WASTEWATER TREATMENT USING NANOMODIFIED NATURAL MATERIALS

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This paper addresses physicochemical and environmental aspects of removal of heavy metals from wastewater using nanomodified natural materials.

A method has been devised to achieve high purity with minimum raw material preparation cost compared with the known methods.

This monograph may be useful for academic researchers, engineers and technicians, undergraduates, post-degree students and professors.

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CONTENTS

INTRODUCTION

According to the World Health Organization, human diseases caused by consumption of low-quality water can account for up to 80% of the total number of health problems. In general, more than half of the world population consume low-quality water, and thus every third inhabitant is endangered by gastrointestinal diseases. Economic damage from morbidity of the population using low-quality water virtually cannot be measured to the full extent due to specifics of the problem and incomplete initial data. Nevertheless, one can say with certainty that this component predominates in the total amount of damage from pollution of water sources.

Sewage of enterprises contain oil products, heavy metal ions, and many different chemical compounds. Harmful chemical elements and substances enter water bodies worsening their sanitary condition, which requires thorough water treatment before using it for household and drinking purposes and for some industrial purposes.

With the growth of technological productions, there is an urgent need to clean up wastewater, which contains petroleum products, heavy metal ions, and many different chemical compounds. Today, there are quite a few efficient technological methods for cleaning up such contaminants, but all these methods clearly depend on the degree of cleaning up on the costs incurred for this process, therefore, in the real economy these methods are used selectively or partially due to the substantial cost of these methods.

The environmental problems of wastewater treatment are considered in papers of Alekseev M.I., Vinogradov S.S., Gubanov L.N., Ilyin Yu.A., Evilevich A.Z., Zainullin Kh.N., Zapolsky A.K., Koganovsky A.M., Kudryavtsev V.N., Ksenofontov B.S., Naidenko V.V., Palgunov P.P., Smirnov A.D., Tarasevich I.Yu., Yakovlev S.V. and others.

The use of natural materials for wastewater treatment is reasonable from the environmental and economical perspectives even though such materials do not offer necessary sorption properties without being modifed or nano activated. Due to modification or nano-activation, the sorbent surface takes on new properties and combines useful properties of the original mineral and synthetic sorbents.

In spite of broad applicability of sorption methods and procedures in industrial wastewater treatment, there is a number of problems in this field. The most critical problems are insufficient sorption capacity of materials, lack of reliable sorbent recovery techniques, sustainable treatment technology which uses sorbents, methods of recycling heavy metals using complex formation.

CHAPTER 1. REMOVAL OF HEAVY METALS FROM WASTEWATER

1.1. Industrial Wastewater Containing Heavy Metal Ions

A variety of chemical industries and an abundance of chemical products (primary, intermediate, and final ones) used and obtained during manufacturing activity are responsible for generation of wastewater which varies in composition and volume and is contaminated with organic and inorganic substances [1].

In most cases, wastewater is a complex system consisting of various subsystems. Impurity concentration in wastewater may vary: wastewater coming from product refrigeration and equipment cooling is scarcely contaminated, while wastewater coming from manufacturing activity is severely contaminated [2]. The basic contaminator is electroplating and pickling industry.

In spite of permanent improvement of current technologies and development of new ones, the electroplating industry is still the least sustainable production [3]. It is characterized by high consumption of quality water [4] and disposal of large volume of wastewater [5]. The average fresh water consumption makes 30-50 percent from industry’s total consumption of water [6]. An electroplating plant produces 600-800 m^3 of wastewater daily on average.

The composition and concentration of impurities in solutions to be decontaminated specify the composition and properties of the sludge produced by neutralization as well as heavy metal content in it [7].

Galvanizing lines produce two types of effluence: industrial wastewater and waste galvanic solutions [8-10]. This effluence contains a number of toxicants, the most environmentally hostile substances are heavy metal ions - cadmium, copper, zinc, chromium, nickel, lead.

After recovery, the part of waste galvanic solutions is reused [11]. Recovery, however, is a challenging and cost-extensive task which is not always practicable. That’s why, in most cases, wasted galvanic solutions are decontaminated together with industrial wastewater at waste treatment facilities, and, as a result, the load on waste treatment facilities increases when the concentration of metal ions is in compliance with the wastewater regulations [12].

The wastewater danger level depends on toxicity of contaminating materials contained in the wastewater [13]. High toxicity of wastewater is caused by substances such as heavy metal salts [14, 15].

Some heavy metal ions have a deleterious effect on growth of many lower organisms if present in watercourse in concentration from 0.01 to 0.1 mg/l, and sometimes have destructive effect if present in concentration of 0,02 mg/l.

The accumulation of chromium in the human organism has toxic effect on its vital organs-damage of central nervous system.

The wastewater produced by engineering plants can contain chromium and copper in concentration up to 400-500 mg/l, and nickel in concentration of a few tens of mg/l [16]. Copper if present in wastewater in concentration above 1.9 mg/l reduces sludge digestion at waste water treatment, concentration of 1.0 mg/l reduces treatment efficiency by 5 %, concentration of 75 mg/l is an instantaneous release of metal and can damage the equipment of wastewater treatment facilities.

1.2. Migration of Heavy Metals in the Environment

The anthropogenic soil anomaly causes partial removal of metal ions, first of all, zinc, and chromium, more even soil profile redistribution and immobilization of the part of metals in persistent inorganic forms [17].

Many factors are responsible for distribution of heavy metals in soil surface. Such distribution depends on the contamination source, regional meteorological conditions, geochemical factors, and landscape-related setting in whole.

The length of stay of particulate pollutants in the environment depends on their mass and physico-chemical properties. The heavier the particles, the faster their deposition.

According to the current understanding, heavy metal migration is basically influenced by the convective mass transfer of solutions in the porous medium, relation of internal and external factors of heavy metal migration: properties of chemical elements and their ability to produce soluble and inert forms, physico-chemical properties of soils [18].

The most important migration type is the liquid phase migration as the most metals get into soil in dissolved form or in form of aqueous slurry. Nearly all interactions of heavy metals with liquid soil constituents occur between liquid and solid phases.

