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Adsorbent technologies for removing toxic substances from wastewater

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Abstract

Education and wastewater treatment is a growing concern in the current century due to the growth of urbanization and industrialization. In order to cope with the situation of increasing danger to the environment, numerous approaches to wastewater treatment are used, i.e. physical, chemical and biological (from primary to tertiary treatment) methods. The various cleaning methods used carry the risk of generating secondary contaminants. The most promising is the use of various materials as adsorbents, which have a higher efficiency of wastewater treatment with minimal formation of secondary pollutants. Biosorption is a key process that is highly efficient and cost-effective. This method mainly uses the process mechanism of adsorption to remove toxic substances from wastewater.

Keywords: Adsorption, agriculture waste and peels, nanotechnology, biosorption mechanism, wastewater treatment, graphene membranes, biological and nanotechnological processes

Introduction

One of the most pronounced problems at the present stage of development of scientific and technological progress is the protection of the natural environment from pollutants entering it. The environmental problem of electroplating attracts attention due to the ongoing pollution of the environment by heavy metal ions. Currently, mechanical, chemical, physico-chemical methods, including expensive electrochemical methods, are used to treat wastewater from galvanic production. Most of them are energy-intensive, technologically complex and rely on imported equipment and expensive reagents. Therefore, in modern economic conditions, priority should be given to cleaning methods that, being effective, would be based on the use of inexpensive local raw materials and production waste. Of considerable interest is the use of renewable waste from the wood processing industry as reagents for the treatment of galvanic waste. Some types of trees are industrially significant species and are intensively used in the national economy. At the same time, a huge amount of sawdust, wood chips, bark, formed during the processing of commercial wood, annually accumulating, is practically not used, is collected in dumps, where it rots or is burned. At the same time, wood processing products are a raw material resource - the richest source of many unique natural compounds. Such raw materials, as a rule, contain natural biologically active substances, the process of which isolation from waste is in most cases more profitable than chemical synthesis. In addition, waste is transferred to the category of secondary material resources, which is relevant from an environmental point of view. In this regard, the study of the possibility of developing and implementing processes for the treatment of electroplating waste using waste from wood processing enterprises seems to be very relevant.

The fuel industry is the main direction of industrial development. At the same time, oil and gas production and processing of raw materials are the main sources of technogenic environmental pollution [1]. For example, water bodies receive a colossal anthropogenic load when untreated or poorly treated wastewater is discharged, which are formed in oil fields, refineries, oil depots and other similar industrial facilities. The concentration of pollution in water sources is several times higher than the established maximum allowable concentrations [2].

In water, oil products can be in free, bound and dissolved states. Free coarse oil products float to the surface of the water and can be removed by gravity settling. Various methods of flotation and coagulation are traditionally used to remove bound fine contaminants. The efficiency of purification processes is more than 70%, while it is possible to reduce the concentration of oil products in water to 20 mg/dm^3. To extract finely dispersed emulsified oil products, mechanical filtration is used, which makes it possible to reduce the content of contaminants to 10 mg/dm^3. Dissolved petroleum products are considered the most difficult to extract from water. High efficiency can only be achieved using expensive methods. Reducing the concentration of substances in wastewater to 1 mg/dm^{3}and lower is possible during sorption or membrane purification [3–5].

Sorption absorption of contaminants from aqueous solutions is the most common way to remove residual oil products from surface and industrial wastewater. Traditional sorbents - activated carbons - have a high sorption activity, but are very expensive. [6]. Sorbents based on vegetable raw materials or phytosorbents are considered acceptable substitutes for expensive coals: peat [6–7], woodworking waste (sawdust, tree trimmings) [8–11], plants (moss, reindeer moss) [12], and agricultural production waste (rice husks, straw, tangerine and coconut peels) [13–16].

Woodworking waste is of particular interest. Among hardwoods, birch and oak prevail, the wood of which is used for the production of veneer, plywood, cellulose, and decorative products. Along with this, the tasks solved by the municipal services of settlements include the disposal of a large amount of wood waste from sawdust of urban plantings at landfills [17, 18]. The secondary use of such materials will allow the introduction of innovative wastewater treatment technologies and significant savings in the economic activities of enterprises.

The main problem of the large-scale introduction of plant-based sorbents is their low sorption capacity compared to activated carbons. Improving the absorbing properties of the samples is achieved through the use of various modifications. Traditional methods are washing, steaming, treatment with solutions of acids and salts in combination with heating, and burning [6–8, 19]. Less common methods of physical influence,such as microwaves, ultrasound, and others [14, 20–24]. For example, according to published data [6], simple washing and drying of peat makes it possible to increase the sorption capacity for dissolved petroleum products from 0.1 to 0.3–0.4 mg/g. When peat is treated with microwaves [25], oil absorption by crude oil increases to 2.5–2.7 g/g. By applying the modification, it is possible to change the water and oil capacity of moss and reindeer moss [12]. Acid-modified ash sawdust improves its sorption properties by 43% [8]. By treating pine sawdust with microwaves, it was possible to achieve an increase in the sorption capacity for oil products by a factor of 3–4 [26].

