Influence of IR radiation on the process of phytoremediation of copper by eichhornia

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Abstract. The effect of infrared irradiation on the process of higher water plants phytoremediation of heavy metal ions is in the focus of this study. The influence of various factors (initial concentration of the solution, duration of the irradiation) on the extraction of copper by eichhornia is discussed.

Introduction
The ability of higher water plants (HWPs) to remove pollutants from water allows them to be used in the practice of cleaning industrial, domestic, sewage and natural waters, both in Russia and throughout the world. In many countries of the Americas, the mine water purification systems on the plantations of eichhornia and reeds are widely used. Facilities with reed vegetation for cleaning domestic sewage in the Netherlands, Japan, Norway, Australia and other countries are described in a number of works [1-3].

In Benton (USA), with a population of 4,700 people, since 1985, domestic wastewater has been treated in ponds with thickets of reeds and water hyacinth (eichhornia). In Ireland (Viljamestown), a system of joint cleaning of domestic water (72%) and surface runoff (28%) is successfully operated, designed in the form of three shallow lagoons, two of which are planted with reeds and cattail, and the third is a bioproduct with floating aquatic plants - eichhornia, lily and duckweed. In China, water hyacinth is used to purify film factory sewage from silver. It was found that the efficiency of water purification from silver, suspended solids, phosphorus and nitrogen compounds, respectively, was 100%, 91%, 53.9%, and 92.9%, with BOD and COD decreasing by 98.6% and 91 %. Australian scientists have developed a method for cleaning surface runoff from highways. The roads are not equipped with curbs; the flow is collected by filtration trenches filled with a depth of 0.8 m of gravel. At the bottom of the trench, prefabricated pipelines with a diameter of 150 mm are laid, which transport the drain for further purification into the bioplatto [1-3].

In Russia the Institute of Cytology and Genetics developed a technology for wastewater treatment using water hyacinth. This technology is widely used in Krasnodar region (a region with a higher
average annual temperature). In spring and summer period this method is also used for sewage treatment plants in the city of Engels, Saratov region.

The main disadvantages of the method are seasonality and low cleaning efficiency. To increase efficiency the processes is stimulated by physical influences. In works [4-6], the effect of a magnetic field (MF) of various intensity and direction on the processes of phytoremediation was studied. It is shown [5,6] that a magnetic field strength of 2 kA/m exerts a stimulating effect on copper recovery processes, as a result of which the cleaning efficiency increases by ~8-12% and reaches 60% in a day in comparison with purification without the influence of MF.

It is also interesting to study other physical effects, for example influence of infrared (IR) radiation on phytoremediation processes.

The purpose of this work was to study the effect of the duration of IR irradiation on the extraction of copper by HWP by eichhornia plant.

**Materials and Methods**

To study the effect of IR on the process of phytoremediation, model solutions based on copper sulfate were prepared. For this purpose, 5 mg/l of CuSO₄ was added to conditionally clean sewage (after biological treatment in sewage treatment plants in the city of Engels, Saratov region). The processes of accumulation and extraction of copper cations from a solution of one liter were investigated. Higher aquatic plant eichhornia of the same mass (20 g) and maturation periods was placed into vessels. The plant was exposed to IR radiation for 1, 5 and 168 hours. Samples were analyzed after 1, 5, 24, 48, 72, 120 and 168 hours. For IR irradiation an artificial source of thermal radiation—an "infrared radiator (a "Minina" lamp with λ = 780-1400 nm) was used. The solution with eichhornia was located at a distance of 1 m from the source of IR irradiation. The scheme of the phytoremediation process under the action of IR irradiation is presented in Fig.1.

![Source of IR irradiation](image)

**Figure 1: The scheme of the effect of IR radiation on the phytoremediation process**

Analysis of water for the residual content of heavy metal ions (HMI) was carried out using photoelectrocolorimetric method (device KFK 3-01) in accordance with Russian State Standard "Drinking water. Methods for determining the mass concentration of copper." To determine the final concentration, 5 ml of the stock solution were placed in a 50 ml flask and adjusted to 50 ml with distilled water. 1-2 drops of aqueous hydrochloric acid HCl (1: 1) was added to the solution, then 1 ml of Rochelle salt (1:1), 5 ml of NH₃ ammonia (25%), 1 ml of starch (0.5%) and 5 ml of Sodium diethylenedithiocarbamate (0.1%). After the performed operations a yellow-brown solution was
obtained. A blue light filter with a wavelength $\lambda = 430$ nm and a cuvette with a working layer thickness of 50 ml was used in the photocolorimetric analysis.

Alongside with the analysis of changes in the concentration of copper in solutions of wastewater, the temperature and pH were fixed by means of an ionometric I-500 transducer of the firm "Aqualon".

