy metal ions, *Universum: Khimiya i Biologiya*, 2018, No. 11, P. 24–27. (In Russ.).
65 Soldatov V., Pawlowski L., Wasag H., Elinson I., Shunkevich A., Prospects of fibrous ion exchangers in water pollution control (chromates sorption by aminocarboxylic fibers examples), Chemistry for the Protection of the Environment 2, Plenum Press, New York, 1996. P. 107–119.
66 Astapov A. V., Peregudov Yu. S., Niftaliev S. I., Sorption of nickel(II) cations with chelate fiber sorbent FIBAN X-I, *Zhurn. Fiz. Khimii*, 2017, Vol. 91, No. 8, P. 1397–1402. (In Russ.).
67 Niftaliev S. I., Astapov A. V., Peregudov Yu. S., Bakaeva Yu. V., Quantum-chemical modeling of complexes formed during the sorption of ammonia on modified ion-exchange fibers, *Kondensir. Sredy i Mezhfaz. Granitsy*, 2012, Vol. 14, No. 2, P. 221–223. (In Russ.).
68 Druzhinina T. V., Smolenskaya L. M., Struganova M. A., Sorption of heavy metals from model solutions with amine-containing chemisorption polyamide fiber, *Russ. J. Appl. Chem*., 2003, Vol. 76, P. 1925–1929.
69 SU Pat. 1623970 A1, 1991.
70 Voropanova L. A., Pukhova V. P., Extraction of copper, cobalt and nickel ions from aqueous solutions by extractant Cyanex 272, *Zapiski Gornogo Instituta*, 2018, Vol. 233, P. 498–505. (In Russ.).
71 Mishra R. K., Rout P. C., Sarangi K., Solvent extraction of zinc, manganese, cobalt and nickel from nickel laterite bacterial leach liquor using sodium salts of TOPS-99 and Cyanex 272, *Transactions of Nonferrous Metals Society of China*, 2016, Vol. 26, No. 1, P. 301–309.
72 Valkov V. A., Borisov M. A., Kuzmin R. S., Extraction of nickel and cobalt with LIX-84-1 and Cyanex 272 mixtures, Scientific Session of Moscow Engineering Physics Institute 2008 (Proceedings, Vol. 4), Moscow, Russia, Jan. 21–25, 2008. P. 75. (In Russ.).
73 Santanilla A. J. M., Tenorio J. A. S., Espinosa D. C. R., Synergistic effect on extraction of nickel and cobalt from synthetic sulfate solution using DEHPA and Cyanex 272 as extractants, TMS 2014: 143rd Annual Meeting & Exhibition, San Diego, USA, February 16–20, 2014. P. 1157–1163.
74 Sun Q., Yang L., Huang S., Xu Z., Li Y., Wang W., Synergistic solvent extraction of nickel by 2-hydroxy-5-nonylacetophenone oxime mixed with neodecanoic acid and bis(2-ethylhexyl)phosphoric acid: Stoichiometry and structure investigation, *Miner. Eng*., 2019, Vol. 132, No. 1, P. 284–292.
75 Sulaiman R. N. R., Othman N., Solvent extraction of nickel ions from electroless nickel plating wastewater using synergistic green binary mixture of D2EHPA-octanol system, *J. Environ. Chem. Eng*., 2018, Vol. 6, No. 2, P. 1814–1820.
76 Pashkov G. L., Fleitlikh I. Y., Grigorieva N. A., Pleshkov M. A., Nickel and cobalt extraction from leaching solutions of oxidized nickel ores with Cyanex 301 systems, *Tsvetn. Metally*, 2018, No. 8, P. 57–62. (In Russ.).
77 Grigorieva N. A., Extraction of nickel, zinc and cobalt in systems with bis(2,4,4-trimethylpentyl)dithiophosphinic acid from sulfate solutions of processing oxidized nickel ores, Thesis for Cand. Sci. Degr. in Chemistry, Krasnoyarsk, 2011. (In Russ.).
78 Preston J. S., Du Preez A. C., Separation of nickel and calcium by solvent extraction using mixtures of carboxylic acids, *Hydrometallurgy*, 2000, Vol. 58, No. 3, P. 239–250.
79 Cheng C. Y., Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime, *Hydrometallurgy*, 2006., Vol. 84, No. 1–2, P. 109–117.
