

## ГІДРОГЕОЛОГІЯ, ІНЖЕНЕРНА ТА ЕКОЛОГІЧНА ГЕОЛОГІЯ

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ELECTROCHEMICAL INVESTIGATION OF COBALT ABSORPTION PROCESSES  
BY SOILS OF UKRAINE

(Рекомендовано членом редакційної колегії д-ром геол. наук, проф. С.А. Вижвою)

In this paper, the processes of cobalt absorption by soils of Ukraine are investigated by using the electrochemical method of pulsed inversion chronopotentiometry. It has been established that the absorption capacity of cobalt by soil varieties from complexing media is 64–98 %. In solutions of  $\text{KNO}_3$ ,  $\text{NH}_4\text{OH}$  and  $\text{CSN}_2\text{H}_4$  mobile compounds of cobalt are part of  $[\text{Co}(\text{H}_2\text{O})\text{n}]^{2+}$ ,  $[\text{Co}(\text{NH}_3)\text{n}]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)\text{n}]^{2+}$ , and in solutions of  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$  and  $\text{EDTA}^{4-}$  anionic complexes  $[\text{Co}(\text{P}_2\text{O}_7)\text{n}]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})\text{n}]^{2-5n}$ ,  $[\text{CoEDTA}]^{2-}$  are formed. The cobalt cationic complexes  $[\text{Co}(\text{H}_2\text{O})\text{n}]^{2+}$ ,  $[\text{Co}(\text{NH}_3)\text{n}]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)\text{n}]^{2+}$  are almost completely absorbed by the soils. Anionic complexes –  $[\text{Co}(\text{P}_2\text{O}_7)\text{n}]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})\text{n}]^{2-5n}$ ,  $[\text{CoEDTA}]^{2-}$  largely remain mobile in the soil profile. The sorption effect depends on the charge of the complex ions, their strength and on the steric parameters of the complex ions. A close positive relationship was established between the cobalt absorption by soils and the cation exchange capacity of soils, the correlation coefficient was 0,7976, and between the cobalt absorption by soils and the humus content (0,7034). In the study of biohumus, it was found that cobalt goes into the solution of 0,02M  $\text{EDTANa}_2 + 0,09\text{M NH}_4\text{Cl}$  by the mechanism of competitive complexation, its transition to the  $\text{HCl}$  solution occurs due to the protonization of the functional groups of biohumus with which the metal is bound. Biohumus has rather high sorption properties of cobalt and may be promising for its use as an effective carrier matrix in various combinations with basic fertilizers. Isotherms of sorption or exchange of cobalt for exchange ions of biohumus in various solutions correspond to isotherms of Langmuir single layer adsorption. The method of IHP analysis is important to use to control the content of trace elements at the level of their trace concentrations necessary for plant development.

**Keywords:** Available content of cobalt, sorption processes, biohumus, cation exchange capacity, electrochemical pulsed method.

**Introduction.** The content of cobalt in soils is influenced by natural and anthropogenic factors. Natural factors include the geology of the territory, the age of soils, climatic conditions, the expansion of the organic fraction of the soil, wind erosion, which result in the distribution of minerals and atmospheric deposition of dust, which includes cobalt. Among anthropogenic human activities, which generally affect the local concentrations of Co in the soil, there is widespread agricultural use of lands and associated chemistry, the use of sewage sludge in the fields as fertilizers, the use of cobalt salts as a feed supplement for bovine animals, as well as air transport (Albanese et al., 2015; Collins and Kinsela, 2010; Perez-Espinosa et al., 2005; Tonkha and Dzyazko, 2014; Tonkha et al., 2018). The average concentration of Co in soils in Europe is 1–20 mg/kg dry weight, in the soil of Ukraine of 0,15–0,86 mg/kg of soil. The part of land in Ukraine, which has very high content of mobile cobalt compounds, is 47,5 % (7,9 million hectares), an average content of cobalt is in 21,8 % of land area, and low content – 9 % (1,5 million hectares) (Collins and Kinsela, 2010).

