

Changes of chemical reactions in soil during electric processing by means of UV-radiation

Anvar Anarbaev^{1*}, Obid Tursunov^{1,3,4}, Dilshod Kodirov¹, Zayniddin Sharipov¹, Farrukh Mukhtarov⁵

¹Tashkent Institute of Irrigation and Agricultural Mechanization Engineers, 100000 Tashkent, Uzbekistan

²Institute of Energetic Problems, Uzbek Academy of Science, 100084 Tashkent, Uzbekistan

³Research Institute of Forestry, 111104 Tashkent, Uzbekistan

⁴Gulistan State University, 120100 Gulistan, Uzbekistan

⁵Tashkent State Technical University, 100097 Tashkent, Uzbekistan

Abstract. The technology of electro-processing by UV-radiation soil of agricultural plants is considered. The mechanism of the effect of UV irradiation to change by redox reactions a chemical potential of the soil is shown. As the result of experimental researches, optimum parameters for processing soils with ultraviolet radiation lamps for increasing the absorption of the most mobile manganese forms in plants are defined.

1 Introduction

Investigations of chemical equilibria are given the most important place in the physical chemistry of soils [1-3]. Among the problems associated with the problem of equilibria is the prediction of the directions of chemical reactions occurring in soils, which are closely related to the thermodynamics of soil solutions and surface phenomena [4-6].

A change in the composition and amount of dissolved substances causes a change in the chemical potential of water. The difference in the chemical potentials of water containing a solute can increase movement in the root system of a plant [7-8]. This will improve the metabolism of nutrients in the plant cells.

Information on the photochemical properties of soils upon exposure to UV radiation is fragmentary. It is known [9] that under the influence of ultraviolet light, colored organic substances are capable of attaching oxygen even in molecular form. This is directly related to the biological activity and soil fertility, because the humus contains amino acids that can inhibit the activity of soil enzymes. This photomethylation changes the number of functional groups, which affects the colloidal-chemical properties of humus.

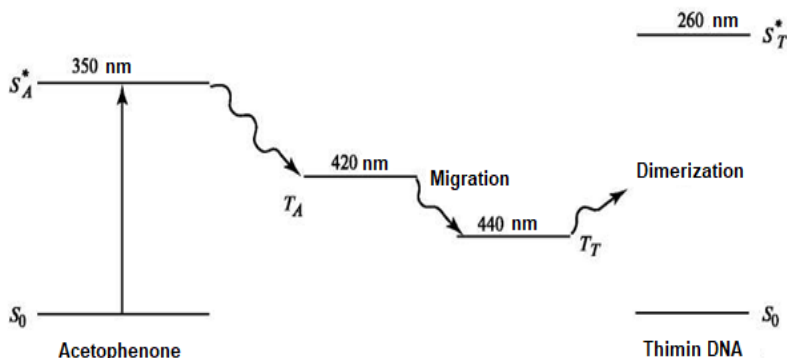


Fig. 1. Scheme of excitation of plant cells when exposed to ultraviolet radiation

The plant is very sensitive to the wavelength of ultraviolet radiation. In Fig. 1, the values of the energies of the levels are given in the wavelengths of quanta of the corresponding energy. When a DNA solution in acetophenone is irradiated with light with a wavelength of 350 nm, quanta are absorbed only by the sensitizer [10].

Redox reactions in soils occur in a complex environment in a multiphase environment with poorly soluble compounds [11]. Along with purely chemical processes in soils, biochemical processes of oxidation and reduction are widely developed. In practice, oxidation is considered as a reaction in which oxygen is added to a substance, or electrons are lost by a substance.

The ability of the soil to undergo redox reactions can be measured using the redox potential.

*Corresponding author: anizan6004@mail.ru

2 Research Methods

The magnitude of the osmotic pressure depends on the composition of the solution and temperature [12]; the relationship between it and the activity of water in solution is expressed most simply by π

$$-R \cdot T \cdot \ln a_w = \int_{\pi}^{\pi+p} v_w dp \tag{1}$$

here p - hydrostatic pressure; π - osmotic pressure; v_w - molar volume of water, R – gas constant, T – temperature. Due to the weak compressibility of water, the integral on the right can be replaced by a difference. With a molecular weight of water equal to 0.018 kg/ mol [13]

$$\pi = -\frac{RT \cdot d}{0,018} \ln a_w \tag{2}$$

where d is the density of the solution, kg/m³.

