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## THE USE OF BROWN COAL IN UKRAINE TO OBTAIN WATER-SOLUBLE SORBENTS

**Purpose.** To develop a method of using salts of humic acids obtained from brown coal of Ukraine for sorption of heavy metal ions and their extraction using ultrafiltration membranes.

**Methodology.** Unique laboratory equipment has been developed to determine the sorption capacity of humic substances with a concentration of 0 to 20 mg/l in relation to heavy metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ) with a concentration of 5 mg/l. The results of proximate and ultimate analyzes, as well as infrared and optical emission spectroscopy were used to assess the quality of brown coal, humic substances and the solution of humic substances with heavy metal ions.

**Findings.** Ukrainian brown coal of Oleksandriia geological-industrial district contains a large amount (about 80 %) of humic acid, which is the basis for obtaining effective water-soluble sorbents. It is proved that humic substances obtained from brown coal of Ukraine allow binding up to 99 % of heavy metal ions in complexes. The most optimal concentration of humic substances in terms of their concentration and selectivity of heavy metal ions extraction is 5 mg/l.

**Originality.** The possibility of practical using of humic substances obtained from brown coal of Ukraine for sorption of heavy metal ions has been proved. As ultrafiltration membranes, UF-20-PAN membranes are used, which are porous polymer films based on polyacrylonitrile with a pore size of 20  $\mu\text{m}$ , the working surface area of the membrane is  $28.26 \cdot 10^{-4} \text{ m}^2$ .

**Practical value.** The introduction of the developed technology will allow, firstly, restoring the practical use of large deposits of brown coal in Ukraine, and secondly, introducing deep treatment of industrial and wastewater.

**Keywords:** *brown coal, sorption, heavy metal ions, membrane, humic substances, IR spectroscopy*

**Introduction.** As of January 1, 2021, the number of brown coal deposits in Ukraine is 80, of which – 3 are being developed. Balance reserves of brown coal in Ukraine are [1]:

- category A + B + C1 – 2,593,359.00 thousand tons;
- category C2 – 299,181.00 thousand tons.

Ukraine's brown coal reserves are concentrated mainly in the Dnieper, partly in the Donetsk (Western Donbas) basins, as well as in the Novodmytrivske deposit of the Dnieper-Donetsk basin and in the Ilnytske, Rokosovske deposits of the Transcarpathian coal-bearing area.

The Dnieper brown coal basin is located within the Ukrainian Shield, which is located in a central position in the structure of the southwestern part of the Eastern European platform. The average thickness of the productive stratum is 15–25 m. The coal-bearing stratum of the Dnieper deposits contains from 1 to 2–3 horizontal coal seams of simple and, less often, complex structure. The average thickness of brown coal seams in the basin is as follows: the lower layer – 4–5 m; the middle one – 3–4 m; the upper layer – 1–2 m. The lower layer, which is characterized by stable planar endurance, is, more often, used industrially. The depth of the strata is from 10 to 160 m, but more often it is in the range of 40–80 m, which allows a significant part of the coal reserves in the basin to be developed in an open way.

Transcarpathian coal-bearing area is confined to the Chop-Mukachevo and Sotolvyno geostructural depressions. Carboniferous are the deposits of the middle sarmatian, paleogene and levantine tier of the neogene.

The Novodmytrivka Oligocene-Miocene brown coal deposit has been explored within the Dnieper-Donetsk basin. The Dnieper-Donetsk depression is part of the Dnieper-Donetsk Trough. The Novodmytrivske deposit is located within the western periclinal of the Korul dome and is confined to the depression of the same name, which is developed above the Devonian salt stem. Two layers are of major industrial importance: III<sub>2</sub> and IV<sub>2</sub>, respectively, with reserves of 75 and 19.6 % of the total balance sheet reserves. The average thickness of layer III<sub>2</sub> is 50 m, that of layer IV<sub>2</sub> is 7.5 m. The maximum depth of bedding of layers is 400 m.

Brown coal mining during 2011–2020 was almost the same and reached 2–15 thousand tons per year. In Ukraine there are only 3 operating sections with balance reserves of categories A + B + C1 equal to 9,331 thousand tons.