80 Mubaroka M. Z., Hanifa L. I., Cobalt and nickel separation in nitric acid solution by solvent extraction using Cyanex 272 and Versatic 10, *Procedia Chemistry*, 2016, Vol. 19, P. 743–750.
81 RU Pat. 2378400 C2, 2010.
82 Radushev A. V., Vaulina V. N., Kharitonova A. V., Chekanova L. G., Gusev V. Y., Direct extraction of nickel from model sulfate solution with hydrazide of versatic tert-carboxylic acids, *Russ. J. Appl. Chem*., 2016, Vol. 89, P. 880–885.
83 RU Pat. 2114199 C1, 1998.
84 RU Pat. 2219259 C2, 2003.
85 RU Pat. 2525307 C2, 2014.
86 Lobana T. S., Bhatia P. V. K., Liquid-liquid extraction of cobalt (II), nickel (II) and copper (II) from basic medium using some β-diketones, *Proc. Indian Acad. Sci., Chem. Sci*.,1995, Vol. 107, No. 1, P. 35–38.
87 Troshkina I. D., Obruchnikova Ya. A., Pestov S. M., Metal sorption by materials with a mobile phase of extractants, *Russ. J. Gen. Chem*., 2019, Vol. 89, P. 2721–2732.
88 Kabay N., Cortina J. L., Trochimczuk A., Streat M., Solvent-impregnated resins (SIRs) – Methods of preparation and their applications, *React. Funct. Polym*., 2010, Vol. 70, No. 8, P. 484–496.
89 Chen J.-H., Chen W.-R., Gau Y.-Y., Lin C.-H., The preparation of di(2-ethylhexyl)phosphoric acid modified Amberlite 200 and its application in the separation of metal ions from sulfuric acid solutions, *React. Funct. Polym*., 2003, Vol. 56, No. 3, P. 175–188.
90 Tanaka M., Huynh H. T., Kobayashi M., Application of solvent extraction and solvent impregnated support to the treatment of effluent from electroless nickel plating processes, TMS (The Material Society) 2003: 132nd Annual Meeting & Exhibition (Proceedings), San Diego, USA, March 2–6, 2003. P. 485–494.
91 Vaughan J., Dieters C., Fu W., Byrne K., Properties of Lewatit TP 272, a commercial solvent impregnated cation exchange resin for cobalt recovery, *Miner. Eng*., 2016, Vol. 88, P. 2–8.
92 Bari M. F., Hossain M. S., Mujtaba I. M., Jamaluddin S. B., Hussin K., Simultaneous extraction and separation of Cu(II), Zn(II), Fe(II) and Ni(II) by polystyrene microcapsules coated with Cyanex 272, *Hydrometallurgy*, 2009, Vol. 95, No. 3–4, P. 308–315.
93 Mu F. T., Jia Q., Tian Y. M., Shang Q. K., Extraction of cobalt (II) and nickel (II) by a solvent impregnated resin containing bis(2,4,4-trimethylpentyl)monothiophosphinic acid, *Adsorption*, 2008, Vol. 14, No. 1, P. 31–36.
94 Yoshizuka K., Sakomoto Y., Baba Y., Inoue K., Distribution equilibria in the adsorption of cobalt (II) and nickel (II) on Levextrel resin containing Cyanex 272, *Hydrometallurgy*, 1990, Vol. 23, No. 2–3, P. 309–318.
95 Farnosova E. N., Development of a combined technology for water purification from heavy metals using membrane methods. Thesis for Cand. Sci. Degr. in Technology, Moscow, 2011. (In Russ.).
96 Golovaneva N. V., Nanofiltration in water purification of heavy metals, *Uspekhi Khimii i Khim. Tekhnologii*, 2014, Vol. 28, No. 2 (151), P. 16–19. (In Russ.).
97 Somin V. A., Development of wastewater treatment technologies for galvanic production of mechanical engineering enterprises on the example of OJSC "Barnaultransmash". Thesis for Cand. Sci. Degr. in Technology, Barnaul, 2009. (In Russ.).
98 Pavlov D. V., Gogina E. S., Modern resource-saving water recycling system for galvanic production, *Vestn. Mosk. Gos.*

Stroit. Univestiteta, 2013, No. 10, P. 175–182. (In Russ.).