Cobalt is found in soils in various compounds, the degree of availability of which for plants is different (Albanese et al., 2015). The soluble salts of cobalt, deposited in the soil, can be fixed due to the formation of insoluble oxides, sulfides, phosphates, carbonates, etc. This leads to the fact that optimal standards for cobalt fertilizers may be inadequate in crop nutrition. The effectiveness of using complex and complex mixed fertilizers containing Co depends largely on the mobility of cobalt compounds and the stability of soil consolidation.

Concentration of cobalt in soils depends on the soil reaction (pH), the content of organic matter, clay and the cation exchange capacity (Копилевичидр., 2015). Since cobalt forms persistent carbonate and hydroxydic minerals that are insoluble in water, most cobalt forms in the soil are not biologically available to plants (Perez-Espinosa et al., 2005), which adversely affects their development. Therefore, there is a need to add cobalt-containing fertilizers to the soil to ensure the full development of plants. The present experience of applying the geospatial methods for soil studying (Pereira et al., 2017) confirmed the requirements of the application of fast geophysical technologies. Soil magnetic properties have relation to the pH, organic matter content, and erosion index (Menshov et al., 2018). Co as a ferromagnetic material can be easily detected with thermomagnetic measurements (Menshov, 2016).

At present, in agrochemical practice, trace elements, integrated in complex compounds, are used. So, the use of chelators of polyethylenepolyamineacetic acid has allowed achieving success in the fight against lime chlorosis of plants (Collins and Kinsela, 2010). The paper (Perez-Espinosa et al., 2005) shows a sharp increase in the flow of the trace element Co to the plants of vicia and oats due to high mobility of  $[\text{CoEDTA}]^{2-}$  in the soil profile. Pre-sowing treatment of corn, sugar beet, cotton seeds with ammoniacal complexes of Co and Mn gave significant increasing in crop yields (Tonkha and Dzyazko, 2014).

At present, microfertilizers are used –  $\text{Co}(\text{NH}_2)_2$ , as well as fertilizers based on polyphosphates, phosphonitrile, phosphamide, and others. They have complex-forming ability. The study of their interaction with  $\text{Co}^{2+}$  ions is of considerable interest, since complex ions of cobalt,

depending on their nature, strength and stereochemical characteristics, varying degrees of oxidation, have different mobility in the soil profile and availability to plants. Chelates formation with organic polydentant ligands to a certain extent simulates many natural processes. Complexes of this type are fairly stable and can be used as self-contained microfertilizers or in combination with macro-components. Therefore, it is important to study the absorption of cobalt from different fertilizers by different types of soils.

**Material and methods.** To determine the cobalt in soil samples, the most easy-to-use, high-precision new electrochemical method of impulse inversion chronopotentiometry (IChP) (*Palanytsia et al., 2014*) using the improved analyzer of heavy metal salts "M-XA1000-5" was used, the principle of which is based on the basic method of inversion chronopotentiometry (IChP method) (*Surovtsev et al., 2007*). The theoretical foundations of the method and the main criterion equation of IChP are presented in (*Копилевич та ін., 2012*). Measurement of cobalt content in soils was carried out in accordance with the methodology developed and approved by Ukrmetrteststandard (*Копилевичидр., 2015*).

Immediately before the measurement of cobalt, a background electrolyte was prepared, consisting of a solution A: (2M HCl + 0,1M NaSCN + 0,4M Na<sub>2</sub>SO<sub>3</sub>) and solution B: (4M NH<sub>4</sub>OH) in the ratio A:B = 3 : 2. In

measurements, a 2-electrode electrochemical cell with an indicator golden solid-state electrode was used. Its working surface was sanded with calcium sulfate chemically deposited, thoroughly washed with bidistilled water. As a comparison electrode, a chloride electrode was used, which was filled with a solution of 2M HCl.

Measurement of Co (II) concentrations in soil samples was carried out using standard additives in the concentration range of 1,0; 0,1; 0,01 and 0,001 µg/cm<sup>3</sup>. Graduating solutions at a concentration of 10.0 1.0 and 0,1 µg/cm<sup>3</sup> were prepared by diluting standard solutions of Co (II) (MSO 0137 : 2000, DSA 022.78-98). The electrolysis potential of Co on a gold electrode is in the range -1,400 ÷ -10000 V.