The types of heavy metal distribution profile in natural and anthropogenic soils vary widely and are determined by several factors: dynamic equilibrium of soil constituents; physico-chemical properties of natural and anthropogenic water, solutions having drainage effect on the landscape; relation of water migration and biogenic migration of heavy metals [19].

The heavy metal migration is also considered in the context of concepts of soil stability [20, 21].

The factors responsible for heavy metal retention in soil are as follows: exchange adsorption of clay and humus surface; forming of complex compounds with humus; forming of insoluble compounds, especially by restoration.

The rate of soluble substance migration in soil layers varies. The average total rate of heavy metal migration in a humus horizon is approximately 3.7 cm per day, in the under horizon, it is twice as large - 7.1 cm per day.

In the profile, a man-induced dispersion train of heavy metals is formed which is influenced for the most part by the organic soil compound [22, 23]. Heavy metal migration in soil mainly occurs in the form of organomineral complexes [24-26].

The organic soil compound forms stable complexes with metals. The humic substances play the leading role in the metal cation fixation [27-30]. They are divided into fractions: humic acids, fulvic acids and humus. Interactions between humic substances and heavy metals are based on ion exchange, sorption, chelation, coagulation and peptization [31].

The acidity is an important factor affecting the behavior of heavy metals in soil. Due to neutral and weakly alkaline reactions, poorly soluble compounds are formed: heavy metal hydroxides, sulphades, phosphates, carbonates and oxalates. If soil acidity increases, the backward process is observed - poorly soluble compounds are transformed into more mobile compounds, so the mobility of many heavy metals increases.

And still, the effect of soil acidity on heavy metal mobility is not so unambiguous. Although mobility of many heavy metals decreases in response to soil pH increase (e.g. Fe, Mn, Zn, Co etc.), mobility of some metals increases in case of soil neutralization. Among these are molybdenum and chromium which have ability to form soluble salts in weak acid and alkaline mediums [32].

Besides, heavy metals such as mercury and cadmium have ability to be mobile in the alkaline medium because they can form complex compounds with soil organic matter. Heavy metals interact with the soil solid phase using specific and non-specific adsorption mechanisms.

Soils with high adsorption ability are rich in clay and organic matter and are able to retain metals especially in the upper layers. This is true for carbonate soils and soils with neutral reaction.

In these soils, less toxic compounds may be washed into the subsoil water and absorbed by plants than in sandy acid soils. In spite of that, it is highly probable that the toxic concentration of the elements will reach its maximum and will cause the imbalance of physical, chemical and biological processes in soil.

Heavy metals retained by the organic colloid part of soil minimize biological activity, inhibit nitrification which is very important for soil fertility.

Retention of heavy metals in sandy soils having high absorption ability like acid soils is very weak except for molybdenum and selenium. That’s why they are adsorbed by plants without difficulty, moreover some of them have toxic effect even in a very small concentration.

The available data concerning soil contamination with heavy metals show that accumulation of a large volume of waste causes transformation of natural systems into natural and man-induced and even industrial ones [33].

One of the basic mechanisms of the observed transformation is the man-induced heavy metal migration in the “industrial waste - soil” system which causes local contamination of soil and has specific character other than naturally occurring physicochemical migration of elements in soil [34]. According to many publications such as [35-38], complex systems such as heavy metal migration in the “industrial waste - soil” system can be researched only using an integrated approach.

Uncontaminated soils contain 6-60 mg/kg of copper on average. The accumulation in upper layers of soil is specific to the distribution of copper in the soil profile. The copper cation (II) is the most abundant movable copper form in surface layers, though other ion forms may be present in soils.

Soil solutions contain copper in concentration of 0.003-0.135 mg/l. More than 90 % of soluble copper forms produce complexes with organic substances. Copper migrates in ionic, colloidal and suspended forms in different layers of soil profile [39].

The critical level i. e. the amount of heavy metals entering the environment which does not result in accumulation of pollution in landscape components and its structural change, is 3-30 kg/km^2 annually for copper [40].

Zinc is wide-spread in all geospheres. Zinc basically migrates through the hydrosphere. Zinc content in soils varies from 10 to 800 mg/kg, though usually it is 30-50 mg/kg, the average content amounts to $5 \cdot 10^{-3}$ %. In the weakly alkaline medium, zinc hydrolyzes, and zinc hydroxide is produced. In the acid medium, zinc is present in a divalent form and can be adsorbed by mineral suspensoids and form complexes with organic substances.

Due to presence of organic substances and calcium, soil has enhanced ability to fix zinc [41, 42]. The organic substance is much more a factor of migration than a factor of accumulation for zinc [43]. Amount of zinc entering the topsoil annually is 9 mg/kg. At the present time, zinc content is 255 mg/g, i.e. 5 times the average values in standard conditions [44-46].

Chemically, nickel has the average activity and is similar to ferrum and copper. In addition to other metals, nickel content in soils is up to 40 mg/kg or $4 \cdot 10^{-3}$ % [47].

In acid soils, nickel's mobility is low, at pH = 6.7 and less, poorly-soluble sedimental nickel oxide (II) is produced.

In the alkaline medium at pH = 7.5-9.5, nickel passes to soluble, mobile and very toxic states. Due to presence of organic acids in soil, highly soluble nickel compounds are produced. In the "soil - water" system, nickel is present in complex forms with inorganic and organic ligands. In forest soils, nickel is present in concentration of 8.5-15.0 mg/kg [48]. The tillable land has the highest nickel content - up to 1000 mg/kg [49].

Due to presence of chromium in soils (up to 50-70 mg/kg of dry soil), chromium moves in the food chain "soil - plant - animal - man". The environmental pollution results in increase of chromium amount that moves in this chain. Gramma grass and other plants may be contaminated (normally, 0.1-0.5 mg/kg of dry matter on average) too, as a result, people may receive higher doses of chromium from food.

Lead content in soil usually varies from 0.1 to 20 mg/kg, background matter content is 10-70 mg/kg, at distance of 50-100 m from motor roads - usually less than 40 mg/kg. Lead content is much greater in soils which, for many years, were fertilized by sewage treatment facility sludge containing lead (usually less than 1000 mg/kg [44].

Lead in soil may be relatively insoluble (sulphate, carbonate, oxides), soluble, occluded on clays and disperse organic matter, or formimg complexes with some organic molecules as well as humic acids and fulvic acids.