99 Kurdiumov V. R., Timofeev K. L., Kraiukhin S. A., Specific features of using reverse osmosis for mine water treatment, *Vodosnabzhenie i Sanitar. Tekhnika*, 2018, No. 11, P. 48–56. (In Russ.).
100 Mavrov V., Erwe T., Blocher C., Chmiel H., Study of new integrated process combining adsorption, membrane separation and flotation for heavy metal removal from wastewater, *Desalination*, 2003, Vol. 157, P. 97–104.
101 Nenov V., Lazaridis N. K., Blocher C., Bonev B., Matis K. A., Metal recovery from a copper mine effluent by a hybrid process, *Chem. Eng. Process.*, 2008, Vol. 47, P. 596–602.
102 Sudilovskiy P. S., Development of a combined flotation-membrane process of wastewater treatment from heavy metals, Thesis for Cand. Sci. Degr. in Technology, Moscow, 2007. (In Russ.).
103 Povorov A. A., Pavlolva V. F., Shinenkova N. A., Treatment of wastewater from electroplating plants, *Ekologiya Proizvodstva*, 2007, No. 5, P. 68–71. (In Russ.).
104 Yenial U., Bulut G., Examination of flotation behavior of metal ions for process water remediation, *J. Mol. Liq.*, 2017, Vol. 241, P. 130–135.
105 Lobacheva O. L., Flotoextraction of nickel ions from dilute aqueous solutions, *Zapiski Gornogo Instituta*, 2006, Vol. 169, P. 156–159. (In Russ.).
106 Hoseinian F. S., Irannajad M., Nooshabadi A. J., Ion flotation for removal of Ni(II) and Zn(II) ions from wastewaters, *Int. J. Miner. Process.*, 2015, Vol. 143, P. 131–137.
107 RU Pat. 2131850 C1, 1999.
108 Chekanova L. G., Radushev A. V., Nasrtdinova T. Yu., Koltashev D. V., Naumov D. Yu., Concentration of Cu(II), Co(II), and Ni(II) ions with N-(2-hydroxyethyl)alkyl amines, *Russ. J. Non-Ferr. Met.*, 2012, Vol. 53, No. 1, P. 8–12.
109 Lesnov A. E., Kudryashova O. S., Birina O. S., Application of synthamide-5 for metals ions flotation, *Vestn. Perm. Universiteta*, 2014, No. 3, P. 80–85. (In Russ.)
110 Santander M., Valderrama L., Guevara M., Rubio J., Adsorbing colloidal flotation removing metals ions in a modified jet cell, *Miner. Eng.*, 2011, Vol. 24, No. 9, P. 1010–1015.
111 RU Pat. 2038328 C1, 1995.
112 RU Pat. 2145942 C1, 2000.
113 Hoseinian F. S., Rezai B., Kowsari E., Chinnappan A., Ramakrishna S., Synthesis and characterization of a novel nanocollector for the removal of nickel ions from synthetic wastewater using ion flotation, *Sep. Purif. Technol.*, 2020, Vol. 240, Art. 116639.
114 RU Pat. 2522630 C1, 2014.
115 CN Pat. 102476838A, 2012.
116 Taseidifar M., Ziaee M., Pashley R. M., Ninham B. W., Ion flotation removal of a range of contaminant ions from drinking water, *J. Environ. Chem. Eng.*, 2019, Vol. 7, No. 4, Art. 103263.
117 Devyatkin P. N., Application of foam flotation for wastewater treatment and production of pure nickel sulfate, *Zapiski Gornogo Instituta*, 2002, Vol. 150, P. 114–115. (In Russ.).
118 Filatova E. G., Soboleva A. A., Dudarev V. I., Antsiferov E. A., Technology of electrocoagulation purification of wastewater of electroplating from ions of heavy metal, *Izv. Vyssh. Uchebn. Zaved., Khimiya i Khim. Tekhnoogiya*, 2014, Vol. 57, No 1, P. 96–100. (In Russ.).
119 Filatova E. G., Soboleva A. A., Dudarev V. I., Electrocoagulation removal of nickel ions from wastewater of electroplating production, *Izv. Vuzov. Priklad. Khimiya i Biotekhnologiya*, 2012, Vol. 2, No. 1, P. 149–157. (In Russ.).