Given the significant deposits of brown coal in Ukraine, as well as practically missing the mining and industrial usage, researchers are trying to find innovative technologies for its application.

The study [2] considered the process of oxidative desulfurization of high-sulfur Ukrainian brown coal, which was performed by treating brown coal with air or air-steam mixture. Fuel without sulfur and resin coal was obtained during the

process of decomposition of organic matter brown coal. The process of brown coal desulfurization provides maximum reduction of sulfur to hydrogen sulfide ( $H_2S$ ) in desulfurized gases with minimal energy consumption. This process also improves the maximum decomposition of resin and sulfur (> 50 %) during the production of electricity from brown coal. Based on the final field research, a block diagram with thermal and material balances of the process was developed. The use of technology in the first stage of brown coal combustion in thermal power plants will allow the utilization of more than 50 % of the extracted coal sulfur in the form of concentrated  $H_2S$  or commodity elemental sulfur. However, this will reduce environmental pollution by sulfur oxide by at least 53–56 %. It has been suggested that the thermal decomposition product of organic brown coal (tar) can be used as a component of furnace fuel oil or as a petroleum-based road bitumen plasticizer.

The results of studies presented in [3] showed that humic acids have a specific effect on the formation of ordered structures in PVA solutions, due to the different nature and characteristics of humic acids. The addition of humic acids to PVA solutions, which contain particles of brown coal residues of varying degrees of dispersion, slows down the effect of ordering the structure. The formation of such particles is due to the presence in some samples of humic acids of a large number of oxygen-containing surfactants that can form weak chemical and/or physical bonds with each other and with brown coal particles, which leads to relatively large dispersed phase aggregates. In PVA solutions with the addition of humic acids with the absence of particles of brown coal residues of varying degrees of dispersion, there is an increase in the processes of ordering the structure. The peculiarities of the influence of humic substances on the processes of structure formation of hydroxypropylmethylcellulose solutions for the production of hybrid ecologically pure biodegradable polymer films were studied. The modifying effect of humic substances, which were obtained from three different samples of brown coal, was studied. Solutions of hydroxypropylmethylcellulose modified with humic substances of various origins were produced to obtain ecologically pure biodegradable polymer films on their basis. The influence of humic substances on the processes of structure formation in hydroxypropylmethylcellulose solutions was studied, on the basis of which it is shown that the differences are due to the different nature and characteristics of humic substances. Appropriate ESMMs have been developed to predict the viscosity and electrical conductivity of PVA solutions with humic acids.

In [4] it was found that the process of gasification of polydisperse systems of coal origin (lignite for heavy coal tars) in the temperature range from 400 to 500 °C and oxidant consumption (air) from 0.0005 to 0.004 m<sup>3</sup>/min has 3 stages, which differ in the values of the rate constant. Mathematical and graphical dependences of the influence of air flow from 0.0005 to 0.004 m<sup>3</sup>/min and temperature 400 to 500 °C on the values of the rate constants and activation energy, solid residue yield, condensed and gaseous products during gasification of polydisperse systems were developed. The component composition of the main condensed products of gasification of polydisperse systems was established.

It is known that soils in many parts of the world are prone to degradation. Replenishment of such soils with organic waste aims to restore soil quality. Organic impurities are heterogeneous environments that are a source of soil organic matter (SOM) that support and restore chemical, physical, biological and environmental functionality. Increasing SOM can affect a soil microclimate, microbial community structure, biomass turnover, and nutrient mineralization. The search for alternatives from local sources continues, as many forms can be expensive or territorially limited. The review [5] focuses on the heterogeneous group of amendments, i.e. brown coal waste. This material has a very high carbon content and soil stability, so it can be used for long-term carbon sequestration to reduce

greenhouse gas emissions and as a conditioner to improve soil quality. However, brown coal can be naturally high in moisture and contaminants. Further research studies should focus on the long-term using of these impurities and determine the physicochemical properties of the soil, the bioavailability of soil contaminants, the diversity of soil groups and the productivity of selected crops. In addition, the development of technologies in situ to reduce the cost of production and processing of brown coal will improve the economic feasibility of its large-scale application.