Soluble lead from sediments and soils is taken by rivers to the World Ocean that receives about 17 thousand tons of lead annually.

The average background lead content in surface water is around 0.02 mcg/l. In surface and underground water, lead content is not higher than 10 mcg/l, lead, however, has ability to accumulate, and the average lead content in land plants is around 0.27 mg/100 g of dry matter.

All heavy metals may impair biological activity in soil, inhibit enzyme activity by reduction of carbon dioxide emission and microbial abundance.

Metal compounds are deposited on soil surface, adsorbed by organic substances, move through the profile with soil solutions, leave the soil profile. Due to migration processes, man-induced heavy metal anomalies are produced in soils.

1.3. Removing Heavy Metals from Wastewater

The basic physicochemical methods for treatment of wastewater containing heavy metals are chemical, membrane, electrochemical, biochemical, and sorption methods [49-54]. Ion exchange and electrolysis have a number of substantial drawbacks in spite of all their benefits [55]. During ion exchange, heavy metal salt solutions (eluate) are produced which are to be disposed of, besides, the reagent consumption is high. The electrochemical method is not always useful when advanced treatment is needed and is very energy-consuming [56].

Treatment of wastewater from electroplating and pickling industries is performed using mainly chemical methods and produces galvanic sludge. The amount of the sludge accumulated by now may be compared with natural mineral deposits [57]. That's why galvanic sludge should be considered as a man-made raw material for production of copper, nickel, zinc, tin, lead, chromium and other metals, that conditions their treatment technologies [58].

The industrial experience of metal abstraction from galvanic sludge by vitriolization and following sulfide precipitation, electrolysis and metal extraction from the solution showed economic inexpediency of the technology [59].

Numerous aspects of use of galvanic sludge as additives for constructional materials and paints, many other methods of application [60-64], as became evident afterwards, do not meet the environmental safety requirements [65-70].

Application in metallurgical industry, where great amounts of non-ferrous metals are needed, is limited by strict sludge composition requirements [71, 72].

Storage of galvanic sludge on industrial sites causes air and water contamination with toxic heavy metals. Waste may be buried at special landfill in metal containers or polypropylene bags. Waste burial using special pits equipped with the shale baffle is a promising method [73-75].

The monographs [76-79] address numerous aspects of removal of heavy metals from industrial wastewater

Ferritization is one of the most efficient methods used for stabilization of galvanic deposits from effluent neutralization station [80]. The method is not new, the manufacturing technology of this process, however, was developed relatively recently at the Ulyanovsk State Technical University [81, 82].

The technology involves treatment of galvanic wastewater (galvanic sludge) using ferrum solution (II) with simultaneous air oxidation of the reaction. On the surface of heavy metal hydroxides of the treated galvanic sludge, mixed oxides of heavy metal ions and ferrum are produced - ferrites with general formula $Me_nFe_{3-n}O_4$.

Ferritization consists of two stages. In the first stage, mixed hydroxides are produced and then are oxidized to form ferrites:

$$(3-n)\ Fe^{2+} + nMe^{2+} + 6OH^{-} \rightarrow MenFe_{3-n}(OH)_6$$

$$Me_nFe_{3-n}(OH)_6 + O_2 \rightarrow MenFe_{3-n}O_4 + 2H_2O + 2OH^{-}$$

Ferrites have spynel type closed-pack lattice. That’s why heavy metal ferrites in contrast to hydroxides are normally insoluble in water and dilute water solutions of strong inorganic acids and alkalies.

The studies of heavy metal ion leaching from ferritized galvanic sludge showed that, in acid medium (pH = 3.5-4.5), they are far less soluble than untreated galvanic sludge. It has been also established that long treatment of the ferritized galvanic sludge using water (up to 60 days) does not result in increase in concentration of heavy metal ions in the extract. The ferritized galvanic sludge is less dangerous for the environment than non-ferritized [83, 84].

Chemical stabilization of galvanic sludge in the ferritized form, physicochemical and structural properties of ferritized galvanic sludge offer possibilities of their landfilling as solid waste [81].

Looking for new ways to use ferritized galvanic sludge is an urgent challenging independent ecological target here is a background of use of this type of galvanic sludge for removing heavy metal ions from wastewater [85, 86].

The technological plans of removal of heavy metal ions from galvanic waste water usually include two stages. During treatment of acid-alkali wastewater, at the the first stage, as a rule, chemical treatment using alkali and alkali-earth metal hydroxides is performed, in most cases, solution of calcium hydroxide (lime milk) in presence of flocculant (polyacrylimide). The process includes mixing of wastewater with the treating agent in the mixer reactor, their interaction after which insoluble compounds are produced and precipitate in the precipitation tank.

At the second stage, a more advanced treatment of wastewater is performed to meet the applicable regulatory requirements. For advanced treatment, application of low-cost and effective sorbents or industrial waste is reasonable, for example, ferritized galvanic sludge [87].

For advanced treatment of galvanic wastewater, a flotation method may be used as well. It is suggested that the coagulation (electrocoagulation) method may be combined with flotation method, for this purpose salts of ferrum, aluminium, magnesium are used and alkaline agents are added [88].

For biological treatment, the following facilities are used: aerotanks, biological filters with loading for preatreatment or final treatment, traditional biological filters, biolite filters for main or additional treatments, lagoons with mixing or aeration for advanced treatment [89].

Heavy metal ions have toxic effect on sludge biocenosis, that’s why it is very important to comply with wastewater regulations and, as best as possible, to remove metals from wastewater entering municipal sewage treatment facilities.

1.4. Sorption Techniques of Wastewater Treatment

Removing metals from wastewater using sorption method become widespread enough because it very effective and does not produce secondary contamination. Sorbents absorb metals from water solutions almost to any residual concentration [90].

Depending on the interaction mechanism of the sorbent with sorbate, sorption processes can be divided as follows [91]: adsorption - concentrating of components on the surface of the chemically inert sorbent due to molecular interaction; extraction - solubilizing of components in the solvent applied on the sorbent; ion exchange - reversible reaction of electrolyte components with mobile cation or ionite anions; deposition - solution component form poorly-soluble compounds during interaction with chemically active substances present in sorbent’s pores.