**Results and Discussion**

Obtained results of the influence of IR radiation (Fig. 2) made it possible to establish that the processes of copper phytoremediation differ from those without IR. During the first hour, extraction of copper by eichhornia under the influence of IR occurs faster by 25%. Most likely this is due to the acceleration of bioelectrochemical processes in plant cells, and this is reflected in their growth, development and reproduction, with thermal exposure to IR irradiation. According to the rule of Vant-Hoff, the rate of chemical reactions increases by 2-3 times with an increase in temperature by 10 °C, and upon reaching the optimum, it begins to decrease. It is known that physiological processes in plant tissues begin at a temperature of +5 °C and are activated at + 10 °C and higher [7]. This fact is confirmed by data on the measurement of temperature. After the first hour, the temperature (T) of the solution in all three cases increased from $T_{ini} = 20$ °C (ambient temperature) to ~ 1.5-1.8 °C, after 5 hours - by ~ 4 °C for samples of IR-1 and IR-2, for which IR irradiation was continued. In the future, a slight increase in temperature was observed only for the IR-1 sample (Table 1).

**Table 1. Dependence of T and pH from the time of IR exposure**

| Hours | T, temperature °C | pH |
|-------|-------------------|----|
|       | IR-1 | IR-2 | IR-3 | IR-1 | IR-2 | IR-3 |
| 1     | 21.8 | 21.9 | 21.8 | 6.94 | 6.94 | 6.94 |
| 5     | 24.3 | 24.5 | 22.0 | 6.83 | 6.83 | 6.85 |
| 12    | 24.7 | 25.0 | 22.3 | 6.97 | 6.73 | 6.93 |
| 24    | 25.0 | 22.4 | 22.4 | 6.8 | 6.98 | 6.88 |
| 72    | 24.8 | 20.6 | 20.7 | 6.96 | 7.09 | 7.11 |
| 120   | 23.8 | 20.1 | 20.2 | 6.98 | 7.32 | 7.14 |
| 168   | 24.2 | 22.0 | 21.6 | 7.05 | 7.30 | 7.07 |

In the Table IR-1 means exposure to the IR throughout the phytoremediation process, IR-2 means exposure to the IR for 5 hours, then the phytoremediation process proceeds without IR, IR-3 means exposure to UV for 1 hour, then the phytoremediation process proceeds without IR exposure.

After 5 hours, the excess copper is discarded by the plant into the solution. On the curves of the concentration change in time, a large peak appears for the samples under IR exposure (Fig. 2), and then there is a gradual decrease in concentration. This fact indicates that during this time, the maximum penetration of infrared radiation into the tissue occurs. It is known that infrared radiation penetrates tissues to a depth of 20 to 50 nm [7], therefore, surface layers are heated to a greater extent. The plant cell contains a large amount of water. The water in the cell is heated evenly, if necessary, the cell evaporates water, protecting plants from overheating by infrared rays [8].

According to the data obtained, penetration of infrared rays and heating of the plant occurs in the first hours of exposure (up to 5 hours). At the same time, the processes of photosynthesis and formation of chlorophyll are accelerated. Bright green color of the leaves of the eichornia is the evidence of it. Therefore, after the first hour, the plant cell, being adapted to conditions after IR exposure, is released of excessively absorbed copper ions (Fig. 2a). In the future, the effect of IR radiation inhibits the processes of phytoremediation and the absorption of copper by a plant without physical effects occurs more quickly (Fig. 2b).
Figure 2: Change in the concentration of Cu\(^{2+}\) in solution in the process of its extraction by eichhonia without and under the influence of IR radiation: a) at the initial time; b) after 168 hours

Measurement of the pH value of the solution in the process of phytoremediation without and under the influence of IR radiation showed that under the influence of infrared radiation a small increase in the pH of the medium occurred (Table 1). Most likely this may be due to the absorption of hydrogen ions by the H\(^+\) plant cell, accompanied by the displacement of copper ions from near the membrane space at the cell surface, and, as a consequence, by a decrease in the rate of extraction of Cu2+ cations. Hydrogen ions have a much smaller size of the ionic radius (r = 0.046 nm) as compared with copper ions (r = 0.128 nm) [9]. After the first hour, a DES is formed on the surface of the plant membrane, which is filled with hydrogen ions. The amount of hydroxyl ions (OH-) increases in the solution and the pH value increases (Fig. 3).

Figure 3: Arrangement of H\(^+\) and Cu\(^{2+}\) ions in an aqueous solution of CuSO\(_4\) at the border of the plant cell / solution
Conclusions

Conducted studies of the effect of IR irradiation on the process of phytoremediation of eichhornia of copper cations allowed us to establish that:

1. After IR irradiation of the HWP of eichhornia within 1 hour, the acceleration of the phytoremediation process is achieved by ~ 25%. Subsequent action leads to a retardation of the purification of effluents from copper ions. The effect obtained is most likely associated with the thermal effect at which the rate of the course of the physico-chemical reactions in the cells varies, since according to the Van't Hoff rule the rate of chemical reactions increases by 2-3 times with an increase in temperature by 10 °C, and decreases upon reaching the optimal state.

2. Influence of infrared radiation leads to a change in the physicochemical properties of water: an increase in temperature and a decrease in the pH of the solution, which in turn affects the growth and development of the plant cell and the processes of bioelectrochemical phytoremediation.

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