According to the authors, one of the perspective methods for using brown coal in Ukraine may be the production of water-soluble sorbents (salts of humic acid) for the sorption of heavy metal ions.

Heavy metal ions are very dangerous toxic substances that have a cumulative effect on aquatic organisms. Insufficiently treated wastewater enters natural reservoirs, where heavy metal ions accumulate in water and bottom sediments, thus becoming a source of secondary pollution. They are not removed from the water by mechanical means, are not removed by biological treatment and traditional water treatment methods such as coagulation and flotation. This necessitates strict control over their entry into the environment, which requires in practice the use of relatively inexpensive, affordable means of capturing them. In addition, the current focus in the implementation of environmental tools to dramatically reduce the discharge of untreated wastewater into the reservoirs, requires intensive efforts to develop schemes for reusable and returnable of treated wastewater, improving the technology of deep treatment. The problem of industrial wastewater treatment is becoming more important every year.

**Literature review.** The results of using of humic acids obtained from brown coal as a sorbent are presented in many scientific publications. In [6], it is presented the results of application of humic acid nanoparticles obtained from brown coal on inert sand by simple impregnation for obtaining a permeable reactive barrier for the purification of groundwater contaminated with copper and cadmium ions. Laboratory studies proved that the sorption efficiency of such sand is 98 % (sorption time – 1 h; sorbent content 0.25 g/50 ml; pH – 7; stirring speed 200 rpm). The results proved that physical sorption was the predominant mechanism of interaction of metal ions and sand with humic acids. The maximum sorption capacity of copper and cadmium was 87.5 and 18.9 mg/l, respectively. In [7], it was shown that the use of commercially available sorbent based on humic acid associated with silica (HAS) allows removing aflatoxins from edible oils (tea, canola, peanuts, sunflower, corn, olive, rice, soybeans, sesame). The use of magnetic nanoparticles (HA-MNP) with iron-based humic acid coating to remove 2- [4- (dimethylamino) styryl] – 1-methylpyridine iodide (2-ASP), as a modular compound for cationic styrylpyridine dyes from an aqueous medium, was studied in [8]. It was proved with fluorescence that HA-MNPs are effective in removing 2-ASP with a maximum adsorption capacity ~8 mg/l. Studies on kinetic behavior and equilibrium have shown that the adsorption process corresponds to the models of the pseudo-2<sup>nd</sup> order and the Langmuir isotherm. Adsorption occurs relatively quickly – 70 % of adsorption is completed within 30 minutes, and the total removal increases due to increasing the pH of the solution. Regeneration of HA-MNP showed that the efficiency of removal remains consistently high after five consecutive cycles. The authors of [9] studied the sorption of Cs and Ba on bentonite from the island of Kimolos (Cyclades, Greece) in aqueous solutions in the presence of  $Na^+$ ,  $Ca^{2+}$  and humic acid. The experiments were performed using <sup>137</sup>Cs and <sup>133</sup>Ba as indicators and  $\gamma$ -spectroscopy. It was found that sorption significantly depends on the initial concentration, ionic strength and temperature of the solutions, and the sorption isotherms satisfactorily reproduced the Langmuir and Freundlich equations. It was shown that the Kimolos bentonite is a good sorbent for Cs and

Ba from heavily contaminated solutions and its sorption capacity is reduced in the presence of humic acid and competing cations. The authors [10] showed that surface-functionalized magnetite nanoparticles treated with humic acid are a perspective sorbent for removing U(VI) from industrial waste streams and polluted water, but the effect of dissolved inorganic carbon on the mechanism and efficiency of adsorption was studied insufficiently. It was found that the adsorption of U(VI) on humic acid-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles does not depend on the ionic strength, but increases with decreasing pH and adsorbent concentration. The degree of adsorption of U(VI) decreases sharply with increasing concentration of added NaHCO<sub>3</sub> and CaCl<sub>2</sub> at pH above 5 and 6, respectively.