The adsorption of contamination containing in wastewater has three processes: external diffusion of molecules from the liquid phase to the surface of the adsorbent due to Brownian diffusion or mixing of the liquid due to eddy diffusion; internal diffusion of molecules along macropores to the surface of micropores, speed of such diffusion is determined by the adsorbent composition and size of sorbate molecules; particularly, adsorption of molecules of the dissolved matter.

Adsorption is influenced by both physical and chemical interactions between the adsorbent and sorbate [92].

In case of physical interaction, contamination is retained on the surface of the sorbent due to weak van der Waals bondings. In case of chemical interaction, contamination is retained due to stable bond between active participants on the surface of the sorbent and contamination [93].

Thus, sorbent effectiveness depends on presence of sufficient surface and sections on this surface which are active in relation to wastewater contamination. Adsorption effectiveness depends not only on sorbent’s properties and quantity but also on chemical properties and concentration of adsorbed substances. The higher concentration of the substance, the higher quantity of this substance is adsorbed per each gram of the sorbent.

Adsorption rate is influenced by rate of the dissolved matter diffusion to the surface of the sorbent through the liquid film which extends around sorbent's particles and may be increased by mixing, in such event, rate of the dissolved matter diffusion from the surface into pores increases. Adsorption rate is also influenced by the size of sorbent particles, rate of liquid flow through sorption loading, contamination concentration, temperature, medium response.

Adsorption is an exothermic reaction during which the decrease of free energy may occur that's why, in case of temperature drop, the adsorption rate increases. The adsorption rate is also influenced by the response of the medium: in most cases, acidity decrease causes increase of adsorption of contamination from wastewater. Substances which are less soluble are adsorpt better [94, 95].

During adsoption from solutions, parallel to adsorption of neutral molecules, ions in the solution may be adsorbed. In this case, the positive ion is adsorbed chiefly on sorbents with negative surface and vice versa. These processes are usually accompanied by ion exchange between adsorbent and solution, so called ion-exchange adsorption [96].

In most cases, sorption methods are used for secondary treatment of wastewater.

Sorption may be performed in static conditions (mixing devices) and in dynamic conditions (filters, devices with fluidized beds) [97-100].

In static conditions, the sorption process includes vigorous mixing of the treated water with the sorbent for some time and the following separation of the sorbent from the water by sedimentation or filtering. If new portions of the sorbent is introduced into the treated water, the water may be decontaminated up to any concentration.

In dynamic conditions, sorption is performed in adsorption devices with different design. For treatment of water with granulated sorbents, devices with dense, looses, mobile, and liquid bed are used. Single-layer and multi-layer adsorbers with dense bed of sorbent operate with upward and downward water flow using parallel and sequential schemes [101].

1.5. Materials Used in Sorption Techniques of Purification

In industrial practice, various sorbents are used which can be divided into two groups: carbon sorbents and inorganic sorbent. The first group includes active carbons, peat and other materials produced mainly by processing of organic materials, the second group includes silica gel, alumogel, zeolite. All sorbents are, to different extents, active in absorbing of both oil products and metal ions.

The basic material used as a sorbent at the present time is the activated carbon (AC). Almost any carbonaceous material may be used as a source material for AC: coal, wood, polymers, waste from food processing, pulp, paper and board, microbiological and other industries. The sorption capacity of granulated AC for hydrocarbons and oil products is high enough: 60-200 mg/g, that's why they can be used for additional treatment of oily wastewater [102-105].

Activated carbon is also widely used for removal of metal ions. At the following initial concentrations of heavy metal ions (given in mg/l): copper - 38.5; nickel - 0.37; ferrum - 87.5; three-valence chromium - 9.6; six-valence chromium - 2.1, the metals are found in the product water in trace quantities. The consumption of powdered carbon is 2 kg/m^3 [92].

Treatment of cyanide-containing galvanic wastewater also shows good results, in particular, removal of copper cyanide by activated carbon layer filtration.

The activated carbon production is an energy-intensive process that results in high enough cost of the final product and the need to reactivate the sorbent. For reactivation of active carbons, thermal, chemical or biological methods are used.

Highly volatile organic substances are removed by high temperature air desorption (120-140 °C), steaming-out (200-300 °C) or using flue gas (300-500 °C). Such methods of reactivation are also energy-intensive and require the complex equipment. The cost of reactivation of the activated carbon in indirect-heating furnaces is a half of the cost of the new sorbent. Reactivation of the activated carbon after heavy metal absorption is performed by heating in the reactor made of stainless steel at a temperature 300 °C within 4 hours in air flow [91].

At chemical reactivation, organic compounds are removed by flushing in acid or alkali solutions.

Biological reactivation includes biochemical oxidation by microorganisms of organic substances within 10-20 hours.

In case of thermal reactivation, more than 50 % of carbon is burnt. It is uneconomical for companies to replace carbon from time to time due to its high cost, that’s why in most cases, instead of thermal reactivation, companies apply flushing in hot water or steaming, though that does not ensure 100 % reactivation but ensures operation of waste treatment facilities.

Many natural materials such as zeolite, sapropeles, peat etc. have sorption properties. The cost of natural sorbents is dozens of times lower than the cost of artificial sorbents, that’s why in most cases the natural sorbents are not reactivated.

The studies [101, 106] present the results of systematic research of sorption properties of natural materials used for removal of various oil products. For improvement of treatment of oil-containing wastewater, the authors have developed combined multilayer sorbents for removal of oil substances having wide range of particle dimensions, with purification degree 92-98%.

It is demonstrated that ultradispersed powder of aluminium oxyhydroxide ensures effective enough removal of both dissolved hydrocarbons (70-80%) and emulsified oil products (60-90%). Application of fragmented materials - natural zeolites such as hongurin and opoka - for filtration treatment of wastewater is more easily producible than application of the powder but it is less effective than the latter. The maximum oil-uptake of aluminium oxyhydroxide is 1.3 g/g, hongurin and opoka - 0.85 g/g.

It is found, that the application of pressed basalt or polypropylene fiber is the most easily producible among the identified fiber materials. Their oil-uptake values are 6.1-7.2 and 3.8-4.5 g/g respectively. Application of carbo fiber with higher oil-uptake (10.2-10.6 g/g) results in more expensive filtration elements.