As an example (table 1), the results of measuring the concentration of Co (II) in model solutions of different concentration ranges are given. It has been established that the method of determining the concentration of Co (II) by impulse inversion chronopotentiometry method according to the developed method can be used in a wide range of concentrations from 0,001 to 1,0 mg/dm<sup>3</sup> with high accuracy.

The results of measurement of the Co(II) mass in the soil sample by the IICP method and atomic absorption analysis, the relative error of measurements, depending on the concentration, varies from 2 to 18 % (Table 2).

Table 1

Measurement errors for Co (II) concentrations in model solutions (n = 5; P = 0.95)		
Parameters of measurements		Co (II), determined by the results of measurements, mg/dm <sup>3</sup>
Indicator	Concentration of Co (II) in solution, mg/dm <sup>3</sup>	
The specified and measured concentration of Co (II) in the model solution, µg/cm <sup>3</sup>	1,0	0,98±0,08
	0,1	0,093±0,006
	0,01	0,0089±0,0005
	0,001	0,00082±0,0001
Relative measurement error, %		2,0-18,0

Table 2

Comparison of the results of the measurement of Co (II) content in sod-podzolic soil by different analytical methods, mg/kg (n = 5; P = 0,95)								
Ion	IChP Method				Atomic-Absorbion Analysis			
	test 1	test 2	test 3	average value	test 1	test 2	test 3	average value
Co <sup>2+</sup>	1,28	1,21	1,18	1,223 ± 0,002	1,31	1,24	1,16	1,236 ± 0,004

As a result of the studies, a sufficient level of coincidence of the results of measuring the concentration of cobalt in soil samples obtained by different methods of analysis has been established. The obtained data will satisfy the satisfactory accuracy and reproducibility of the results of the determination of cobalt under the proposed conditions, while the lower limit of determination of the element according to the developed method is set at the level of  $1 \cdot 10^{-3}$  µg/dm<sup>3</sup>. For studies of the absorption of cobalt by different types of soils from complex-forming environments the soil samples from a layer of 0–30 cm were taken.

*In the first series of studies*, aqueous solutions of KNO<sub>3</sub>, NH<sub>4</sub>OH and (CSN<sub>2</sub>H<sub>4</sub>) were prepared, which are used as ligands in agrochemical practice. The experiments were carried out according to the following method: 10 g of air-dry soil was filled with 60 ml of a solution containing Co in the amount of 70 µg (at the rate of 7 mg/kg soil) and the corresponding ligand.

The mixture was shaken on a rotator for 1 hour and filtered through a folded filter. The filtrate was determined content of Co. Analysis of Co from solutions containing KNO<sub>3</sub>, NH<sub>4</sub>OH and (CSN<sub>2</sub>H<sub>4</sub>) was performed using a new method of impulsed inversion chronopotentiometry (*Копилевичидр., 2015; Карнаухов та ін., 2000*).

*In the second series of studies*, there were prepared solutions of polyphosphates Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> and Trilon B

(disodium salt of ethylenediaminetetraacetic acid) as a universal organic complexone. Since the polyphosphate and trilonate complexes of Co do not regenerate on the electrode in the favorable potential range (up to -2,0 V), a special method of their analysis was developed. The method is the following: from 20 ml of a polyphosphate solution Co was extracted by 20 ml of dithizone in CCl<sub>4</sub> solution during 5 minutes at a pH of 8,8 (control with using a pH-meter "pH-150M").

The extract was washed with 10 ml of water to remove completely the phosphates and then the samples were evaporated on a plate in glasses to the state of wet salts. The wet residue was mineralized by adding 1 ml of conc. HNO<sub>3</sub>, 1 ml of 30 % H<sub>2</sub>O<sub>2</sub> and 1 ml of conc. H<sub>2</sub>SO<sub>4</sub>. The contents were heated until sulfuric acid vapor appeared and then 1 ml of H<sub>2</sub>O<sub>2</sub> was added again. Trilonate solutions were burnt in a muffle furnace without prior treatment with concentrated acid solutions. The residue was dissolved in 2 M NH<sub>4</sub>OH and Co was determined by the IChP method (*Kopilevich et al., 2015*) using a gold solid electrode.