For arid soil solutions (from the Latin aridus "dry", or desert climate), and semiarid (steppe) regions, where the system Ca, Mg, Na || Cl, SO₄-H₂O water activity can be calculated using the expression [14]

$$\ln a_w = -0,018 \cdot I \cdot \sum_{j=1}^N \frac{v_j}{p_j} \eta_j \times \left\{ 1 + \ln 10 \left[\frac{v_j + v_{j-}}{\nu} \cdot I \left(b_j^0 + \sum_{k=2}^N \alpha_{jk}^0 \cdot y_k \right) - |z_j + z_{j-}| A \sqrt{I} \sigma(r_j^0 \cdot B \sqrt{I}) \right] \right\}$$

A - the value of the ionic strength associated with the different number of electrons in the reaction.

The electrical conductivity EC of these solutions closely correlates with the value of the osmotic pressure of soil solutions, so, according to [15], the root-mean-square error of the formula was 15%. $E_c = 23,4\pi$

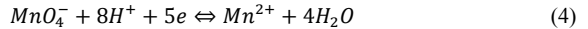
Since the activities of the substances (activity coefficients) participating in the reaction are unknown, we will use the concentration form of the Nernst equation [16] with the substitution of the apparent standard redox potential E^0 as a constant:

$$E = E^0 + \frac{2,303 \cdot R \cdot T}{n \cdot F} \cdot \lg \frac{[Ox]}{[Red]} \tag{3}$$

The quantity $\frac{2,303 \cdot R \cdot T}{n \cdot F}$ for brevity, denoted by the symbol ϑ . In general, the redox potential is a complex function of the activities of various oxidized and reduced forms of substances involved in the reaction [17]. With the participation of hydrogen ions in the reaction, their activity also affects the value of the redox potential.

3 Results

The system $MnO_4^- \rightleftharpoons Mn^{2+}$ was chosen as a typical example for calculations. In this case, the reaction proceeds with the participation of eight hydrogen ions [18]:

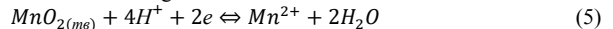


The magnitude of the oxidative potential is determined in this case by the equation

$$\begin{aligned} E &= E^0 + \frac{\vartheta}{5} \lg \frac{a_{MnO_4^-} \cdot a_{H^+}^8}{a_{Mn^{2+}}} = E^0 + \frac{\vartheta 8}{5} \lg a_{H^+} + \frac{\vartheta}{5} \lg \frac{a_{MnO_4^-}}{a_{Mn^{2+}}} = \\ &= E^0 - \frac{\vartheta 8}{5} pH + \frac{\vartheta}{5} \lg \frac{a_{MnO_4^-}}{a_{Mn^{2+}}} \end{aligned}$$

at 18^oC: $E = E^0 - 0,0923 \cdot pH + 0,0115 \cdot \lg \frac{a_{MnO_4^-}}{a_{Mn^{2+}}}$

Manganese compounds also form other redox systems. Solid state manganese dioxide is reduced to Mn^{2+} :



then $E = E^0 + \frac{\vartheta}{2} \lg \frac{a_{H^+}^4}{a_{Mn^{2+}}}$, since the activity of manganese dioxide in the solid phase is taken to be unity.

According the known ongoing reaction based on the values of normal oxidation potentials in determining the amount of divalent manganese in the soil

$$E = 0,991 + 0,0581\sqrt{I} - 0,116pH - 0,029 \lg[Mn^{2+}] \tag{6}$$

Table 1. Normal potentials of a number of redox soil systems

Element symbol	Highest oxidation state	+n · e ⁻	Lowest oxidation state	E ⁰ , V
Cu	Cu ²⁺	+2 · e ⁻	Cu ↓	+0.345
	Cu ²⁺	+e ⁻	Cu ⁺	+0.159
	Cu(NH ₃) ₄ ²⁺	+e ⁻	Cu(NH ₃) ₂ ⁺ + 2NH ₃	-0.01
Mn	Mn ³⁺	+e ⁻	Mn ²⁺	+0.151
	Mn(OH) ₃ ↓	+e ⁻	Mn(OH) ₂ + OH ⁻	+0.1
	Mn(OH) ₃ ↓ + 3H ⁺	+e ⁻	Mn ²⁺ + 3H ₂ O	+1.84
	MnO ₂ ↓ + 4H ⁺	+2e ⁻	Mn ²⁺ + 2H ₂ O	+1.23
	MnO ₄ ⁻	+e ⁻	MnO ₄ ²⁻	+0.558
	MnO ₄ ⁻ + 4H ⁺	+3e ⁻	MnO ₂ ↓ + 2H ₂ O	+1.69
	MnO ₄ ⁻ + 8H ⁺	+5e ⁻	Mn ²⁺ + 4H ₂ O	+1.51