Clay materials (diatomite, opoka, bergmeal) are the most popular inorganic sorbents used for water treatment. In terms of physicochemical properties, they may be divided into several groups.

Dispersed silica of sedimentary origin that 68-99% consists of amorphous silica. Of these, opoka has high concentration of magnesium oxide and ferrum oxide (III), and bergmeal is characterized by high concentration of aluminium oxide (up to 15.7%).

Layered and band alumino-ferrum-magnesium silicate are divided into minerals with expanding structure (vermiculite, montmorillonite) and minerals with rigid structure (kaolinite, agilite, mica)

The mechanism of sorption of contamination from water using clay materials is complicated and includes van der Waals interactions between carbon chains and the extended surface of silica microchips as well as Coulomb interactions between charged and polarized molecules of sorbate and positively charged parts of sorbent surface containing ions H^+ and $A1^{3+}$.

Biosorption filtration using natural zeolites or other sorbents is applied for intensification of biological treatment of sewage and industrial wastewater [107]. Sorption of heavy metals from solutions using biological technology is an ever-expanding research field [108-111].

In spite of variety of used adsorbents, many of them do not meet all requirements for such materials, that's why research and development of new sorption materials is a continuous process [112, 113].

Production of comparatively inexpensive sorption materials from industrial waste is of higher priority as in this case waste is reused [114, 115]. Industrial waste used as adsorbents is free of the main disadvantage present in the most used adsorbents, especially ionites, - high cost.

Comminuted rubber and tyre char produced after waste tyre pyrolyses may be used as carbon sorbents.

Transition metal ferrites becoming more common in current technologies. One of the ferrite applications is sorption from liquid and gas media. The ability of ferrites to adsorb heavy metal ions is used for removal strontium and uranium from water [116]. Powdered ferrites obtained from galvanic sludge are used for removal of hydrogen sulfide released during hardcoal combustion [117].

Regularities of processes of oleinic, linolic and octadecatrienoic acid adsorption-desorption from organic media on the surface of magnetite and ferrites of ferrum, manganese and copper have been studied. [118].

It is found that in areas of low equilibrium concentration, adsorption for all systems means volume filling of pore space of ferrites by sorption solutions, and adsorption equilibrium stays within the theory of micropore volume filling. In case of higher concentrations, condensation of adsorbent solutions occurs in mesopores and on the external surface of particles of ferrum, manganese and copper ferrites.

To intensify settlement of metal ions and other contaminants from galvanic wastewater, flocculants are added to wastewater. In international water treatment practice, natural [119] and synthetic polymeric flocculants, in particular polyacrylimide, are extensively used.

The adsorption and adsorption layer structure depend on the molecular weight of the polymer and molecular-mass distribution. The adsorption layer gets thicker if molecular weight increases.

1.6. Sorbent Activation and Modification

Some clay materials are active enough in their natural state, but most of them must be activated by chemical or thermal methods to increase and adapt their porous structure [120-123]. Due to different methods used for modification of natural materials, including activated carbon, the sorbents are produced which have specific sorption properties suitable for wide range of organic and inorganic substances [124-128].

The easiest way which does not require additional reagents and complex equipment is the thermal modification of different materials. Materials produced are characterized by better sorption properties in relation to various organic and inorganic substances. Opoka and bergmeal are inciderated at 1000 °C in presence of chloride and carbonate of sodium: the incinerated minerals do not expand in water.

The research [129] shows that thermally modified (400-600 °C) brucite can be used for removal of ferrum and manganese from natural water. Influence of thermal treatment of natural silicate and carbonate minerals on their sorption properties was studied. The results from this study shows that thermal treatment at high temperatures (500-800 °C) reduces sorption capacity of silicate minerals such as wollastonite and diopside as related to metal cations [130].

Among the natural minerals, special attention is paid to zeolite which is due to its wide occurrence and economic expediency of technological application [131-134]. Heating of natural zeolites up to 700 °C increases specific suppression and improves their sorption properties [135]. To produce durable and waterproof materials from natural zeolites, they are heated in furnaces with chloride and carbonate of sodium at 1000 ºC. In case of fast heating of source materials, they foam and as a result the volume and porosity increase by 5-20 times.

In the research [136], aluminosilicate sorbents were used for removal of oil products from the water surface: expanded pearlite, waste produced from silicate mineral inclusions as a result of hardcoal combustion.

Chemical treatment together with heating in water solutions at high temperatures (hydrothermal treatment) is also used. During hydrothermal modification of aluminosilica gels with various composition, porosity and specific suppression of sorbents produced depends on the silica and alumina relation [137].

Heavy metal sorption is increased due to modification of kaolinite by phosphate and sulphate of sodium [138].

Treatment of diatomite by manganese oxide is used in removal of lead ions and [139] paints from textile industry wastewater [140].

The authors [141] suggest that activated aluminosilica adsorbent produced from adding of various activators (magnesite and dolomite) to natural clay may be used for removal of heavy metal ions from wastewater.

There is much evidence concerning the use of organic substances in modification of natural and other substances. The microstructure of montmorillonite can be changed under the action of SAA [142]. Due to treatment of granulated aluminosilicate sorbents using various silicoorganic compounds (sodium alkilsililiconate, polyethylhydroxyloxane etc.), the sorbents take on water-repellent property and their oil-uptake increases. Due to treatment of the surface of zeolites using silicoorganic compounds, it becomes hydrophobic and as a result oil sorption from water improves. Zeolites treated with amin [143] are successfully used for removal of ion lead and cadmium from solutions.

Except chemical treatment, there are other methods of modification of clay materials which help to improve their sorption properties. The authors [144] studied influence of ultrasound, microwave and hydro-thermal treatment on the properties of montmorillonite. In study [145], ultrasound was used for regulation of the porous structure of vermiculite.

One of the most prospective directions in the field of sorbent and catalyser synthesizing is production of semisynthetic sorbents - composite materials made of natural mineral materials by chemosorption modification of organic and inorganic compounds, deposition of simple and complex oxides on them or other treatment.

The new field of application of nanomaterials based on carbon and inorganic nanostructures has been developed very intensively [146-149].

As a result, the sorbent is produced which have porous structure other than the source minerals do and combine useful properties of the source materials and synthetic sorbents [150, 151].