*In the third series of studies*, 100 g of biohumus was saturated with cobalt ions with an active contact of 0,5 M Co(NO<sub>3</sub>)<sub>2</sub> solution for 48 hours. The solid phase was filtered, washed until negative reaction on NO<sub>3</sub><sup>-</sup> ion, dried on the air. The obtained samples were used to study the extraction of cobalt ions from biohumus by solutions of 1M CaCl<sub>2</sub>; 1M CH<sub>3</sub>COONH<sub>4</sub>; 1M HCl; 0,02M EDTANa<sub>2</sub> + 0,09M NH<sub>4</sub>Cl,

which are widespread in agrochemical practice for diagnostics of the movable cobalt forms in soil. Ratio solid phase: extractant was 1 : 10 by volume.

In the fourth series, the biogumus was previously saturated by calcium ions. 100 g of biogumus were treated with 1M solution of  $\text{CaCl}_2$  at shaking, filtered; the solid phase was washed with distilled water to negative reaction on calcium ions and dried in air. The obtained calcium-

biohumus was used to study the specific adsorption of Co by humus in a solution of 0,01 M  $\text{CaCl}_2$ . The experiments were carried out according to the regulations, as in the system: biohumus – 0,01M  $\text{CaCl}_2$  –  $\text{Co}^{2+}$ .

**Results and discussion.** As a result of the experiments carried out by the above methods, the percentages of absorbed Co by various soils (table 3) from various complexing media (table 4) were calculated.

Table 3

Basic physical and chemical properties of the studied soils (n = 5; P = 0,95)

No	Soil	Soil reaction, pH ( $\text{H}_2\text{O}$ ), %	Humus content, %	Cation exchange capacity, mmol/100 g soil
1	Chernozemic-Meadow medium loamy	7,8±0,2	4,75±0,15	27,1±0,4
2	Sod-Podzolic light loamy	5,1±0,15	1,95±0,11	9,4±0,3
3	Dark-Chestnut sodisity affected heavy loamy	8,6±0,3	5,15±0,12	25,8±0,2
4	Meadow sodisity affected medium loamy	7,6±0,2	4,98±0,16	27,3±0,4
5	Dark-Grey Podzolized light loamy	5,9±0,2	2,98±0,2	14,9±0,2
6	Sodic crust solonets heavy loamy	8,8±0,3	2,12±0,11	8,8±0,2
7	Chernozem Southern low-humus heavy loamy	8,0±0,2	4,12±0,09	31,8±0,2
8	Grey Podzolized light loamy	5,4±0,15	2,58±0,11	11,8±0,3
9	Chernozem Podzolized medium loamy	6,8±0,15	3,78±0,11	21,8±0,2
10	Chernozem Halpic medium loamy	6,6±0,15	4,18±0,09	29,8±0,2

Table 4

Absorption of Co by soils from different complexing media

No	Soil	1M $\text{KNO}_3$ pH 7,9, %	1M $\text{NH}_4\text{OH}$ pH 11,8, %	1 M $\text{CSN}_2\text{H}_4$ pH 7,6, %	0,15 M $\text{Na}_4\text{P}_2\text{O}_7$ pH 9,2, %	0,25M $\text{Na}_5\text{P}_3\text{O}_{10}$ pH 8,6, %	0,1 M EDTA pH 4,5, %
1	Chernozemic-Meadow medium loamy	97,7	92,7	83,6	58,0	50,7	4,8
2	Sod-Podzolic light loamy	79,0	67,0	80,8	65,0	29,3	1,2
3	Dark-Chestnut sodisity affected heavy loamy	93,6	80,6	85,3	20,5	14,2	2,8
4	Meadow sodisity affected medium loamy	97,6	95,7	89,8	62,5	62,5	7,5
5	Dark-Grey Podzolized light loamy	89,7	92,6	95,5	51,3	43,6	6,9
6	Sodic crust solonets heavy loamy	88,1	97,9	89,5	48,1	43,0	4,8
7	Chernozem Southern low-humus heavy loamy	98,0	88,0	88,6	50,0	15,5	3,1
8	Grey Podzolized light loamy	82,7	64,4	70,1	37,0	9,8	6,5
9	Chernozem Podzolized medium loamy	97,3	93,5	82,1	58,4	55,0	4,8
10	Chernozem Halpic medium loamy	97,3	96,9	82,1	54,7	39,2	1,9