In any case, the economic feasibility of using one or another modification requires a thorough analysis, taking into account the further utilization of the spent sorbent of plant origin. In this regard, this review article proposes various adsorbent technologies for wastewater treatment.

Water as an important natural resource

Water is an important natural resource; therefore, it must be saved. As an important reserve for the prevailing flora and fauna, pollution by organic and inorganic pollutants must be prevented. However, some technologies used for this purpose emit secondary pollutants or by-products that further pollute the environment [27, 28]. Therefore, economical and efficient wastewater treatment technologies are urgently needed [29, 30]. There is an acute shortage of water around the world, which highlights the urgent need for adequate food production throughout the year to combat hunger, deprivation and malnutrition, requiring the reuse of wastewater for irrigation [31]. The reuse of water through the recycling of industrial wastewater has attracted the attention of the scientific community in the past few decades. Wastewater treatment has a great advantage in agricultural activities, since it contains sufficient nutrients [32], so its treatment with subsequent use in agriculture must be carried out with great care to ensure its environmental friendliness, economy and increase in agricultural production [31]. The problem of wastewater treatment is much more complicated than it seems. There are two main sources of pollutants in wastewater: natural, including but not limited to volcanic activity, soil erosion and rock weathering, and the spread of mineral pollutants from human activities, waste disposal sites, urban runoff, mining, circuit board manufacturing, agricultural activities, metal surface treatment and plating, fuel combustion, textile dyes, semiconductor manufacturing, etc. [32, 33]. Wastewater generated in agriculture, industry and the domestic sector contains various amounts of harmful inorganic (heavy metals and excess nutrients) and organic (pigments, polyaromatic hydrocarbons, etc.) pollutants, which pose a serious danger to the environment and health [34, 35, 36, 37]. Among heavy metals (potentially toxic elements or PTEs) and metalloids, PTEs belong to the group of trace elements with a density >4 ± 1 g cm−3. These include copper (Cu), mercury (Hg), cadmium (Cd), zinc (Zn), tin (Sn), iron (Fe), lead (Pb), silver (Ag), manganese (Mn), chromium (Cr), cobalt (Co), arsenic (As), aluminum (Al), and nickel (Ni).Due to their persistence, higher mobility and solubility, wastewater containing these PTEs is not treated properly and is released into freshwater resources with various environmental and health consequences. In addition, these PTEs are taken up by aquatic organisms, crops and other plant species and enter the human food chain, thereby affecting human health [38, 39, 40]. In addition to natural and anthropogenic sources, There are two main types of wastewater pollutants – organic and inorganic pollutants. Organic pollutants include pesticides, phenols, herbicides, petroleum, dyes, oils, biphenyls, fats, proteins, starches, and drugs, while inorganic pollutants contain chemical fertilizers, PTEs, and excess nutrients. They cause deterioration of water quality and serious environmental problems [41, 42]. To reduce the environmental and health risks associated with wastewater, various technologies are used based on various degrees of purification, chemical reactions and processes, such as membrane filtration, reverse osmosis, chemical precipitation, solvent extraction, oxidation and adsorption [43, 44, 45, 46]. Organic pollutants include pesticides, phenols, herbicides, petroleum, dyes, oils, biphenyls, fats, proteins, starches, and drugs, while inorganic pollutants contain chemical fertilizers, PTEs, and excess nutrients. They cause deterioration of water quality and serious environmental problems [41, 42]. To reduce the environmental and health risks associated with wastewater, various technologies are used based on various degrees of purification, chemical reactions and processes, such as membrane filtration, reverse osmosis, chemical precipitation, solvent extraction, oxidation and adsorption [43, 44, 45, 46]. Organic pollutants include pesticides, phenols, herbicides, petroleum, dyes, oils, biphenyls, fats, proteins, starches, and drugs, while inorganic pollutants contain chemical fertilizers, PTEs, and excess nutrients. They cause deterioration of water quality and serious environmental problems [41, 42]. 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Organic adsorbents for wastewater treatment

