Estimation of anti-chlorosis action of iron-lignosulfonate complex synthesized by anodic dissolution of iron

Yu G Khabarov, V A Veshnyakov and A E Shergin
Northern (Arctic) Federal University named after M.V. Lomonosov, 17 Northen Dvina Emb., Archangelsk, 163002, Russia
E-mail: khabarov.yu@mail.ru

Abstract. Iron-lignosulfonate complexes are used as trace element fertilizers to control plant chlorosis caused by iron deficiency. In this study, iron-lignosulfonate complexes were synthesized by anodic dissolution of iron in solutions of sodium lignosulfonates or lignosulfonic acids. The resulting solutions of the iron-lignosulfonate complex do not contain extraneous ions that are present in similar preparations synthesized chemically from salts. Electrosynthesis of iron-lignosulfonate complexes was carried out with two iron electrodes with alternating polarity, changing the period of switching the polarity of the electrode, temperature and the duration of electrolysis. The anti-chlorosis action of the synthesized iron-lignosulfonate complex was tested while growing lupine on calcareous soil. The plants were treated with solutions of the synthesized complex by the non-root method after 10 and 20 days of their cultivation. For comparison, lupine was also grown on normal soil and on calcareous soil without iron-lignosulfonate complex treatment. The content of chlorophyll, the content of carotenoids and the mass of the ground part of the plants treated with the synthesized complex were the same or higher than those of the plants grown on normal soil. In addition, all these parameters were 2-3 times higher than that of the plants grown on calcareous soil without treatment.

1. Introduction
The iron deficiency leads to the development of chlorosis in plants, which is manifested in the yellowing of the leaves due to a decrease in the content of chlorophyll. This decrease leads to the fall of the crop [1]. Chlorosis is usually observed in plants growing on calcareous soil that has a high concentration of bicarbonate anions [2, 3] and pH of 7.5–8.5 [4] or higher. Iron in this soil is in an insoluble form of hydroxycarbonate, therefore it is inaccessible to plants. Chlorosis control is a global problem as calcareous soils occupy about 1/3 of all agricultural areas. For this purpose, iron complexes with synthetic organic compounds that provide solubility are commonly used. However, synthetic complexones are poorly biodegradable and quite expensive.

The use of iron complexes with natural organic compounds is a more ecofriendly alternative. In particular, many studies have been devoted to the use of iron lignosulphonates for the control of chlorosis [5]. At the same time, iron lignosulfonates are usually obtained by mixing technical lignosulfonates with iron salts. As a result, these solutions contain extraneous ions. In this study, we used anodic dissolution of iron to synthesis iron-lignosulfonate complex without extraneous ions, and the resulting solutions with high iron concentrations were tested when lupine was grown on calcareous soils.

2. Materials and methods
2.1. Materials

The studies were carried out with industrial sodium lignosulfonates with the content of functional groups determined by known methods [6], %: total acid 5.51±0.07, sulfo groups 2.88±0.09, carboxyl 1.47±0.02, phenolic hydroxyl 1.16, carbonyl 1.43±0.04, methoxy 9.35±0.06. The solution of lignosulfonic acids was prepared by decationization of the sodium lignosulfonates solution with cation-exchange resin KU-2-8. The sodium lignosulfonates solution had pH 4.3 and contained, %: dry substances 62.5±0.4 including reducing substances 0.58±0.02 and ash content relative to dry substances 14.40±0.4. The lignosulfonic acids solution had pH 1.1 and contained, %: dry substances 50.9±0.2 and ash content relative to dry substances 0.33±0.03.

2.2. Electrochemical synthesis

Electrochemical synthesis of iron-lignosulfonate complexes was carried out in a 300 mL temperature-controlled flow cell with two iron electrodes (the iron content of 99.1%, the diameter of 5 mm, the length of 70 mm, the interelectrode gap was 5 mm) with continuous electrolyte circulation. The power supply served as an electronic unit, which allows to vary the constant voltage, control the current strength and change the polarity of the electrodes with a predetermined time interval. The concentration of the sodium lignosulfonate solution was 6%, the concentration of lignosulfonic acids was 5%. The iron concentration in resulting solutions was determined by photometry [7].