In solutions of  $\text{KNO}_3$ ,  $\text{NH}_4\text{OH}$  and  $\text{CSN}_2\text{H}_4$ , cobalt is a part of the complex cations  $[\text{Co}(\text{H}_2\text{O})_n]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_n]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)_n]^{2+}$ , and in solutions of  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$  and  $\text{EDTA}^{4-}$  anionic complexes  $[\text{Co}(\text{P}_2\text{O}_7)_n]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})_n]^{2-5n}$  i  $[\text{CoEDTA}]^{2-}$  are formed. The complexity of Co in all cases is close to 100 %. The absorption capacity with different soil types from the complexing environments was 64–98 %. Chernozem has 18–28 % more absorption of Co then Sod-Podzolic.

A high percentage of absorption of complex cations can be explained mainly by the cationic type of the soil absorbing complex of the main types of soils of Ukraine. With an increase in the size of ligands in the series  $\text{H}_2\text{O} < \text{NH}_3 < \text{CSN}_2\text{H}_4$ , the sizes of complex ions increase and, regardless of the soil specificity, the sorption effect decreases. Between the cation exchange capacity of soils and the absorption

capacity of cobalt a close positive correlation was established, the correlation coefficient was 0,7976 (fig. 1).

Also, the absorption capacity depended on the content of humus in the soil, with the increase of soil humus content more mobile compounds of cobalt were found in the soil, the correlation coefficient was 0,7034 (fig. 2).

In the case of cobalt-containing complexes of anionic character, the sorption effect is a function of the strength of complex ions. Pyrophosphate complexes ( $\text{pK} = 6,1-7,2$ ) and tripolyphosphate complexes ( $\text{pK} = 6,6-6,89$ ) (Карнаухов та ін., 2000) are sorbed by soils much more than trilonate, which is in accordance with high strength of  $[\text{Co EDTA}]^{2-}$  ( $\text{pK} = 16,1$ ) (Копілевич та ін., 2012).

At the results of the experimentseries 3, an assessment of the possibilities of biohumus as a carrier matrix of cobalt was carried out (table 5).

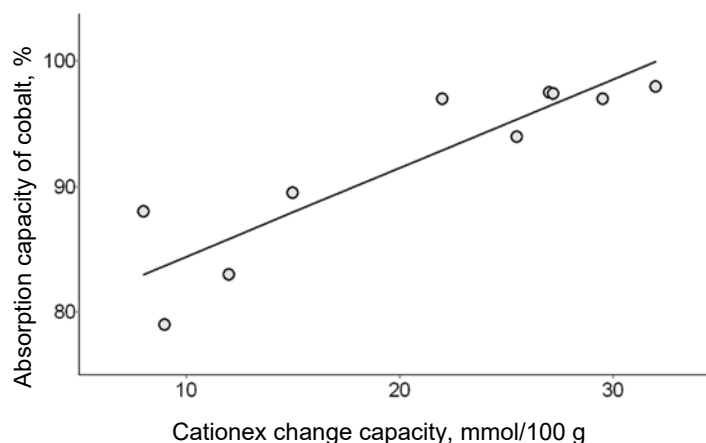


Fig. 1. Dependence of the absorption capacity of mobile compounds of cobalt by soils from cation exchange capacity of soils

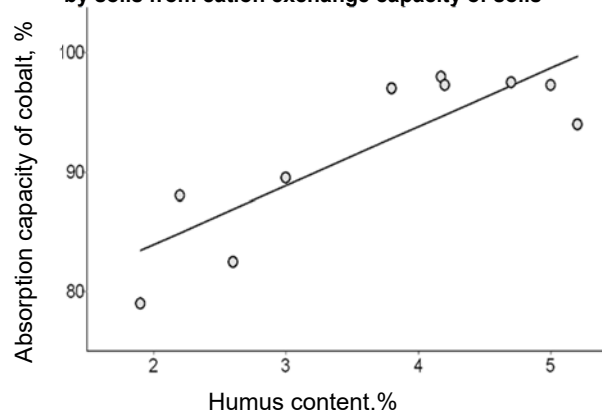


Fig. 2. Dependence of the absorption capacity of mobile compounds of cobalt by soils on the content of humus