1. Forestry and wood waste adsorbent

Forestry waste (such as tree branches, twigs, leaves and bark) accumulates in large quantities as solid waste and can be used as feedstock for the production of adsorbents for wastewater treatment. Polysaccharides (pectin, cellulose) and polyphenolic complexes (flavonoids, tannins, lignin, terpenes) have specific functional groups in combination with hydroxyl (-OH) or carboxyl (-COOH) groups with passing ions. These wastes have a high potential for adsorption of metal ions through ion exchange or chelation process [47]. Various types of forest wastes were used as adsorbents for PTEs removal, i.e. bark, chestnut bloodworm, sawdust, pine pectin and pine needles. Among these biological wastes, chestnut tow has the highest absorption value, i.e. 16.18 mg g. −1— and its bark has a value of 9.31 mg g −1 [48]. Forestry waste is also used to produce biochar, an absorbent carbon material produced by slow pyrolysis. Biochar has the highest removal efficiency in PTEs removal, i.e. 264 mg/g.−1 from wastewater [49]. Waste produced from forest products has been reported to have been used with over 69% efficiency.

2. Agricultural waste as an effective wastewater adsorbent

Fruit and vegetable skins. In most kitchen waste bins, fruit and vegetable waste and skins make up the largest proportion. The skins of many fruits and vegetables are thrown into the trash or fed directly to livestock. Vegetable and fruit waste and by-products, which are generated in significant quantities during industrial processing (production of secondary products), are a problem. They must be managed or recycled due to their harmful effects on the environment. Peel and peel of fruits and vegetables are a natural, environmentally friendly and economical source of adsorbents that can eliminate various types of water pollutants and reduce pollution, and therefore are a renewable and promising resource [50]. Fruit shell, i.e. coconut shell, contains dynamic functional groups -OH and -COOH, present in cellulose, hemicellulose and pectin, which are involved in the binding and removal of PTEs (Cd, Pb, As, Cr, Cu and Fe, Ni). Feng *et al*. [50] investigated the effectiveness of fruit shell adsorbents for removing Cu(II) from electroplating wastewater. In 50 ml of wastewater samples containing 14.33 mg l−1 Cu (II) ions, the adsorption efficiency was up to 97.1%. To evaluate the cost-effectiveness, the same process was repeated to test the reusability of the adsorbent, and it was concluded that the adsorbent could be reused several times in the same process. Shanti and Manonmani [50] reported that 6 g of the adsorbent is sufficient to remove 90–95% Cr(VI) from wastewater.

Since the above functional groups can be located in different positions with respect to each other, an assumption was made about their joint participation in the interaction with metal ions to form complex structures of the chelate type. Thus, an organic ligand can have several metal binding sites, i.e. can be at least bidentate. The joint participation of -COOH and -OH groups in the formation of complex structures of the chelate type is shown in Figure 1.

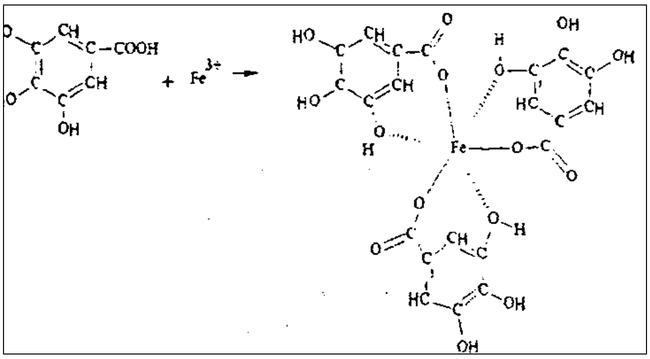


Fig 1: A chelate-type complex during the interaction of gallic acid with iron (III).

3. Coal based adsorbents

Coal is an organic material that contains various minerals. Moreover, organic materials typically make up 85–95% (w/w) of dry coal biomass. Coal is a complex sedimentary rock, which mainly consists of by-products of plant residues and their derivatives. It is a source of carbon, although it also contains various elements such as hydrogen, oxygen, sulfur and nitrogen. Coal and its derivatives are used not only as fuel, but also as precious materials in various environmental protection processes. Coal is cheap and plentiful, even in some countries there are abundant coal reserves in the form of mines. However, it has interesting properties that make it an effective adsorption material for removing various organic contaminants and PTEs. Coal can form stable complexes with several PTEs due to -COOH groups and phenolic groups associated with its highly cross-linked aromatic structures (Figure 2). Carboxyl or hydroxyl groups can participate in ion exchange reactions. Arpa and others [50] reported that the use of low-quality Turkish coal can effectively remove Hg (II), Cd (II) and Pb (II) ions from mining wastewater. Karabulut *et al* reported that poor quality Turkish coal can also remove Cu and Zn from sewage sludge. The adsorption phenomenon seems to correspond to the Langmuir isotherm model. Analysis of raw coal and exchangeable coal by FTIR showed that a significant amount of PTEs was removed and visible on the surface of the coal due to the formation of exchangeable metal carboxylates.