2.3. Estimation of anti-chlorosis action

Vegetation studies were carried out in greenhouse conditions on a gray forest soil (original soil). A calcareous soil was created artificially by adding 20% (by volume) of calcium carbonate to the original soil. Yellow lupine (Lupinus luteus, cultivar Martin 2, cultivar Kopylovsky) was used as an object of research. On the 10th day of cultivation, half of all plants growing on calcareous soil were treated with a non-root method with a solution of the synthesized iron-lignosulfonate complex with an iron concentration of 0.02%. The second similar treatment of the same plants was carried out on the 20th day of cultivation with a solution of the synthesized iron-lignosulfonate complex with an iron concentration of 0.03%. After 20 and 30 days of growing plants on the original and calcareous soils (without and with treatment), the contents of chlorophyll and carotenoids were determined after extraction with acetone [55]. The height and absolutely dry weight of the aerial parts of plants were measured after 30 days of cultivation.

3. Results and Discussion

The dissolution of the iron anode occurs directly under the action of the applied voltage. In the processes of electrochemical machining of metals, the voltage does not exceed 48 V. When using an alternating voltage, there was practically no dissolution of the anode, therefore, studies were carried out at a constant voltage. During the experiments, a rapid decrease in the magnitude of the anode current and the formation of a film on the anode were noted. This is apparently due to the fact that when an electric field is applied, the lignosulfonate polyanions move to the anode and settle on its surface to form a film that leads to an increase in resistance and thereby a decrease in the anode current density. The efficiency of anodic dissolution of a metal is proportional to the anodic current density.

To increase the rate of anodic dissolution, it is necessary to remove the resulting film from the surface of the anode. To solve this problem, a setup was used in which the polarity of the electrodes changes with a given period. The first experiment showed that the efficiency of electrochemical processing increases by 5–7 times. With an increase in voltage in the region of 4–30 V, the amount of iron transferred to the solution increases. The dependence of the concentration of iron on the switching period of the polarity of the electrodes (SPPE) passes through a maximum. At higher voltages, the maximum shifts towards lower SPPE. Obviously, as the voltage increases, the rate of formation of a lignosulfonate film at the anode increases, therefore, to maintain the process speed at the maximum level, a more frequent change in the polarity of the electrodes is necessary.
Subsequently, experiments were carried out at a voltage of 16 V. A full factorial experiment was implemented to systematically study the dependence of anodic dissolution of iron in solutions of lignosulfonic acid and lignosulfonates on temperature, process duration, and SPPE. Independent variables were changed in the following intervals: temperature was from 30 to 80°C, process duration was from 5 to 60 min, SPPE was from 1 to 41 s for lignosulfonic acid and from 1 to 170 s for lignosulfonate (in coded values from −1.683 to 1.683). Polynomials of 1–3 degrees were calculated from experimental data. The approximation error of the dependence of the iron concentration on variable factors was about 5% using third-order polynomials.

All selected independent factors have a significant impact on the output value. Moreover, their influence is not the same for solutions of lignosulfonates and lignosulfonic acids. SPPE has the greatest influence on the lignosulfonates solution, and in the case of lignosulfonic acids the duration of the process has the greatest effect. For both samples, there are coefficients with different signs for SPPE, which indicates the presence of an extremum on the dependence. An increase in both the temperature and the duration of the process leads to an increase in iron concentration. The optimal SPPE decreases with increasing electrolysis time. An increase in temperature also leads to a decrease in the optimal SPPE value for the lignosulfonates solution to 14–20 s at a temperature of 80°C, while for the lignosulfonic acids solution this parameter remains unchanged (7–8 s) with a process time of 20 min. The dissolution rate of the iron anode is significantly higher in lignosulfonic acids solutions than in lignosulfonates solutions. This is due to the lower pH value and high proton mobility.