Table 5

The amount of cobalt that has been converted into solution from biohumus (n = 5; P = 0,95)

Extractant	The amount of cobalt that has been converted into solution from biohumus, g/kg
1H CaCl <sub>2</sub>	4,25
1M CH <sub>3</sub> COONH <sub>4</sub>	8,35
1M HCl	22,50
0,02M EDTA Na <sub>2</sub> + 0,09M NH <sub>4</sub> Cl	16,18

In experiment 4, an analysis of isotherms of sorption or exchange of Co<sup>2+</sup> on exchangeable ions of biohumus in the various solutions that are given in fig. 3, which correspond to the isomers of the Langmuir monolayer adsorption, and hence are described by the equation:

$$a = \frac{a_m C}{A + C}, \quad (1)$$

where  $a$ ,  $a_m$  – current and maximum adsorption of cobalt by a biohumus;  $A$  – energy constant;  $C$  – the equilibrium concentration of Co<sup>2+</sup> in the solution.

From the fig. 4 it is seen that the assumption of the Langmuir character of adsorption is well established. Thus, there is a high affinity of the Co<sup>2+</sup> ions to biohumus both in its initial polyionic form and in the saturated by Ca<sup>2+</sup> ions form. The growth of adsorption of Co<sup>2+</sup> in a number of colloidal solutions of biohumus Ca – 0,01M CaCl<sub>2</sub> < biohumus – 0,01M CaCl<sub>2</sub> < biohumus – 0,03M NaCl due to the greater ability of these ions to exchange on monovalent sodium ions than on two-valent ions.

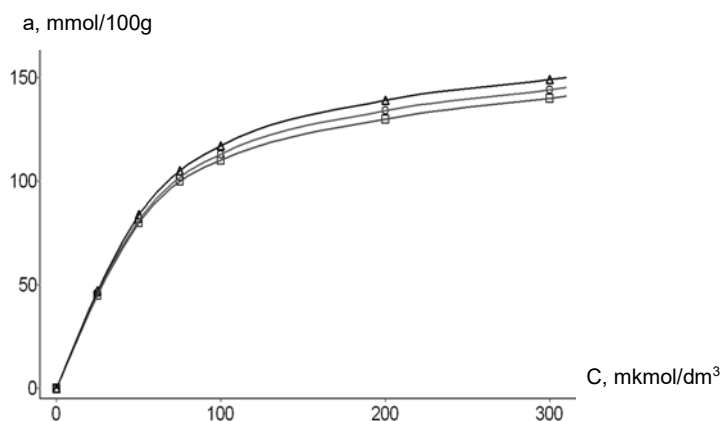


Fig 3. Isotherms of cobalt sorption in the systems:

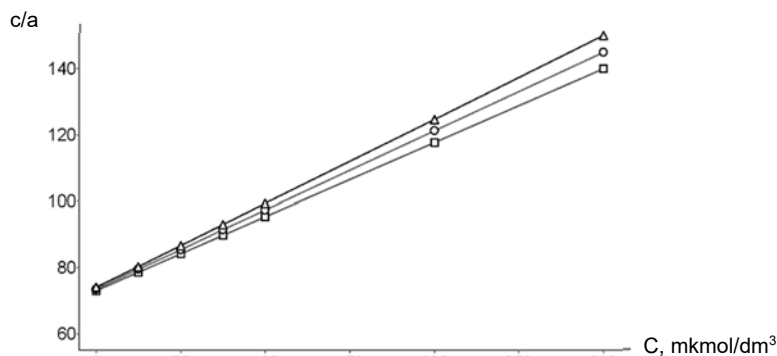
1 – biohumus Ca – 0,01 M $\text{CaCl}_2$  –  $\text{Co}^{2+}$ ; 2 – biohumus – 0,01 M $\text{CaCl}_2$  –  $\text{Co}^{2+}$ ; 3 – biohumus – 0,03M NaCl –  $\text{Co}^{2+}$ 

Fig. 4. Isotherms of sorption of cobalt in the linear interpretation of the Langmuir equation.