The main directions of practical application of surface-modified materials: selective sorbents, chromotographic materials, chemical and biological sensors, catalysers, self-cleaning, biononcontaminated and anticorrosive coatings, implants, adhesives and antiadhesives, carriers of enzimes and cells.

Based on the analysis of the current state of the problem of removing oil products and heavy metals from wastewater, a conclusion about prospectivity of application of natural minerals including modified ones in treatment systems is made. The use of industrial waste as sorbents for removal of heavy metal ions from wastewater is another promising direction.

Development of these directions will contribute to minimization of pressure made by industrial wastewater and dangerous waste on the environment.

CHAPTER 2. WASTEWATER USING NANOMODIFIED NATURAL MATERIALS

2.1. Method of Removal of Heavy Metal Ions from Wastewater Using

In this paper, a technique of wastewater treatment from heavy metal ions using nanoactivated complexes of natural zeolite and diatomite is proposed. This technique can reduce significant costs in preparation of raw materials and its subsequent chemical modification. Technological solutions are proposed for disposal and recycling of industrial wastewater allowing obtaining water treated to the necessary regulatory water content of impurities and returning it to the process cycle. The uniqueness of the method and techniques is in the use of nanoactivated natural sorbents for treatment of both ion-exchange water, and also natural water from heavy metal ions that pollute it.

Some natural materials are quite active in the natural state, but most of them are advisable to activate by chemical or thermal means to increase and adjust their porous structure and change the chemical nature of the surface [152-157]. Various methods of modifying natural materials, including activated carbons, lead to production of sorbents with specific sorption properties to a wide range of organic and inorganic substances. A new field of application of nanomaterials based on carbon and inorganic nanostructures is developing especially intensively. As a result, sorbents with a porous structure different from the original mineral are obtained, combining the useful properties of the initial material and synthetic sorbents.

One of the most promising methods of treating natural and waste water is sorption on various natural materials, to re-use treated water in closed water systems of enterprises. The increase in the scale of application of natural sorbents is due to the fact that, with a developed specific surface, they have good sorption properties and are ten times cheaper than synthetic ones. In this regard, their technological application is simplified often excluding the regeneration stage.

The simplest method which does not require additional reagents and complex hardware design, is thermal modification of various materials. The obtained materials are characterized by increased sorption properties with respect to various organic and inorganic substances.

The main problem of modern technological systems of application is the development of environmentally safe technologies with the most closed cycle and the minimum amount of waste. The current situation in this field of research has necessitated the improvement of sorption technologies and selective processes for treatment of contaminated solutions and process fluids for the integrated solution of resource-saving and environmental problems. As a result of target of studies of a wide range of sorption materials in relation to wastewater treatment, the processes of adsorption of oil products and heavy metal ions on natural sorbents and their analogs have been further developed.

Often, these methods involve natural sorbents with subsequent mechanical grinding, thermal and/or chemical modification to obtain high rate of adsorption at the output. The chemical modification must be chosen for the different types of contamination separately which also increases the treatment process cost. The developed method allows creating a nanoactivated complex of natural zeolite and diatomite. Its production is tens of times cheaper than that of the existing methods in the absence of costs for expensive grinding, expensive chemical components and chemical modification process.

In this paper, a sorbent for water treatment from heavy metal ions is produced from a natural zeolite and diatomite nanoactivated using an ultrasonic through-flow disperser in the following ratios of components (wt. %): diatomite - 20-30, zeolite - the rest. The resulting sorbent allows trapping arsenic ions of different valences, cadmium, cesium, copper, zinc, nickel, lead, chromium, sulfate ions, chloride ions, and others.

The main difference of the result in the output sorbent of this method is an expanded list of heavy metal ions captured to a high degree of treatment, and also the most concentration of contamination of effectively treated water which is greater than 20 mg/l, i.e., 3-4 times higher than that of most of the previously proposed methods. Furthermore, when using the proposed sorbent obtained in this method, no metal ions release, and absorption of metal ions actively continues. These technical results are achieved because a sorbent for water treatment from heavy metals ions is produced from natural zeolite and diatomite nanoactivated in the through-flow ultrasonic disperser.

Moisture is separated by passing the slurry through a separator which also divides the resulting prepared sorbent into fractions followed by calcination for 4 hours at 250-300 °C. Thus, the proposed technique makes it possible to obtain fractions of nanoactivated natural sorbent with particle size of classes: 0.5-1 nm, 0.005-0.01 microns, 0.5-1 micron. Reduction in sizes is done by ultrasonic cavitation in the flow regime; the percentage ratio of the mass fraction of solids to water is 70:30.

The sorbent samples of nanoactivated complexes of natural zeolites and diatomites were tested for the adsorption capacity with respect to heavy metal ions as follows. Absorption of the specified heavy metal ions was studied from model solutions at a concentration of 20 mg/l. 100 g of the sorbent was placed in 10 l. of the test solution in the pH range of 5-7 and stirred with a mechanical submersible stirrer for 30 minutes. The solution was then settled for 20 minutes and analyzed by stripping voltammetry for residual content of heavy metal ions. The concentration was evaluated by adding the standard solution of the specified heavy metal ions with a concentration of 20 mg/l (50 ml). The minimum detectable concentration was 0.001 mg/l. The sorption percentage was calculated while taking the initial concentration of heavy metal ions as 100%.

Depending on the data obtained, the degree of extraction was determined to determine the dynamic characteristics of the adsorption process. Experimentally, the amount of adsorption (A) of contaminants and the degree of extraction (α) were calculated as follows:

$$A = (C_{init} - C) \cdot V_{sol} / m_{sorb}$$

$$\alpha\ (\%) = (C_{init} - C) \cdot 100 / C_{init},$$

where C_{init} and C are the initial and the equilibrium concentration of heavy metal ions in the solution; V_{sol} - solution volume; m_{sorb} - sorbent mass.

Data on the sorption capacity of the obtained sorbent samples with different concentration of diatomite and zeolite is given in Table 1.