120 Akbal F., Camci S., Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation, *Desalination*, 2011, Vol. 269, No. 1–3, P. 214–222.
121 Kim T., Kim T.-K., Zoh T.-D., Removal mechanism of heavy metal (Cu, Ni, Zn, and Cr) in the presence of cyanide during electrocoagulation using Fe and Al electrodes, *J. Water Process Eng.*, 2020, Vol. 33, Art. 101109.
122 Kobya M., Demirbas E., Parlak N. U., Yigit S., Treatment of cadmium and nickel electroplating rinse water by electrocoagulation, *Environ. Technol.*, 2010, Vol. 31, No. 13, P. 1471–1481.
123 Shahriari T., Methods of nickel removal from valerian irrigating wastewater, *J. Med. Plants & By-products*, 2014, Vol. 3, No. 1, P. 79–83.
124 Zhilinskiy V. V., Slesarenko O. A., Electrochemical wastewater treatment and water treatment, BGTU, Minsk, 2014. (In Russ.).
125 Ozeryanskaya V. V., Kolbasin A. V., Sogomonyan A. A., Rybalkina I. S., Study on galvanochemical treatment efficiency for wastewater purification in galvanic production, *Vestn. Donskogo Gos. Tekhn. Universiteta*, 2010, Vol. 10, No. 7, P. 1089–1093. (In Russ.).
126 Khalturina T. I., Bobrik A. G., Intensification of purification of sewage water-generation manufacturing enterprises of metallurgy enterprises and machine-building complex containing ions of chromium, copper, nickel and zinc, *Gradostroitelstvo i Arkhitektura*, 2018, Vol. 8, No. 2, P. 27–34. (In Russ.).
127 Kozodaev A., Andrushko A., Firsova A., Research of reagent-free wastewater treatment methods of the chrome plating line for mineralizing the rod of hydraulic cylinders, *IOP Conf. Ser.: Mater. Sci. Eng.*, 2019, Vol. 492, Art. 012021.
128 Didenko A. F., Investigation of the process of galvano-coagulation of heavy metals in sewage waters, *Vestn. Nauki i Obrazovaniya*, 2018, No. 5, P. 26–31. (In Russ.).
129 Abramov V. O., Abramova A. V., Keremetin P. P., Mullakaev M. S., Vexler G. B., Mason T. J., Ultrasonically improved galvanochemical technology for the remediation of industrial wastewater, *Ultrason. Sonochem.*, 2014, Vol. 21, No. 2, P. 812–818.
130 CN Pat. 100390075C, 2008.
131 RU Pat. 2033480 C1, 1995.
132 RU Pat. 2205236 C1, 2003.
133 Kolesnikov A. V., Il'in V. I., Brodskiy V. A., Kolesnikov A. V., Electroflotation during wastewater treatment and extraction of valuable compounds from liquid technogenic waste: A review, *Theor. Found. Chem. Eng.*, 2017, Vol. 51, No. 4, P. 369–383.
134 RU Pat. 2363665 C1, 2009.
135 RU Pat. 2445273 C1, 2012.
136 Kolesnikov A. V., Vorob'eva O. I., Kapustin Y. I., Electroflotation purification of wastewater from copper and nickel ions in the presence of surface-active compounds and oil products, *Theor. Found. Chem. Eng.*, 2011, Vol. 45, No. 5, P. 794–799.
137 Benvenuti T., Krapf R. S., Rodrigues M. A. S., Bernardes A. M., Zoppas-Ferreira J., Recovery of nickel and water from nickel electroplating wastewater by electrodialysis, *Sep. Purif. Technol.*, 2014, Vol. 129, P. 106–112.
138 Vergun A. P., Tikhonov G. S., Dorofeeva L. I., Deionization of nickel-containing solutions of galvanic production, *Bulleten Tomsk Polytech. Universiteta*, 2003, Vol. 306, No. 2, P. 38–39. (In Russ.).
139 Lu H., Wang J., Yan B., Bu S., Recovery of nickel ions from simulated electroplating rinse water by electrodeionization process, *Water Sci. Technol.*, 2010, Vol. 61, No. 3, P. 729–735.