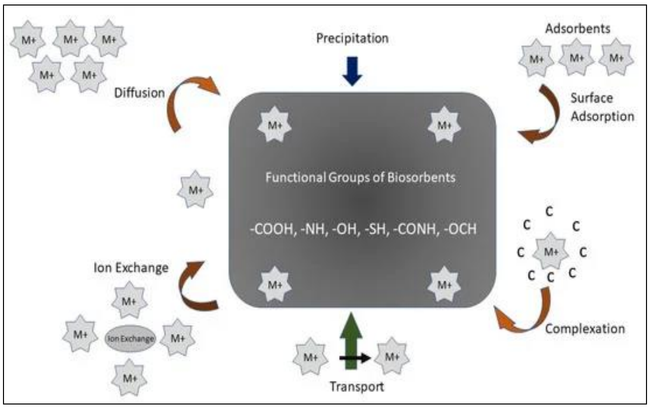


Fig 2: Schematic diagram of the biochar/biosorbent mechanism for decontamination of contaminants.

Nanocomposites in wastewater treatment

Nanotechnology is defined as a set of methods and techniques that make it possible to create objects in a controlled way, including components with sizes less than 100 nm (at least in one dimension) and, as a result, acquire fundamentally new qualities. Studies conducted in many laboratories around the world show that such properties of synthesized nanomaterials as a large specific surface area, high permeability, catalytic activity, resistance to biofouling, the possibility of functionalization, etc., allow them to be effectively used to obtain pure water. Nanomaterials and nanocomposites are proposed for adsorption and removal of cations, anions, purification from petroleum products (carbon, nano-zeolites, metal oxide nanoparticles).

Silver nanoparticles are used to disinfect water at points of consumption and to reduce biofouling of membranes. Nano-TiO_2 has a high photocatalytic activity; based on it, commercial products for wastewater treatment from organic impurities have been developed.

To monitor water quality, sensors are offered that use the magnetic, optical, electronic properties of nanoparticles (nano-Au, -SiO_2, -CdSe, etc.) and nanocomposites (commercial products are available). All these nanomaterials cannot be considered within the framework of one article. Two allotropic modifications of carbon will be presented here - nanotubes and graphene, which are promising for creating membranes and filters of a new generation, and have fundamentally new qualities [47].

Graphene is a two-dimensional crystal consisting of a single layer of carbon atoms. It can be thought of as a single plane of graphite separated from the crystal. Carbon nanotubes (CNTs) are seamless cylinders of one or more graphene layers with a diameter of 0.7 nm to 100 nm and a length of up to several centimeters with open or closed ends (Figure3).

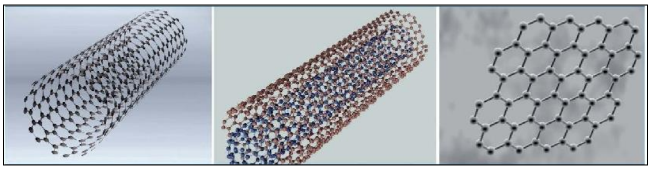


Fig 3: Carbon nanotubes, single-walled and multi-walled, graphene on the right

It is believed that carbon nanotubes were first discovered and described in the early 1990s. Soon their unique electrical, mechanical, optical and other properties were demonstrated. We quickly moved from laboratory research to implementation. CNTs production volume from 2006 to 2012 increased by at least 10 times. Carbon nanotubes in the form of films, coatings, as part of composites are used in microelectronics, automotive, aerospace and defense industries, as well as in the production of workwear, sports equipment, and medical goods. According to experts, a new and important area of application is water treatment. The experts of the RUSNANO project on the use of nanotechnologies in water purification singled out carbon nanotubes as a promising material. The unusual behavior of gases and liquids inside carbon nanotubes has long attracted the attention of scientists. First, theorists showed that the transport of molecules through CNTs can be orders of magnitude greater than through other known materials with pores of the same size. Then, these predictions were experimentally confirmed on membranes of vertical nanotubes placed in a dense film of polymers or silicon nitride. The rate of water flow through a membrane of close-packed nanotubes <2 nm in diameter in silicon nitride exceeded the value corresponding to Poiseuille's law by more than three orders of magnitude.For a membrane with pores 7 nm (nanotubes in a polystyrene film), the excess turned out to be even greater, by 4-5 orders of magnitude. The authors suggested that the effect is associated with the absence of friction between water molecules on the smooth inner surface of nanotubes and the creation of ordered hydrogen bonds between water molecules. Theorists continue to study the mechanisms of transport. The authors of a recent paper used molecular dynamics simulations and proposed a new mechanism for fast water transport. In their opinion, the competition between the processes of interaction of water molecules with each other and with a crystalline substrate leads to local changes in particle density. In other words, water molecules do not move in a continuous, uniform flow, as other theories suggested, but in intermittent jumps. The study of the principles of nanohydrodynamics is very important for solving the problem of water desalination. Certainly, For the practical use of the remarkable transport and other properties of carbon nanotubes, it is necessary to develop economical methods for obtaining membranes and methods for scaling them up. In recent years, certain successes have been achieved in the synthesis of various types of membranes.