Table 1

Sorption capacity of the obtained sorbent samples with different concentration of diatomite and zeolite

Zeolite, % of content	Diatomite, % of content	α (%), sorption
100	0	62,3±0,5
95	5	71±0,5
90	10	89±0,5
85	15	90,1±0,5
80	20	97,8±0,5
75	25	100±0,5
70	30	100
65	35	96±0.5

As we can see from the results of experiments, the best results are shown by samples of diatomite in concentrations ranging from 20-30%. The minimum absorption is observed with a decrease in the proportion of diatomite less than 20%, but also with its significant increase of more than 30%.

The experiment showed that there is a degree of extraction ratio on the sorbent sample processing temperature. The data is given in Table 2 and graphically in Fig. 1.

Table 2

Degree of extraction ratio on the sorbent sample processing temperature

T, ^{0}C	100	150	200	250	300	350	400	500	600
α, %	83,5	91,7	95,8	98,6	99,4	97,1	91,8	85,1	83,7

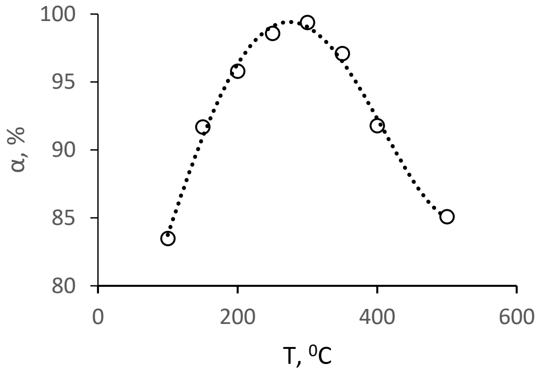

***Fig. 1.* Degree of extraction ratio on the sorbent sample processing temperature**

2.2. Application of Wastewater Treatment System Using Nanomodified Natural Sorbents for Economic Entities

Protection of water resources from contamination is considered as one of the global problems of the present day. Wastewater of almost all economic entities contains oil products, heavy metal compounds and other pollutants. Many effective wastewater treatment systems can provide purification index up to 99.9%, but operation of such systems entails significant costs, therefore many economic entities neglect environmental protection standards despite heavy penalties.

The main task of modern technological systems is the development of environmentally safe technologies with the most closed cycle and the minimum amount of waste. The current situation in this field of research has necessitated the improvement of sorption technologies and selective processes for treatment of contaminated solutions and process fluids for the integrated solution of resource-saving and environmental problems. The target studies of wide range of sorption materials applied in wastewater treatment resulted in further development for processes of adsorption of oil products and heavy metal ions on natural sorbents and their analogs.

That is why design of cost-effective wastewater treatment systems that would ensure high purity is a challenge for all countries.

This paper suggests a multi-stage treatment system based on nanoactivated natural sorbents employed in a closed-loop water cycle. The advantage of using such treatment system as compared to the existing ones is demonstrated on the example of economic entities operating in the machine building industry in Russia, the USA and Israel.

The issue related to the construction of a water treatment system is solved differently at different economic entities, because the technology of water treatment depends not only on the requirements for the quality of treated water, but also on the technological and economic feasibility of water treatment. Such methods as water treatment based on biological sludge, centrifugation, sorption, flotation, ultraviolet water treatment or ozonization, micro- and nanofiltration are successfully used for wastewater treatment. The most popular and effective methods of water and wastewater treatment are as follows: physicochemical treatment methods, biological methods, both aerobic and anaerobic, wastewater treatment based on membranes, thermal methods of water treatment, wastewater treatment based on ozone, absorption methods of treatment based on activated carbon, ion-exchange methods for the selective extraction of contaminants. Each of the methods above has its advantages and disadvantages. Selection of one or another method depends on a number of factors, such as the scale of contamination, its specificity and economic feasibility. The existing environmental protection standards require economic entities to implement new treatment facilities or modernize the existing ones [158-163].

In Russia the most popular methods of wastewater treatment are chemical and physicochemical methods. Chemical treatment is carried out with the use of a variety of chemical reagents that react with contaminants. As a result of their action insoluble deposits form. Physicochemical treatment of water combines several methods: coagulation - adding of coagulants to effluents during reaction that produces deposits in the form of flakes, which can simply be removed, flotation - passing of air bubbles through effluents. When moving up they take oils, surfactants and other contaminants with them. As a result, foam is formed on the surface of effluents, and sorption - the use of materials that can absorb contaminants. First, mechanical treatment is carried out.

Israel was recognized as the best country in terms of industrial wastewater treatment in 2010 and subsequent years. Today Israel remains one of the world leaders in this area. The main methods are as follows: chemical, mechanical, physicochemical, and biological. In addition to the traditional methods of water and wastewater treatment, new and more environmentally friendly and economically viable methods have been developed in Israel: membrane, electrochemical, magnetic treatment, ozonation, treatment with selective sorbents. Each of these methods allows removal various contaminants effectively with minimal harmful effect on the environment.

In the United States the most popular industrial method of wastewater treatment is the membrane treatment method. Growing interest to the technology of ultrafiltration among US specialists is caused by an increasing scale of its application. The method of membrane filtration is based on the following: when wastewater is passing through the membrane, it gives preference to some substances and retains impurities that are foreign for it. The main advantage of this method is almost complete treatment of liquid from foreign impurities and compounds. Thorough filtration prevents pollutants ingress to water.

An analysis of data on industrial wastewater treatment was conducted at economic entities of such countries as Russia, the United States and Israel. The data collected at five economic entities of the machine building industry in each country are presented in Table 3, where C_{in} - input impurity concentration, C_{out} - output impurity concentration, α - extraction degree.

Table 3

Concentrations of heavy metals in wastewater before and after treatment at economic entities of the machine building industry by country

Extracted substance	Russia			USA			Israel		
	C_{in}, mg/l	C_{out}, mg/l	α, (%)	C_{in}, mg/l	C_{out}, mg/l	α, (%)	C_{in}, mg/l	C_{out}, mg/l	α, (%)
	pH = 3-11								
Fe	150.4	0.3	99.8	75.9	0.1	99.9	75.0	0.1	99.9
Cu	10.3	0.4	96.1	9.7	0.35	96.4	13.6	0.3	97.8
Zn	22.8	0.8	96.5	20.6	0.5	97.6	21.4	0.6	97.2
Cr_{total}	95.3	0.3	99.7	89.5	0.2	99.8	90.7	0.2	99.8
Ni	1.06	0.07	93.4	1.09	0.06	94.5	1.15	0.07	93.9
Pb	2.6	0.1	96.1	2.9	0.08	97.2	2.2	0.04	98.2
Cr^{6+}	3.5	0.1	97.1	2.5	0.05	98.0	2.5	0.05	98.0
Other	6	0.2	96.6	4.5	0.02	99.6	4.7	0.01	99.8

The data in Table 3 are organized according to the average value of concentrations at the selected economic entities in the industry most polluted with heavy metals. The above results indicate that the methods used for treatment in Russia are inferior to the level of wastewater treatment at economic entities in the United States and Israel. All the methods used are quite expensive, especially in the USA and Israel. Searching for and development of new economically viable and highly effective water treatment methods is of top-priority importance for these countries.