140 Alkatsev M. I., Cementation Processes in Nonferrous Metallurgy, Metallurgiya, Moscow, 1981. (In Russ.).
141 RU Pat. 2503731 C1, 2014.
142 Pan L. S., Komarova E. A., Biochemical method of wastewater treatment from heavy metals using sulfate-reducing bacteria, *Vestn. Perm. Natsion. Issled. Politekhn. Universiteta*, 2012, No. 14, P. 198–203. (In Russ.).
143 Barbosa L. P., Costa P. F., Bertolino S. M., Silva J. C. C., Guerra-Sa R., Leao V. A., Teixeira M. C., Nickel, manganese and copper removal by a mixed consortium of sulfate reducing bacteria at a high COD/sulfate ratio, *World J.*

Microbiol. Biotechnol., 2014, Vol. 30, P. 2171–2180.
144 RU Pat. 2603249 C1, 2016.
145 Zhang D., Wang J., Zhao J., Cai Y., Lin Q., Comparative study of nickel removal from synthetic wastewater by a sulfate-reducing bacteria filter and a zero valent iron–sulfate-reducing bacteria filter, *Geomicrobiology*, 2016, Vol. 33, No. 3–4, P. 318–324.
146 Aronbaev S. D., Biosorption concentration of heavy metals and radionuclides by microorganisms and sorbents based on their basis, *Molodoy Ucheniy*, 2015, No. 294, P. 31–50. (In Russ.).
147 Cayllahua J. E. B., Torern M. L., Biosorptive flotation of nickel and aluminum ions from aqueous solutions, *Desalination*, 2011, Vol. 279, No. 1–3, P. 195–200.
148 Rodriguez C. E., Quesada A., Nickel biosorption by *Acinetobacter baumannii* and *Pseudomonas aeruginosa* isolated from industrial wastewater, *Braz. J. Microbiol.*, 2006, Vol. 37, No. 4, P. 465–467.
149 Joshi P. K., Kumar R., Rajput V. D., Removal of heavy metals – lead, cadmium and nickel by fungi and bacteria from liquid medium, *J. Soil Salin. Water Qual.*, 2013, Vol. 5, No. 1, P. 60–64.
150 Marrero J., Diaz A., Valle A., Cantero D., Gomez J. M., Coto O., Nickel and cobalt removal capacities of native metal-resistant bacteria, *Adv. Mater. Res.*, 2009, Vol. 71–73, P. 617–620.
151 RU Pat. 2521653 C2, 2014.
152 Ramadoss R., Subramaniam D., Removal of divalent nickel from aqueous solutions using blue-green marine algae: Adsorption modeling and applicability of various isotherm models, *Sep. Sci. Technol.*, 2019, Vol. 54, No. 6, P. 943–961.
153 Filipovic-Kovacevic Z., Sipos L., Briski F., Biosorption of chromium, copper, nickel and zinc ions onto fungal pellets of *Aspergillus niger* 405 from aqueous solutions, *Food Technol. Biotechnol.*, 2000, Vol. 38, No. 3, P. 211–216.
154 Mogollon L., Rodriguez R., Larrota W., Ramirez N., Torres R., Biosorption of nickel using filamentous fungi, *Appl. Biochem. Biotechnol.*, 1998, Vol. 70–72, P. 593–601.
155 Sujatha P., Kalarani V., Kumar B. N., Effective biosorption of nickel (II) from aqueous solutions using *Trichoderma viride, J. Chem.*, 2013, Vol. 9, Suppl., Art. 716098.
156 Al-Fakih A., Biosorption of Ni^{2+} and Cd^{2+} from aqueous solutions using NaOH-treated biomass of *Eupenicillium ludwigii*. Equilibrium and mechanistic studies, *Open J. Appl. Sci.*, 2015, Vol. 5, No. 7, P. 376–392.
157 Ahmad I., Ansari M. I., Aqil F., Biosorption of Ni, Cr and Cd by metal tolerant *Aspergillus niger* and *Penicillium* sp. using single and multi-metal solution, *Indian J. Exp. Biol.*, 2006, Vol. 44, No. 1, P. 73–76.
158 Padmavathy V., Biosorption of nickel(II) by baker's yeast: Kinetic, thermodynamic and desorption studies, *Bioresour. Technol.*, 2008, Vol. 99, No. 8, P. 3100–3109.