1. Graphene membranes

The second carbon nanomaterial promising for creating membranes for water purification, disinfection, and desalination is graphene.

As you know, in 2004, the future Nobel Prize winners A. Geim and K. Novoselov obtained it by separating the layers from ordinary graphite using adhesive tape. The award "for advanced experiments with a two-dimensional material, graphene," was awarded to them in 2010. By that time, many laboratories around the world had obtained results indicating the unique electronic, optical, mechanical, thermal, and other properties of graphene. Recently, unique membranes based on graphene have been obtained. The authors of created pores 0.4 nm in diameter (pore density 1012/cm2) in graphene using ion bombardment and subsequent etching and, for the first time, demonstrated selective fast ion transport in a membrane of one atom thickness. The permeability is 50 times greater than conventional membranes used for desalination. The authors consider that their membranes are especially promising for biomedicine because Nanofiltration or desalination processes require large membranes. The scaling problem can be solved if, instead of graphene, so-called graphene oxide is used, which is easily obtained by exfoliating pre-oxidized graphite into separate sheets. The authors of created a micron-thick membrane consisting of layers of graphene oxide interconnected like a multilayer mother-of-pearl structure. Such a membrane is impermeable to all gases, vapors and liquids, but water passes through it unhindered. The researchers attribute this to the formation of a network of graphene nanocapillaries inside the layers of graphene oxide. Diffusion of other molecules is blocked by constriction of capillaries at low humidity and/or by filling them with water. In a new paper,it was demonstrated that

that such a membrane is distinguished not only by a high water transmission rate, but also by exceptional selectivity. Hydrated ions whose radius exceeds 0.45 nm cannot penetrate through it, while smaller ions are absorbed into the capillaries with a very high efficiency (according to the authors of, the phenomena correspond to a pressure on the ions > 50 atm). The next task for the researchers is to reduce the size of the capillaries so that such membranes can be used for desalination of sea water.

2. Graphene/polymer composite membranes

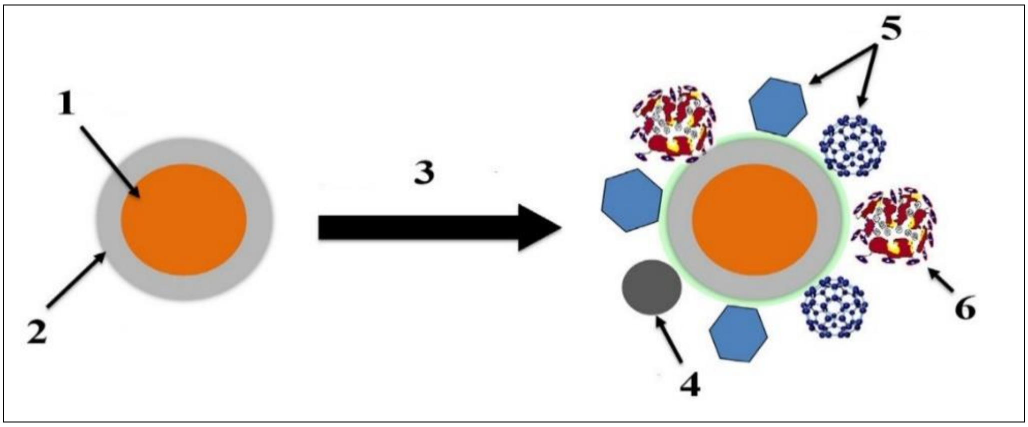
Graphene can be used to create composite membranes with strong antimicrobial properties. The authors of [47-50] synthesized polyamide membranes with graphene nanoplatelets on the surface (the bond is provided by the interaction of the hydroxyl groups of graphene oxide with the hydroxyl groups of the polyamide active layer). Experiments have shown that 65% of bacteria die on the surface within 1 hour, while the transport properties of the membrane do not deteriorate. Such composite membranes, like multilayer graphene ones, can be produced on an industrial scale, because the oxidized form of graphene is obtained using well-known relatively inexpensive methods of chemical oxidation of graphite.

