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Investigation of phytoremediation processes by microalgae

Water is the basis of life and when various toxic chemicals get into the water, the consequences are inevitable. Phytoremediation of reservoirs based on algae was analyzed in this study. It has been established that algae are not fastidious in growth and at the same time effective in application. It is worth noting that algae do not clean the water body of a specific pollutant, their diversity allows for the isolation of a number of other dangerous pollutants. So, we can say that phytoremediation with the use of algae gives a chance for the existence of all mankind.

Currently the high rate of urban population growth is generating very large amounts of waste that must be treated before discharge. Wastewater(WW) and greenhouse gases(GHG) e mainly carbon dioxide(CO₂) e are two of the main wastes that pose a major challenge to global environmental sustainability. Human economic activity disrupts natural biogeochemical cycles, pollutes water bodies with various organic and inorganic substances. The use of various toxic chemicals in agriculture and in everyday life, waste from internal combustion engines of vehicles, including space, mining and processing of minerals, urban sewage of megacities, military operations, etc. lead to disruption of natural cycles and balanced environmental conditions. So, for example, heavy metals and chemical pollutants of the environment, accumulating and moving along the food chain (water - plants - animals - humans), affect various organs of animals and humans, causing diseases. The environmental issue is becoming more and more acute. The emergence of such a concept as phytoremediation and knowledge related to it gives humanity a chance to save the Earth's biosphere and its representatives[1].

Phytoremediation is a set of methods for cleaning water, soil and atmospheric air using green plants. Recent studies have shown that phytoremediation is one of the most promising methods of wastewater treatment, which allows for the removal or significant reduction of pollutants in a natural way, thereby reducing man-made pressure on water bodies. As a rule, for water purification in phytoremediation systems, higher aquatic plants are used, the basis of which are reeds, rushes, cattails, and rushes. However, one of the most effective methods of phytoremediation of wastewater is algae.

It has long been studied that standard methods of wastewater treatment have their drawbacks, which are listed in the table.

Table 1

Disadvantages of standard wastewater treatment methods[2]

| Methods of wastewater research | Disadvantages |
|---------------------------------------|-------------------------------|
| Mechanical method | Low level of cleaning |
| Chemical method | The use of chemical reagents |
| Physical-mechanical method | High cost |
| Biological methods | The need for large land plots |

Such methods are quite diverse, but their development does not keep up with the evolution of pollutants, which are multiplying faster and faster following scientific and technological progress. And then humanity began to take the first steps to find a method with a high level of purification, low cost, and most importantly, with minimal waste. And so the first scientific research on phytoremediation was carried out in the 1950s in Israel, but the active development of the technique took place only in the 1980s of the 20th century. In connection with the birth of efficient and cost-effective technology, a new term "environmental phytoremediation" appeared, which suggests the restoration of anthropogenically disturbed ecosystems with the help of plants. Already in those years, it was investigated that the concentration of heavy metals in the body can lead to the following diseases: cancer, autism, acute and chronic kidney failure, intrauterine death of the fetus, metabolic disorders, diseases of the cardiovascular and nervous systems[3]. The phytoremediation method can stop such a pattern, but the main step in this case is choosing the right plant that will be suitable in all parameters.

Recently, there has been a growing interest in the use of algae to clean water bodies. Microalgae allow not only to purify water from heavy metals, but they are also a good bioindicator. At the beginning of their use, the first thing that was noticed was that algae are characterized by the speed of their growth, they have a low cost for implementation and, at the same time, high efficiency[4]. In addition, it should be noted that algae do not compete on the market. The use of aquatic plants, especially micro- and macroalgae, has attracted much attention due to their ability to absorb metals and toxic elements from the environment or make them less harmful[5].

Microalgae can simultaneously grow in WW and produce valuable biomass while they remove organic carbon and inorganic nutrients (nitrogen and phosphorus) from the WW, therefore microalgae can play a very important phytoremediation role, particularly during the final tertiary treatment phase of the WWTP[6].

The treatment of WW with microalgae offers many advantages over conventional treatments:

1. Nitrogen and phosphorous can be converted into biomass without any external source of organic carbon;
2. Nitrogen and phosphorus are removed from WW simultaneously;
3. The effluent discharged into receiving water bodies is oxygenated;
4. High-value products can be extracted from the biomass generated such as protein and lipids.

Macroalgae are widely used to measure heavy metal pollution and marine environments worldwide. In recent years, several species of green algae *Enteromorpha* and *Cladophora* have been used to measure heavy metal levels in many parts of the world. The ability of macroalgae to accumulate metals in their tissues has led to their widespread use as biomonitors of availability metals in marine systems[7,8]. Chlorophyta and Cyanophyta are hyperabsorbers and hyperaccumulators of arsenic and boron, absorbing and accumulating these elements from the environment in their bodies. These algae can be hyperphytoremediators, and their presence in water reduces the water pollutant arsenic and boron[9].