159 Durmaz-Sam S., Sayar N. A., Topal-Sarikaya A., Sayar A. A., Biosorption of Ni(II) by *Schizosaccharomyces pombe*: Kinetic and thermodynamic studies, *Bioprocess Biosyst. Eng.*, 2011, Vol. 34, No. 8, P. 997–1005.
160 Podgorskii V. S., Kasatkina T. P., Lozovaia O. G., Yeasts – biosorbents of heavy metals, *Microbiol. Zhurn.*, 2004, Vol. 66, No 1, P. 91–103. (In Russ.).
161 Donmez G., Aksu Z., Bioaccumulation of copper(II) and nickel(II) by the non-adapted and adapted growing *Candida* sp., *Water Res.*, 2001, Vol. 35, No. 6, P. 1425–1434.
162 RU Pat. 2509734, 2014.
163 Kadukova J., Horvathova H., Biosorption of copper, zinc and nickel from multi-ion solutions, *Nova Biotechnol. Chim.*, 2012, Vol. 11, No. 2, P. 125–132.
164 Guarin-Romero J. R., Rodriguez-Estupinan P., Giraldo L., Moreno-Pirajan J. C., Simple and competitive adsorption study of nickel(II) and chromium(III) on the surface of the brown algae *Durvillaea antarctica* biomass, *ACS Omega*, 2019, Vol. 4, No. 19, P. 18147–18158.
165 Karaca M., Bisorption of aqueous Pb^{2+}, Cd^{2+} and Ni^{2+} ions by *Dunaliella salina*, *Oocystis* sp., *Porphyridium cruentum* and *Scenedesmus protuberans* prior to atomic spectrometric determination: Thesis for Master of Science in Chemistry, Izmir, 2008. 95 p.
166 Ofer R., Yerachmiel A., Shmuel Y., Marine macroalgae as biosorbents for cadmium and nickel in water, *Water Environ. Res.*, 2003, Vol. 75, No. 3, P. 246–253.
167 Ahmady-Asbchin S., Tabaraki R., Jafari N., Allahverdi A., Azhdehakoshpour A., Study of nickel and copper biosorption on brown algae *Sargassum angustifolium*: Application of response surface methodology (RSM), *Environ. Technol.*, 2013, Vol. 34, No. 13–16, P. 2423–2431.
168 Kleinubing S. J., Vieira R. S., Beppu M. M., Giubal E., Da Silva M. G. C., Characterization and evaluation of copper and nickel biosorption on acidic algae *Sargassum filipendula*, *Mater. Res.*, 2010, Vol. 13, No. 4, P. 541–550.
169 Pahlavanzadeh H., Keshtkar A. R., Safdari J., Abadi Z., Biosorption of nickel (II) from aqueous solutions by brown algae: Equilibrium, dynamic and thermodynamic studies, *J. Hazard. Mater.*, 2010, Vol. 175, No. 1–3, P. 304–310.
170 Mohammed A. A., Najim A. A., Al-Musawi T. J., Alwared A. I., Adsorptive performance of a mixture of three nonliving algae classes for nickel remediation in synthesized wastewater, *J. Environ. Health Sci. Eng.*, 2019, Vol. 17, No. 2, P. 529–538.
171 Al Hawari A., Biosorption of lead, copper, cadmium and nickel by anaerobic biomass, PhD Thesis, Montreal, 2004.
172 RU Pat. 2097338 C1, 1997.
173 Yang L., He L., Xue J., Wu L., Ma Y., Li Y., Peng P., Li M., Zhang Z., Highly efficient nickel(II) removal by sewage sludge biochar supported α-Fe_2O_3 and α-FeO(OH): Sorption characteristics and mechanisms, *PLoS One*, 2019, Vol. 14, No. 6, Art. e0218114.
174 Zhuikova L. I., Wastewater treatment using activated sludge biopolymers. Thesis for Cand. Sci. Degr. in Technology, Shchelkovo, 2007. (In Russ.).
175 Liu Y., Lam M. C., Fang H. H. P., Adsorption of heavy metals by EPS of activated sludge, *Water Sci. Technol.*, 2001, Vol. 43, No. 6, P. 59–66.