Table 1 [19] shows the values of the normal potentials of a number of redox systems that are of interest from the point of view of transformation into mobile forms of trace elements in the soil.

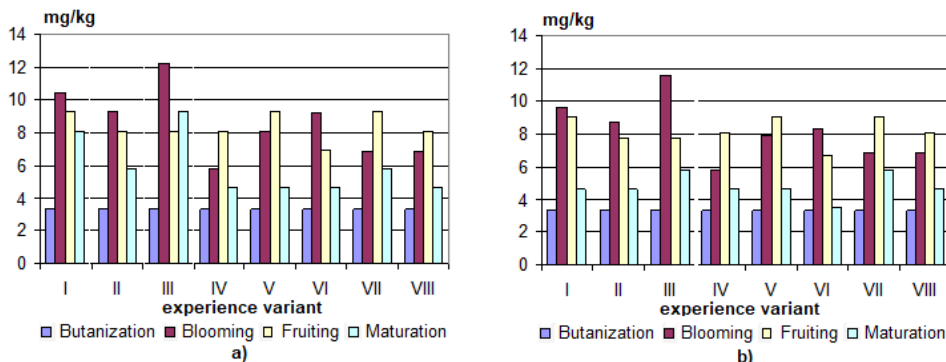


Fig. 2. Influence of electrical treatment with UV radiation on the microelement (manganese) composition of the soil by the phases of development (in mg Mn per kg of soil) a) at a depth of the arable layer 0÷30 cm b) at a depth of the soil horizon of 30 ÷50 cm: I - control (soil without plants and UV treatment), II - control (soil with a plant and without UV treatment), III - UV treatment of soil without plants, IV - UV treatment of soil and cotton seeds, V – pre-sowing UV treatment of soil and cotton seeds, soil during sowing, VI - UV treatment of soil and plants during their growing season, VII - UV treatment of soil during plant growing season, VIII - pre-sowing UV treatment of cotton seeds + UV treatment of soil and plants during the growing season of plants

Ultraviolet soil treatment is able to influence the oxidation-reduction processes in the soil in terms of preserving the mobile forms of microelements in it [20-22]. This is shown by the results of experiments on seed treatment carried out in the experimental field base of the agricultural enterprise “BMKB-Agromash” (Fig. 2).

Field test results set for the phases of plant development confirm the above models.

As can be seen from Fig. 2, at the initial phase of the appearance of plant buds, there is no change in the amount of manganese under different variants of experiments, which means the duration of redox processes in the soil from 70 to 95 days.

Compared to control measurements, UV treatment of the soil significantly increases the Mn content (variant III).

Due to the achieved electric potential in the soil, oxygen is separated from oxide compounds from Mn and forms water molecules with hydrogen. When electro treating cotton seeds and soil with UV radiation (option IV), the microelement composition of the soil (for example, manganese) is minimal. This suggests that it is possible to change the chemical equilibrium of the soil towards the formation of an aqueous solution of Mn, which passes from the soil to the plant.

4 Conclusions

It is possible to evaluate the light effect of UV radiation as follows.

The zone of direct penetration of UV radiation into the soil is limited (5÷10 mm). Consequently, the effect of light on soil processes is complex. Among the components in the upper layer of the arable layer, which can be affected by UV radiation, are primarily humic substances that cover solid phase particles with films. UV irradiation allows in formulas

(4 ÷ 6) due to an additional quantum of energy $h\nu$ lead to an excited state an additional electron e^- in microelements of the soil, thereby increasing the value of the potential E to the required values, allowing changing the chemical equilibrium of the soil in the direction of water release. Redox processes ensure the appearance of an aqueous solution of trace elements, which are more actively assimilated by plants. At the same time, their productivity and the quality of the grown fruits increase significantly.

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