The use of nanomaterials with unique physicochemical and surface properties provides new opportunities in wastewater treatment. Implementation of nanotechnologies in wastewater treatment is a promising area for the improvement of the quality of treatment. So, paper [164] proposes to use sorption treatment with the help of nanomodified natural sorbents - a nanoactivated complex of zeolite and diatomite - for the treatment of wastewater containing a wide range of pollutants. Natural zeolite and diatomite are distinguished by an increased ion-exchange capacity, the ability to exchange cations, low price and high popularity.

The main component of the selected natural sorbents is silicon oxide. Its content in diatomite reaches 80%, in zeolite - about 70%. These minerals also contain oxides of aluminum, iron, titanium, calcium, magnesium, sodium, potassium, and other oxides.

According to the method proposed in paper [164], the capacity of the sorbent to absorb large concentrations of heavy metals as compared to the concentrations at the selected economic entities specified in Table 3 was tested. The results of the tests are given in Table 4.

Table 4

Results of sorption of heavy metals by nanoactivated complex of natural sorbents

Extracted substance	pH = 3-11		α, (%)
	$C_{in,}$ mg/l	C_{out}, mg/l	
Fe	200	0.1	99.9
Cu	15	0.15	99
Zn	27	0.15	99.4
Cr_{total}	105	0.1	99.9
Ni	5	0.01	99.8
Pb	5	0.01	99.8
Cr^{6+}	5	0.01	99.8
Other	10	0.01	99.9

According to the data presented in Table 4, the results of testing of the adsorption capacity of a nanomodified sorbent with respect to extracted substances showed that this sorbent can be successfully used for wastewater treatment from ions of heavy metals. So, the method of industrial wastewater treatment from heavy metals presented in paper [164] is the most effective.

It is proposed to introduce water cycles based on multi-stage treatment systems presented in paper [165] with the use of nanoactivated complexes of natural sorbents, as well as to reuse treated water in circulating cooling water systems, etc. This system, which scheme is shown in Fig. 2, is the most cost-effective method of wastewater treatment for economic entities.

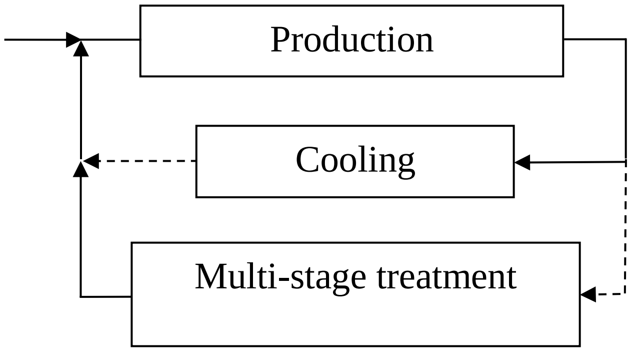

Fig. 2. **Scheme of a closed-loop water cycle**

As distinct from a once-through water-supply system, which is usually used in case of low water consumption and closely located water sources, a full circulating water system presupposes water reuse for the purposes of production. Technologies that allow reusing treated wastewater or regenerating process solutions are of great importance. Most modern economic entities are active consumers of water resources. For the purposes of economic and environmental expediency it is advisable to give preference to a progressive method of recirculating water supply implying the repeated use of this resource. Reuse of wastewater after its treatment for the purposes of the same process operations or for other production needs is an effective way to reduce the number of industrial effluents discharged into reservoirs, as well as reduce costs of economic entities.

The main advantages of multi-stage systems in a close-loop water cycle for industrial effluents treatment based on nanomodified natural sorbents are as follows: a possibility to remove various compounds of heavy metals simultaneously on the first stage, heavy metal compounds are clathrated in the form of crystalline non-leachable products, dispersed suspensions and emulsified pollutants are removed effectively with dissolved heavy metals, the process is not sensitive to the influence of other salts that may be present in effluents in large concentrations [166, 167].

The analysis of the current state of wastewater treatment from heavy metals at the selected economic entities leads to a conclusion about the prospects of using the developed system based on nanomodified natural sorbents, as well as allows recommending them for practical use for wastewater treatment at economic entities of Russia, the United States and Israel.

CONCLUSION

By analyzing the data obtained it can be concluded on the best sorption properties of the obtained sample at a temperature of 250-300 °C. All samples of various concentrations of diatomite and zeolite were tested at different temperatures. We can say that there is a dependence on the sorbent heating time and pH of the solution being treated. Optimal time of the sorbent heat treatment is from 2-4 hours, further heating does not impair the degree of treatment. The data obtained are well correlated with the results [168-170].

Is known to use zeolite-containing sorbent treated by calcination at a temperature of 250 °C for 2-4 hours for water treatment from metal ions [171], but the disadvantage of this invention is the low sorbent efficiency. Also known are methods where a chemically modified zeolite is used [172] and [173]. The disadvantages of these methods include a narrow list of elements to be treated, as well as low sorbent efficiency and high cost of production.

The developed method allows obtaining a high degree of treatment at minimal cost for preparation of raw materials compared to the known methods. The most efficient modes for the sorbent production by the above method were obtained.

The results of new treatment system testing proved more usefulness with respect to those ones used at economic entities in Russia, the United States and Israel. The degree of extraction is 99.9% combined with a high economic efficiency. Moreover, heavy metals are not released if the proposed sorbent is used, and the process of heavy metals absorption is actively continuing.

The optimally effective regimes to produce nanoactivated sorbent by the presented method were obtained.

The use of nanomaterials has high economic potential [174-181].

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