3. Nanoadsorbents based on metal oxides

Metal oxides such as iron oxide, titanium oxide, and alumina are effective and inexpensive adsorbents of heavy metals and radionuclides. The adsorption process is controlled by the complexation between the dissolved metal and the oxygen of the oxides. The process proceeds in two stages: adsorption of metal ions on the outer surface, followed by a limiting stage of diffusion into the particles along the walls of micropores.

Analogues of metal oxides at the nanoscale are characterized by higher adsorption capacity and adsorption kinetics due to a larger specific surface area and a larger number of surface adsorption centers. For example, with a decrease in the size of a magnetite nanoparticle from 300 to 11 nm, the adsorption capacity for arsenic increases by a factor of 100. This effect is largely due to an increase in the specific surface area. However, besides this, if nanoparticles with a size of 300 and 20 nm have the same adsorption capacity for arsenic per unit surface (3.6 atoms per square nm), then with a further decrease in the size of nanoparticles to 11 nm, this indicator reaches 11 atoms per square nm. This "nanoscale" effect is associated with a change in the surface structure of magnetite, which leads to the creation of new adsorption centers.

Along with a high adsorption capacity, nanoparticles of some iron oxides (magnetite, maghemite) have the property of superparamagnetism, which occurs when the particle size decreases below 40 nm. This circumstance allows the separation of nanoparticles in a low-gradient magnetic field. Magnetic nanoparticles can be directly used asadsorbents. On their basis, core-shell structures are also created, in which the shell is given certain functions (catalytic, biocidal, selective adsorption), and the core provides magnetic separation. The shell can consist of silica, which has a wide range of chemical properties, and related nanoparticles with the required properties.



1 – core with magnetic properties; 2 – silica shell; 3 – functionalization process; 4 - nanoparticles with antimicrobial properties; 5 – nanoparticles with (photo)catalytic properties; 6 – nanoparticles-selective adsorbents.

Fig 3

Metal oxide nanoparticles can be pressed into granules with virtually no change in properties, which is convenient for industrial applications. They outperform activated carbon in terms of adsorption of As, Pb, Hg, Cu, Cd, Cr, Ni. Especially noticeable is the superiority over activated carbon, for example, of TiO_2 nanoparticles in the adsorption of As, primarily As(V). Nanoparticles of oxides or hydroxides can be introduced into the structure of activated carbon, which allows simultaneous removal of, for example, As and organic substances. The regeneration of metal oxide nanoparticles is carried out by changing the pH. Many reports note that the adsorption capacity remains at an acceptable level after several cycles of adsorption/regeneration.

4. Nanoparticles of metallic iron

According to numerous reports, metallic iron nanoparticles (MIN) can be successfully used to remove or destroy antibiotics, azo dyes, chlorine-containing pesticides, organophosphorus compounds, nitroamines, nitroaromatic compounds, para-chlorophenol, polybrominated diphenyl ethers, polychlorinated biphenyls, nitrates, perchlorates, Ba, Be, Cr, Co, Cu, Pb, Mo, Ni, Ag, Tc, V, Z n, Cd, As, Se, U, Pu, and inactivation of viruses and bacteriophages.

These materials are used for groundwater treatment, which suggests that nanoparticles have certain properties, namely, high reactivity, sufficient mobility in porous media, the necessary durability, and low toxicity. A necessary property is also the ability of nanoparticles to form aqueous colloidal suspensions. In addition, the technologies for the production and use of nanoparticles in terms of their costs should be competitive with traditional methods. Not all types of nanoparticles meet these requirements. For example, silver nanoparticles are highly reactive and stable in the form of colloidal suspensions. Their cost, however, at a consumption for groundwater treatment at the level of kilograms, is too high. In the natural aquatic environment, MIN undergo a process of corrosion, i.e. interact with oxygen and water to form Fe(II), Fe(III) and hydrogen ions, as well as insoluble oxides and hydroxides (on the surface of metal nanoparticles). It is these corrosion products that are involved in chemical (reduction, complex formation, precipitation) and physical (adsorption) processes of interaction with pollutants. Due to the large specific surface area (up to 100 m^2/g), when significant amounts of nanoparticles are introduced into the aquatic environment, a reducing environment quickly arises due to the formation of hydrogen, which is favorable for the destruction of contaminants. The main mechanisms for removing pollutants in the presence of MIN are chemical processes and adsorption by the surface layer of oxides and hydroxides. Organic pollutants undergo regenerative degradation. Heavy metals and radionuclides bind (complexation, precipitation, adsorption) on the surface of nanoparticles without physical destruction. In this regard, it should be noted that such pollution is not removed from the aquatic environment subjected to purification, since the extraction of nanoparticles (with retained pollution) is practically impossible. Thus, in principle, when geochemical conditions change, in the presence of complexing agents or other heavy metals or radionuclides that can replace those already bound, there is a possibility of remobilization of contaminants. The processes of binding, degradation, and remobilization can proceed with the participation of microorganisms. According to 2004 data, the cost of 1 kg of MIN obtained by various methods varied from £15 to £100. Counts,