**Unresolved aspects of the problem.** In [11] it was proved that the content of humic acids in local effluent solutions inhibits the sorption of metal ions such as Cd, Cr, Cu, Ni, Pb, Zn when using solid commonly used sorbents (BFS, CCF, WTCR, BC). This is due to the formation of stable complexes of humic acids with metal ions, which prevents their sorption by sorbents. Humate particle sizes range from 10 to 1,000 nm [12]. Given the above, the authors consider a perspective direction to develop a method of water purification by delaying complexes of humic substances with heavy metal ions by ultrafiltration membranes.

**Purpose.** The purpose of the research is to develop a method for using salts of humic acids obtained from brown coal of Ukraine for sorption of heavy metal ions and their extraction using ultrafiltration membranes.

**Methods.** Samples of Ukrainian brown coal of the Oleksandriia geological-industrial district were studied. Indicators of proximate (W<sup>a</sup>, A<sup>d</sup>, S<sub>d</sub><sup>d</sup>, V<sup>d</sup>) and ultimate (C<sup>daf</sup>, H<sup>daf</sup>, N<sup>daf</sup>, S<sub>d</sub><sup>d</sup>, O<sup>daf</sup>) analyses of brown coal, and the yield of humic acids (HA<sub>f</sub><sup>daf</sup>) are shown in Table 1.

Analyzing the quality of brown coal, it is necessary to note the increased yield of humic acids (79.44 %), which will contribute to the economic feasibility of their using for sorption of heavy metal ions.

Model solutions of metal ions (Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>) with a concentration of 5 mg/l in distilled water were prepared and a complexing agent – humates (sodium salts of humic acids) with different concentration from 0.0 to 20 mg/dm<sup>3</sup> was added.

UF-20-PAN (Belarus) membranes were used as ultrafiltration membranes in the purification of solutions from ions of copper (Cu<sup>2+</sup>), lead (Pb<sup>2+</sup>), mercury (Hg<sup>2+</sup>), cadmium (Cd<sup>2+</sup>), zinc (Zn<sup>2+</sup>) and cobalt (Co<sup>2+</sup>). This membranes are porous polymer films based on polyacrylonitrile with a pore size of 20 μm, the working surface area of the membrane is 28.26 × 10<sup>-4</sup> m<sup>2</sup>. Polymer membranes are characterized by increased thermal and aggressive resistance, non-toxic, safe to operate and can be operated at pH from 2 to 12 and a maximum water temperature of 100 °C. The minimum productivity of distilled water is 60 dm<sup>3</sup>/m<sup>2</sup> · h.

The research was performed in an experimental setup (Fig. 1), which is a non-flowing cell with a volume of 0.2 dm<sup>3</sup> at an ambient temperature of 25 °C. The separation solution was poured through a fitting into a transparent cylindrical cell body made of polycarbonate. To reduce the effect of concentration polarization, the cell was equipped with an electromagnetical stirrer and a propeller 3–5 mm away from the membrane. The required pressure (0.2 MPa) above the membrane was created by passing a certain portion of compressed air from the compressor valve with special tubes through the fitting. During

the separation process, the filtrate that passed through the membrane and the drainage through the hole in the lower flange was collected in a sampler and analyzed.

The degree of separation (selectivity, *R*) of the membrane for the corresponding metal was calculated by the formula

$$R = \frac{C_o - C_f}{C_o} \cdot 100, \quad (1)$$

where *R* is metal ions extraction factor (selectivity), %; and are the concentration of metal ions in the initial solution and in the filtrate, respectively, mg/l.

The IR absorption spectra were recorded on a “Nicolet 380” spectrometer from “Thermo Electron Corporation” (USA). Parameters of the analysis are as follows: resolution – 4; write speed – 0.6329; gain – 4; number of scans – 32. The studied samples of brown coal, humic substances obtained from brown coal, both before and after interaction with the metal ions were pre-dried and ground. All spectra were recorded in the range of 4,000–400 cm<sup>-1</sup>. Deciphering of IR spectra was conducted according to own experience, and also works of known research studies.