Nielsen suggested that brown algae such as *Fucus* often dominate the vegetation of habitats polluted by heavy metals[10]. Mei suggested that *Platymonas subcordiformis*, a marine green microalgae, has a very high strontium uptake capacity, although high strontium concentrations cause oxidative damage to the alga itself, and reduced growth rate and chlorophyll content[11]. Some types of algae can convert mercury ions into metallic mercury, which then evaporates from the cell[12,13]. The blue-green algae *Phormidium* can successfully accumulate heavy metals such as Cd, Zn, Pb, Ni and Cu[14]. *Dunaliella salina*, a green microalgae, has a high tendency to accumulate zinc, followed by copper and cobalt, the lowest tendency was for cadmium, this may be related to the importance of zinc as a hydrogen carrier in photosynthesis[15]. Therefore, it can be concluded that different types of algae and algae of the same species can have different adsorption capacity[16].

Table2

Absorption of metals by some types of algae[17]

| Species | Metal |
|----------------------------------|--------------------------------------------------------------------------|
| <i>Ascophyllum nodosum</i> | Gold (Au) Cobalt (Co) Nickel (Ni) Lead (Pb) |
| <i>Caulerpara cerosa</i> | Boron (B) |
| <i>Daphnia magna</i> | Arsenic (As) |
| <i>Fucus vesiculosus</i> | Zinc (Zn) Nickel (Ni) |
| <i>Laminaria japonica</i> | Zinc (Zn) |
| <i>Micrasterias denticulata</i> | Cadmium (Cd) |
| <i>Phormidium bohner</i> | Cromium (Cr) |
| <i>Platymonas subcordiformis</i> | Strontium (Sr) |
| <i>Sargassum filipendula</i> | Copper (Cu) |
| <i>Sargassum fluitans</i> | Copper (Cu) Iron (Fe) Zinc (Zn) Nickel (Ni) |
| <i>Sargassum natans</i> | Lead (Pb) |
| <i>Sargassum vulgare</i> | Lead (Pb) |
| <i>Spirogyra hyalina</i> | Cadmium (Cd) Mercury (Hg) Lead (Pb) Arsenic (As) Cobalt (Co) |
| <i>Tetraselmis chuil</i> | Arsenic (As) |

Removal of metals can be achieved by bioaccumulation and biosorption. In the process of bioaccumulation, metal ions are transported across cell membranes through passive and active transport systems and accumulate inside cells.

Extracellular and intracellular metal binding approaches (such as complexation, physical adsorption, ion exchange and chelation) have been used by algae to reduce metal-induced toxicity. These mechanisms effectively transform toxic metals into less or non-toxic forms [18]. Detoxification of metal by algae is carried out in various ways, such as binding to a specific intracellular organelle, transport to specific cellular components such as polyphosphate vacuoles/bodies, leaching into solution by an efflux pump[19].

Biosorption is a physicochemical property that leads to the removal of metals by covalent or ionic bonding. Cell walls of algae have a net negative charge due to the presence of PO_4^{3-} , COO^- and other functional groups that bind to metals through ion exchange. Algae minimize metal-induced damage by sequestering and excreting metals, and by synthesizing proteins and other binding compounds such as glutathione (GSH) and metallothioneins (MTs). The ability of algae to metabolize and adsorb metals is related to their high surface-to-volume ratio, efficient metal uptake, storage systems, and the presence of high-affinity metal-binding groups on their cell surfaces. During physical adsorption, metal ions in aqueous solution bind to polyelectrolytes on the algal cell wall through weak forces such as redox interaction, covalent bonding, biomineralization, and van der Waals forces. The pH of the adsorbing medium strongly affects the adsorption of metal ions [20].

Although algae have excellent potential for metal accumulation, they have some limitations, such as low biomass and sensitivity to high metal concentrations. These problems can be solved by some advanced interventions such as genetic modifications that enhance biomass production.

Conclusion. Pollution of water bodies with heavy metals is a serious global environmental problem. Because they are non-biodegradable, they can accumulate in food chains, causing various signs of toxicity in exposed organisms, including humans. Due to its efficiency, low cost and ecological aspect, phytoremediation, or the use of ecological functions of microalgae in the treatment of metal-contaminated waters, is one of the most recommended processes. Phytoremediation helps to improve the ecological situation and reduce the anthropological load on water bodies. In addition, it is safe to say that the emergence of phytoremediation is a chance for the biosphere. The accumulation of heavy metals by micro- and macroalgae provides an advantage of phytoremediation over other methods, which are more expensive and harmful to the environment. Currently, research is ongoing in the direction of the development of technologies for microalgae-biocleaners of water bodies, but the results of the conducted research are pleasantly surprising.

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