Actually MIN have very limited mobility in porous media, not exceeding a few meters. The reason lies in the aggregation of nanoparticles, the formation of bulk deposits as a result of oxidation/corrosion of nanoparticles, and the adsorption of nanoparticles on the surface of minerals and carbon-containing materials. An increase in the mobility of MIN is achieved by modifying their surface. For this purpose, coatings in the form of surfactants or polymers are applied to the surface of nanoparticles. For these purposes, for example, carboxymethylcellulose and guar gum have become widespread. Successful experiments were carried out with chitosan. It is reported about the use of a biodegradable surfactant to stabilize MIN which contributes to the biodegradation of organochlorine compounds as a carbon source for microorganisms, and polyacrylic acid. In the latter case, the influence on the mobility of stabilized nanoparticles of a biofilm, which is present in real natural media in almost all cases, is considered. It has also been found that nanoparticles with a particle size of 100–200 nm have the highest mobility in porous media. In addition, such fractions of nanoparticles are characterized by significantly lower toxicity. The technology of their injection is greatly simplified.

A recognized method for increasing the reactivity of nanoparticles is the alloying of metallic iron with metals from among Pd, Pt, Ag, Ni, Cu, etc. In the US, approximately 40% of groundwater treatment projects involve the use of bimetallic nanoparticles. In European countries, this approach is not widespread. Instead of using alloying additives, their thermal treatment is also used to improve the physicochemical properties of nanoparticles.

5. Combination of biological and nanotechnological processes

There are various technologies for harvesting algal biomass, such as sedimentation, centrifugation and air flotation, which use condensed chemicals as a carrier. However, these technologies cannot be used on a large scale due to their high cost [50]. In these advanced technologies, membrane technology is the most advantageous method of algae cultivation and biomass production, in which the cultivation of algae at high density is carried out only with the help of membrane bioreactors. The advantage of membrane technology is that no coagulants need to be added for membrane filtration, which facilitates the reuse of filtered water and simplifies the separation of algae biomass. Scientific and technological technologies at the nanoscale show that many existing problems with water quality can be solved using nanostructured catalytic membranes, nanocatalysts, nanoabsorbents, nanotubes, nanopowders and micromolecules.These are all NPs and colloids that have a significant impact on water quality in the purification procedure. The study showed that the combination of wastewater treatment processes with advanced nanotechnologies can create highly efficient water treatment systems. Growing algae in wastewater is one of the most beneficial approaches to energy production and wastewater treatment. Many species of algae are effective due to the presence of PTEs. Nutrients mix with water to form a solution that provides the right conditions for algae to grow. In addition, algae biomass is recovered more efficiently, than conventional methods without damaging cells, and the energy requirement for harvesting algae is less than with other methods. Polyvinylidene fluoride, polysulfone, and polyethersulfone membranes are widely used due to their physicochemical stability, although the main problem lies in the membrane material and microbial cells between the hydrophobic mechanism and membrane fouling.Studies have shown that nanoparticles can improve hydrophilicity and reduce membrane fouling, such as CNTs and TiO.The performance of microbial fuel cells can be improved by using inexpensive NCs such as nanosized carbon in electrodes, since the electrodes are mechanically stable and have a large surface area, high electrical conductivity, and good electrochemical catalyst activity. Due to all the unique properties of platinum (Pt), commercial Pt cathode catalysts can be replaced by CNT or Pt in microbial fuel cells.To increase microbial adhesion and reduce toxicity, CNTs have also been coated with numerous anemic polymers, such as polyaniline and polypyrrole, to make NCs. These NCs are composed of negatively charged CNTs, which combine electrostatically with positively charged polycationic polymers as anodes. microbial fuel cells.

Unresolved technical issues

The main reason for the high reactivity of nanoparticles is their large specific surface area; however, aggregation in an aqueous medium significantly reduces the value of this parameter. This is typical for both titanium dioxide and fullerenes. On the other hand, dispersed nanoparticles, due to their size, are difficult to isolate from the aqueous medium, which requires an additional stage of membrane filtration, which ensures the return of the suspension of nanoparticles to the technological process and prevents their entry into drinking water, which is associated with corresponding costs. At the same time, a number of studies indicate the toxicity of some nanomaterials. Immobilization of nanoparticles on the surface of the reactor or membrane eliminates the need for their separation. In this case, however, the available surface area of the nanoparticles is limited,

Another problem, as noted, is the lack of residual disinfectant concentration, leading to the re-development of microorganisms in water distribution networks in the case of non-reagent disinfection. This problem can be solved by the parallel use of a chemical disinfectant to create the required concentration in the process of transporting water.