For example, in [13], petroleum ether, carbon disulfide, methanol, acetone and acetone/sulfur carbon were selected as solvents for the ultrasonic extraction of acid-washed brown coal of Hefeng deposit. The extract and residue were identified as *E<sub>i</sub>* and *R<sub>i</sub>* (*i* = 1, 2, 3, 4, 5) for each stage. Using FT-IR characteristics *E<sub>i</sub>* and *R<sub>i</sub>* the molecular structure of the extracted product was analyzed by segmented peak selection. The results show that the hydroxy bond in the fifth order extract is dominated by the self-associated hydroxy bond; in aliphatic substances only *E<sub>3</sub>* was dominated by aliphatic –CH<sub>3</sub> and asymmetric –CH<sub>2</sub> valence vibration, and in other extracts symmetric and asymmetric –CH<sub>2</sub> valence vibration prevailed.

Symmetrical bending vibrations of the end of the aliphatic chain –CH<sub>3</sub> and asymmetric deformation vibrations –CH<sub>3</sub> and –CH<sub>2</sub> dominate in *E<sub>1</sub>*, which indicates that petroleum ether mainly breaks easily breakable chemical bonds in brown coal samples; CS<sub>2</sub> dissolves most of the aromatic structure containing aliphatic side chains. The functional groups contained in the five residues are the same, indicating that the basic structure of the brown coal sample does not change due to stepwise extraction. The extraction has an obvious effect on the aromatic structure and the hydroxy bond in the residue. Aromatic structures vary from dominant disubstituted benzene to dominant tetrasubstituted benzene. Before the extraction in the hydroxyl hydrogen bond, hydroxy-ether hydrogen

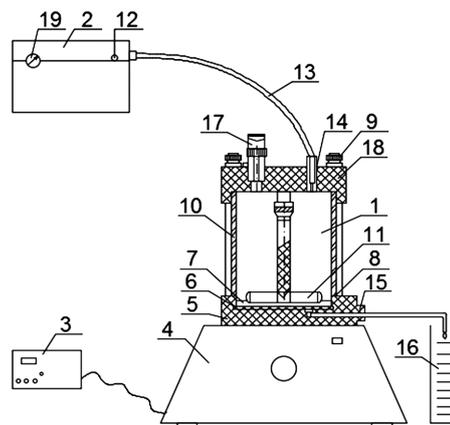


Fig. 1. Scheme of the installation for filtration:

1 – membrane cell; 2 – compressor; 3 – strobe tachometer; 4 – magnetic stirrer; 5 – the lower base of the cell; 6 – porous fluoroplastic; 7 – membrane; 8 – silicone rubber; 9 – bolts; 10 – cell body; 11 – propeller; 12 – the valve; 13 – tube; 14 – fitting; 15 – hole; 16 – sample collection; 17 – safety valve; 18 – upper flange; 19 – manometer

Table 1

Indicators of brown coal quality

W <sup>a</sup>	A <sup>d</sup>	V <sup>d</sup>	C <sup>daf</sup>	H <sup>daf</sup>	N <sup>daf</sup>	S <sub>d</sub> <sup>d</sup>	O <sup>daf</sup>	(HA <sub>f</sub> <sup>daf</sup> )
16.8	48.7	29.1	61.13	5.56	0.51	3.64	29.16	79.44

bonds dominated in acid-washed brown coal, and after extraction it was transformed into self-associated hydroxyl. In addition, sequential extraction has little effect on oxygen-containing functional groups and aliphatic functional groups. Comparing the structural parameters, it was found that  $E_1$ ,  $E_3$  and  $R_3$  have a higher degree of aromatic condensation, and  $E_4$  has a longer straight and less branched chain.

In [14], attempts were made to construct molecular structures of vitrinite samples from four bituminosites of different ranks and to investigate the relationship of molecular structure with thermoplastic properties of vitrinite using a number of advanced analytical methods combined with theoretical methods.

Plastometry and Gieseler fluidity index showed that Evirgol vitrinite had high fluidity ( $F_{\max} = 17,675$  ppm), a wide range of ductility ( $\Delta\tau = 105.1$  °C) and good caking properties ( $G = 99.32$ ). Various analytical techniques, such as solid-state spectroscopy of nuclear magnetic resonance  $^{13}\text{C}$ , infrared spectroscopy with Fourier transform, X-ray diffraction analysis, and Raman spectroscopy provided comprehensive structural information for molecular models of vitrinite samples with functional density theory. These molecular models showed that Evirgol's vitrinite had more cyclic aliphatic structures that significantly contribute to the development of fluidity. These cyclic aliphatic structures can be precursors of aromatic rings in liquid molecules during coking and provide hydrogen that saturates free radicals in the thermoplastic range. Cyclic aliphatic structures can promote the formation of such molecular structures with an appropriate molecule size that supports the mobile phase in the thermoplastic range for the development of fluidity.