Denominations of lines correspond to the fig. 3

**Conclusions.** The cobalt cationic complexes  $[\text{Co}(\text{H}_2\text{O})\text{n}]^{2+}$ ,  $[\text{Co}(\text{NH}_3)\text{n}]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)\text{n}]^{2+}$  – are almost completely absorbed by the soils. Anionic complexes –  $[\text{Co}(\text{P}_2\text{O}_7)\text{n}]^{2-4\text{n}}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})\text{n}]^{2-5\text{n}}$  i  $[\text{Co} \text{ EDTA}]^{2-}$  – remain largely mobile in the soil profile. The sorption effect depends on the charge of complex ions, their strength, and also on the steric parameters of complex ions.

The use of complex-forming macro-fertilizers is perspective, in our opinion, not only to partially prevent the fixation of Co, but also from the point of view of its possible activation from fixed forms in the soil profile. A comprehensive study of the behavior of Co, depending on soil parameters and the physiological characteristics of plants, will greatly optimize the microelemental nutritional process of plants.

A high percentage of the absorption of complex cations of cobalt by different soil species is due to accumulation under the conditions of the chemical industry and the near humus. The tight positive links were established between absorptivity of the cobalt and cation exchange capacity (the correlation coefficient was 0,7976) and between absorptivity of the cobalt and humus content (the correlation coefficient was 0,7034).

In the study of biohumus, it was found that in solution of 0,02M EDTA  $\text{Na}_2$  + 0,09M  $\text{NH}_4\text{Cl}$ , cobalt switches over to the mechanism of competitive complexation, and its transition to epy HCl solution occurs due to protonation of the functional groups of the biohumus with which the metal is bound. The obtained results indicate that biohumus has relatively high sorption properties relative to cobalt and may be perspective for its use as an effective carrier matrix in various combinations with mineral fertilizers.

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## ЕЛЕКТРОХІМІЧНЕ ДОСЛІДЖЕННЯ ПРОЦЕСІВ ПОГЛИНАННЯ КОБАЛЬТУ ҐРУНТАМИ УКРАЇНИ

Досліджено процеси поглинання кобальту ґрунтами України за допомогою електрохімічного методу імпульсної інверсійної хронопотенціометрії. Установлено, що поглинальна здатність  $\text{Co}$  різновидами ґрунтів із комплексоутворювальних середовищ становить 64–98 %. У розчинах  $\text{KNO}_3$ ,  $\text{NH}_4\text{OH}$  і  $\text{CSN}_2\text{H}_4$  рухомі сполуки кобальту входять до складу  $[\text{Co}(\text{H}_2\text{O})_n]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_n]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)_n]^{2+}$ , а у розчинах  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$  і  $\text{EDTA}$  утворюються аніонні комплекси  $[\text{Co}(\text{P}_2\text{O}_7)_n]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})_n]^{2-5n}$  і  $[\text{Co}(\text{EDTA})_n]^{2-}$ . Катионні комплекси кобальту –  $[\text{Co}(\text{H}_2\text{O})_n]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_n]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)_n]^{2+}$  – практично повністю сорбуються ґрунтами. Аніонні комплекси –  $[\text{Co}(\text{P}_2\text{O}_7)_n]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})_n]^{2-5n}$  і  $[\text{Co}(\text{EDTA})_n]^{2-}$  значною мірою залишаються мобільними в ґрунтового профілі. Сорбційний ефект залежить від заряду комплексних іонів, їхньої міцності, а також від стереометричних параметрів комплексних іонів. Установлено тісний позитивний зв'язок між поглинанням кобальту ґрунтом і ємністю катіонного обміну ґрунту, коефіцієнт кореляції становить 0,7976, і між поглинанням кобальту ґрунтом і вмістом гумусу (0,7034). При дослідженні біогумусу встановлено, що в розчин  $0,02\text{M}$   $\text{EDTA}$   $\text{Na}_2$  +  $0,09\text{M}$   $\text{NH}_4\text{Cl}$  кобальт переходить за механізмом конкурентного комплексоутворення, його перехід у розчин  $\text{HCl}$  відбувається за рахунок протонізації функціональних груп біогумусу, з якими зв'язаний метал. Біогумус має досить високі сорбційні властивості щодо кобальту і може бути перспективним для використання його як ефективної матриці – носія в різних сполученнях з основними добривами. Ізотерми сорбції або обміну  $\text{Co}^{2+}$  на обмінні іони біогумусу в різних розчинах відповідають ізотермам монослоєвої адсорбції Ленгмюра. Метод ІХП аналізу важливо використовувати для контролю вмісту мікроелементів на рівні їхніх слідових концентрацій, які є необхідними для розвитку рослин.