The anti-chlorosis action of the synthesized iron-lignosulfonate complex was evaluated with lupine cultivation. Lupine was chosen as an object of vegetative research, since it is calciphobous, i.e. iron deficiency develops when it is grown on calcareous soil. For non-root treatment, we synthesized iron-lignosulfonate complexes with a maximum iron content (3 g/L), which were then diluted to the required concentration. The first treatment of plants growing on calcareous soil with the iron-lignosulfonate complex was 10 days after planting. At this point, chlorosis of plants growing on calcareous soil had already begun, and the chlorophyll content in plants was 30% lower than that of plants growing on the original soil. It was enough to carry out one foliar treatment so that the chlorophyll content in 3 days would increase by more than 2 times compared with control plants growing on calcareous soil without treatment. After 20 and 30 days of lupine cultivation, the total content of chlorophyll and carotenoids in the treated plants grown on calcareous soil was much higher than in the control plants grown on calcareous soil without treatment, and even exceeded those in plants grown on the original soil (figure 1).

![Figure 1](image.png)

**Figure 1.** The relative content of pigments in lupine grown on original and calcareous soils without and with iron-lignosulfonates complex treatment of plant.
The weight of the ground part of the plants after treatment with iron-lignosulfonate complex increased 2.2 times compared with plants grown on carbonate soil and almost reached the mass of plants grown on the original soil (table 1).

Table 1. Height and weight of the ground part of plants grown on the original and calcareous soils without and with iron-lignosulfonates complex treatment of plant.

| Type of soil               | Height relative to plants grown on calcareous soil, cm | Weight relative to plants grown on calcareous soil, g | % |
|----------------------------|------------------------------------------------------|-----------------------------------------------------|---|
| Original soil              | 13.9±0.9                                             | 2.5±0.3                                             | 125 | 227 |
| Calcareous soils           | 11.1±1.1                                             | 1.1±0.2                                             | 100 | 100 |
| Calcareous soils (treated plants) | 12.1±0.6                                           | 2.4±0.5                                             | 109 | 218 |

4. Conclusion
Anodic dissolution of iron in a solution of lignosulfonic acids or lignosulfonates can be used to obtain iron-lignosulfonate complexes to avoid introducing additional anions, which occurs when using iron salts. The rate of anodic dissolution of iron is higher in a solution of lignosulfonic acids than in solutions of lignosulfonates. An increase in the concentration of iron in solution occurs with increasing temperature and the duration of electrolysis. It is necessary to use a direct current with periodic polarity reversal in order to avoid coating the electrodes with a lignosulfonate film. The dependence of the concentration of dissolved iron on the duration of the period of switching the polarity of the electrodes has a maximum, which shifts toward a shorter duration with increasing voltage. The synthesized iron-lignosulfonate complexes have a pronounced anti-chlorosis effect. The contents of pigments, the height and weight of the ground part of the treated plants grown on calcareous soil were close to those of plants grown on the original soil.

References
[1] Zuo Y and Zhang F 2011 Plant and Soil 339 83-95.
[2] Briat J F, Dubos C and Gaymard F 2015 Trends in Plant Science 20 33-40.
[3] Lucena J J and Hernandez-Apaolaza L 2017 Plant and Soil 418 1-4.
[4] McCauley A, Jones C and Jacobsen J 2009 Nutrient management module 8 1–12
[5] Rodriguez-Lucena P, Hernández-Apaolaza L and Lucena J J 2010 J. Plant Nutr. Soil Sc. 173 120-6.
[6] Zakis G F 1994 Functional analysis of lignins and their derivatives (Atlanta: Tappi Press).
[7] Khabarov Yu G, Komarova G V and Mashyanova E A 1988 Lesnoy Zhurnal-Forestry Journal N5 124–5.
[8] Pochinok H N 1976 Methods of biochemical analysis of plants (Kiev: Naukova Dumka).