In [15], it was found that intrinsic alkali and alkaline earth metals (AAEM) have an obvious catalysis in the pyrolysis of low-grade coal. Due to differences in the degree of dispersion and chemical form, the catalytic effects of AAEM with different states of occurrence may be different. The chemical structure of coal is the most direct evidence of AAEM catalysis. However, the quantification and evaluation of these structures, especially asymmetric functional groups, has always remained an unresolved issue. In this study, Zhundong coal's FT-IR spectra containing various forms of native AAEM were selected, functional group structures of these samples were semiquantitatively characterized by a series of original infrared structural parameters, and volatile products during pyrolysis were detected by TG-FTIR. Complex analysis of functional group structures, weight loss rate and volatile product concentration indicates that water-soluble and ion-exchange AAEMs in coal prevent the release/decomposition of  $-\text{COO}-$  and aliphatic  $\text{C}-\text{H}$  groups and promote thermal cracking of  $\text{C}-\text{H}$  aromatic groups. Inhibition of ion-exchange AAEMs during the release/decomposition of  $\text{Ar}-\text{O}-$  groups and dehydrogenation/polycondensation of aromatic clusters in carbon is also confirmed. It is expected that the method of infrared structural parameters proposed in this paper will be a reasonable, efficient, comprehensive and universal method for quantitative characterization of structures of functional groups of coal and coal, as well as improving the existing system of coal quality analysis, respectively, creating a new tool for evaluation and connection of chemical structures of coal and coal.

The pH value was determined using an ionometer "I-160M" (Ukraine).

The concentration of metal ions in aqueous solutions was determined on a PlasmaQuant PQ 9000 Elite (Germany) high-resolution optical emission spectrometer with an inductively coupled plasma.

**Results.** Using infrared spectroscopy, samples of brown coal (lignite) from the Oleksandriia deposit and humic substances obtained from it were studied (Fig. 2).

According to the results of IR spectroscopy, the main functional groups of the studied brown coal and humic acids are:

1. Aromatic carbonyl- and phenol-containing hydrocarbons, which is confirmed by the presence of an intense band of valence vibrations  $\text{C}=\text{C}$  bonds at  $\approx 1,600$   $\text{cm}^{-1}$ ; bands of valence oscillations of  $\text{C}-\text{O}$  bonds in the region  $1,705-1,650$   $\text{cm}^{-1}$ ; intensive absorption in the region of valence vibrations of  $\text{OH}$ -groups ( $\approx 3,300$   $\text{cm}^{-1}$ ),  $-\text{C}-\text{O}$ -groups ( $1,200-1,100$   $\text{cm}^{-1}$ ), as well as bands of valence and deformation oscillations of  $\text{C}_{\text{ar}}-\text{H}$  bonds at  $\approx 3,050$   $\text{cm}^{-1}$  and  $900-700$   $\text{cm}^{-1}$  respectively. Absorption bands at  $\approx 900$   $\text{cm}^{-1}$  are responsible for the oscillations of one isolated hydrogen atom, at  $\approx 830$   $\text{cm}^{-1}$ ,  $\approx 800$   $\text{cm}^{-1}$ ,  $\approx 770$   $\text{cm}^{-1}$  – for the oscillations of two, three, four hydrogen atoms in aromatic rings.

2. Aliphatically saturated  $\text{C}_{\text{ar}}-\text{H}$  groups, identified by the presence of absorption bands in the range of  $3,000-2,800$   $\text{cm}^{-1}$  ( $\text{CH}_3$ ,  $\text{CH}_2$ ,  $\text{CH}$  groups), as well as asymmetric bands ( $\approx 1,400$   $\text{cm}^{-1}$ ) and symmetric ( $\approx 1,380$   $\text{cm}^{-1}$ ) deformation oscillations of  $\text{CH}_3$  groups,  $\text{CH}_2$  groups  $\approx 1,485-1,445$   $\text{cm}^{-1}$  and  $\text{CH}$ -groups  $-\approx 1,340$   $\text{cm}^{-1}$ . We can note the bands of  $\text{C}-\text{O}$ -groups ( $1,750-1,700$   $\text{cm}^{-1}$ ) – aldehydes, ketones, carboxylic acids, esters.