Ключові слова: доступний вміст кобальту, сорбційні процеси, біогумус, катіонообмінна ємність, електрохімічний імпульсний метод.

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## ЕЛЕКТРОХІМІЧЕСКОЕ ИССЛЕДОВАНИЕ ПРОЦЕССОВ ПОГЛОЩЕНИЯ КОБАЛЬТА ПОЧВАМИ УКРАИНЫ

Исследованы процессы поглощения кобальта почвами Украины с помощью электрохимического метода импульсной инверсионной хронопотенциометрии. Установлено, что поглощающая способность кобальта разновидностями почвы из комплексообразующих сред составляет 64–98 %. В растворах  $\text{KNO}_3$ ,  $\text{NH}_4\text{OH}$  и  $\text{CSN}_2\text{H}_4$  подвижные соединения кобальта входят в состав  $[\text{Co}(\text{H}_2\text{O})_n]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_n]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)_n]^{2+}$ , а в растворах  $\text{Na}_4\text{P}_2\text{O}_7$ ,  $\text{Na}_5\text{P}_3\text{O}_{10}$  и  $\text{EDTA}$  образуются анионные комплексы  $[\text{Co}(\text{P}_2\text{O}_7)_n]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})_n]^{2-5n}$  и  $[\text{Co}(\text{EDTA})_n]^{2-}$ . Катионные комплексы кобальта –  $[\text{Co}(\text{H}_2\text{O})_n]^{2+}$ ,  $[\text{Co}(\text{NH}_3)_n]^{2+}$ ,  $[\text{Co}(\text{CSN}_2\text{H}_4)_n]^{2+}$  – практически полностью сорбируются почвами. Анионные комплексы  $[\text{Co}(\text{P}_2\text{O}_7)_n]^{2-4n}$ ,  $[\text{Co}(\text{P}_3\text{O}_{10})_n]^{2-5n}$  и  $[\text{Co}(\text{EDTA})_n]^{2-}$  в значительной степени остаются мобильными в почвенном профиле. Сорбционный эффект зависит от заряда комплексных ионов, их прочности, а также от стереометрических параметров комплексных ионов. Установлена тесная положительная связь между поглощением кобальта почвами и ёмкостью катийного обмена почвы, коэффициент корреляции составил 0,7976, и между поглощением кобальта почвами и содержанием гумуса (0,7034). При исследовании биогумуса установлено, что в раствор  $0,02\text{M}$   $\text{EDTA}$   $\text{Na}_2$  +  $0,09\text{M}$   $\text{NH}_4\text{Cl}$  кобальт переходит по механизму конкурентного комплексообразования, его переход в раствор  $\text{HCl}$  происходит за счет протонизации функциональных групп биогумуса, с которыми связан металл. Биогумус имеет достаточно высокие сорбционные свойства кобальта и может быть перспективным для использования его в качестве эффективной матрицы – носителя в разных сочетаниях с основными удобрениями. Изотермы сорбции или обмена кобальта на обменные ионы биогумуса в различных растворах соответствуют изотермам монослойной адсорбции Ленгмюра. Метод ИХП анализа важно использовать для контроля содержания микроэлементов на уровне их следовых концентраций, необходимых для развития растений.

Ключевые слова: доступное содержание кобальта, сорбционные процессы, биогумус, катионообменная ёмкость, электрохимический импульсный метод.