This issue determines the direction of research. Work is underway in the field of improving various coatings containing nanomaterials, minimizing membrane fouling by immobilizing functional nanomaterials, incorporating nanoparticles into filter media (activated carbon,ion exchange resins). To solve the problem of separation of nanomaterials, nanoparticles with a core-shell structure are synthesized. At the same time, the core has magnetic properties, which creates conditions for magnetic separation, and the shell includes various functional nanomaterials that provide photocatalysis, disinfection, etc.

A significant problem is to increase the scale of production and reduce the cost of nanomaterials. Here they see a promising use of iron nanoparticles in the composition of composite materials for the inactivation of bacteria and viruses.

At present, it is impossible to talk about the near prospects for the widespread introduction of processes based on nanotechnology in the field ofwater purification and disinfectionbecause there are too many technical problems to solve. Noteworthy, however, is the almost synchronous growth of two information flows in foreign scientific and technical periodicals. On the one hand, data on the diversity and toxicity of micro- and nanoconcentrations of pollutants and by-products of water disinfection are multiplying. On the other hand, an increasing number of research works are devoted to alternative methods of water purification and disinfection, and among them nanotechnologies play a significant role.

Toxicity of nanomaterials

The growing use of artificial nanoparticles and nanomaterials in water treatment and disinfection is causing concern about their toxicity due to the lack of technology to remove them from the aquatic environment. This concern is based on assumptions about the high mobility of nanoparticles in porous media and their corresponding ability to spread in suspended form over long distances. At the same time, it is reported that there is no significant mobility of nanoparticles since a relatively high value of the diffusion coefficient leads to frequent contacts with the surface of porous media in the natural environment or with filter materials in water purification schemes. In addition, there are data on increased retention of nanoparticles in porous media at high ionic strengths and in the presence of divalent ions. At real values of ionic strength in underground and surface waters and in the presence of significant concentrations of calcium and magnesium, favorable conditions are created for the sedimentation of nanoparticles. According to some authors, there is no reason to believe that the use of nanomaterials in water treatment technologies will cause the appearance of significant amounts of these "new" pollutants.

At the same time, there are a number of works devoted to the identification of the negative consequences of contact with nanomaterials as a result of inhalation, penetration through the skin, and absorption in the digestive tract, as well as the physicochemical characteristics of nanoparticles, which cause the corresponding risks to human health.

Despite the wide variety of different nanoparticles and nanomaterials, the toxic effect has been studied only for a very limited number of them. These include carbon-based nanomaterials and metal oxide nanoparticles, including TiO_2.

The results of laboratory studies with rodents indicate the potential danger of developing neoplasms, lung diseases, and inflammatory processes. The results of experiments on tissue samples and cell cultures indicate oxidative stress (associated with the formation of highly reactive oxygen compounds) as the cause of these phenomena. It should be noted, however, that the toxicological studies performed used high concentrations of nanomaterials, which are hardly characteristic of real conditions. In addition, most of the experiments were carried out with rats known for their hypersensitivity to effects on the lungs.

Recently, studies have begun to appear on the potential danger of nanomaterials for aquatic organisms. Much more work is devoted to the impact of nanomaterials on microorganisms that are the basis of ecosystems and participate in global biogeochemical cycles. A particular case of various interactions between nanomaterials and microorganisms are the properties of nanomaterials, which determine their use in the process of water disinfection. In general, the toxicology of nanomaterials is a relatively new discipline, and the accumulated material is not enough to formulate generally accepted conclusions and recommendations.

However, there is evidence of a negative impact on biological treatment processes from Ag nanoparticles contained in wastewater. It has been shown that the rate constants of biological nitrification and oxidation of organic substances decrease exponentially with increasing concentrations of Ag nanoparticles. In this case, even low concentrations of Ag nanoparticles (less than 1 mg/L) affect the course of nitrification.

The long-term effect of Ag nanoparticles on bacteria was assessed in activated sludge in an SBR reactor using two substrates favorable for the development of heterotrophic and autotrophic bacteria. After continuous operation for 50 days, it was found that heterotrophic bacteria involved in the process of removing organic substances are more resistant to Ag nanoparticles than nitrifying bacteria. After 50 days, the microbial diversity significantly decreased, and the effectiveness of wastewater treatment also decreased

An increase in the use of nanotechnologies in the area under consideration will inevitably lead to an increase in the content of nanomaterials in the natural aquatic environment. In this regard, the development of analytical methods for the determination of nanoparticles becomes an independent problem. The methods currently proposed are, as a rule, complex, very costly, and associated with a number of limitations.

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