3. IR spectra have bands of absorption of  $\text{C}-\text{O}$  bonds in simple and complex ethers and phenolic  $\text{C}-\text{O}$  groups with a maximum in the region  $\approx 1,280$   $\text{cm}^{-1}$ .

The results of purification of aqueous solutions from metal ions depending on the concentration of humic substances (0–20 mg/l) are given in Table 2 and in Fig. 3.

Analyzing the shown graphic dependences in Fig. 3, we can conclude that with increasing concentration of humic substances from 0.0 to 20 mg/l the selectivity of metal extraction increases, namely:  $\text{Cu}^{2+}$  from 9.08 to 95.80 %;  $\text{Pb}^{2+}$  from 14.82 to 94.86 %;  $\text{Cd}^{2+}$  from 4.82 to 89.76 %;  $\text{Hg}^{2+}$  from 10.70 to 84.92 %;  $\text{Zn}^{2+}$  from 11.56 to 89.16 %;  $\text{Co}^{2+}$  from 18.76 to 82.70 %.

It should be noted that based on the graphical dependencies shown in Fig. 3, the degree of extraction of heavy metal ions depending on the concentration of humic substances varies nonlinearly. The most optimal concentration of humic substances in terms of extraction of metal ions is 5 mg/l, further increase in concentration to 20 mg/l practi-

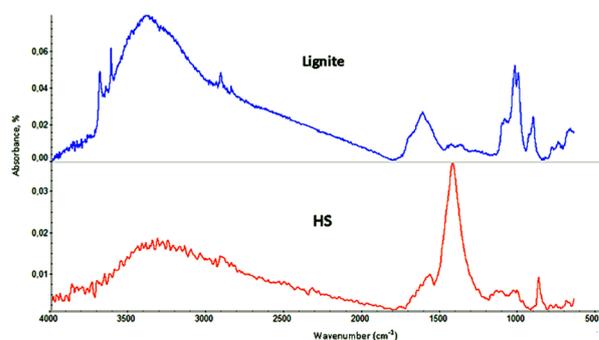


Fig. 2. IR spectra of brown coal and humic substances

Table 2

Concentration of heavy metal ions (mg/l) depending on the concentration of humic substances (mg/l)

Ion	Concentration of humic substances, mg/l				
	0.0	2.5	5.0	10.0	20.0
$\text{Cu}^{2+}$	4.456	3.193	1.189	0.573	0.210
$\text{Pb}^{2+}$	4.259	3.449	1.071	0.541	0.257
$\text{Cd}^{2+}$	4.759	3.868	2.211	1.123	0.512
$\text{Hg}^{2+}$	4.465	3.693	1.772	1.437	0.754
$\text{Zn}^{2+}$	4.422	3.823	2.088	1.477	0.542
$\text{Co}^{2+}$	4.062	3.661	1.985	1.233	0.865

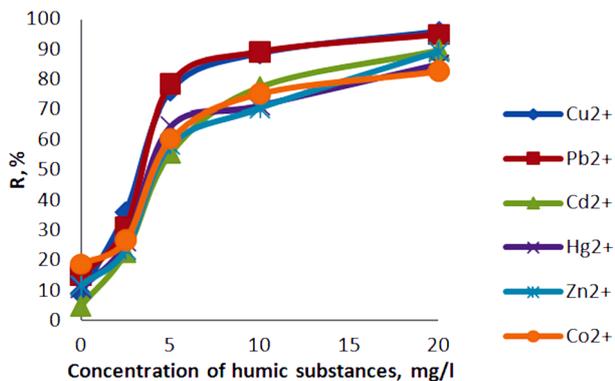


Fig. 3. Selectivity of metal ions extraction depending on the concentration of humic acids substances

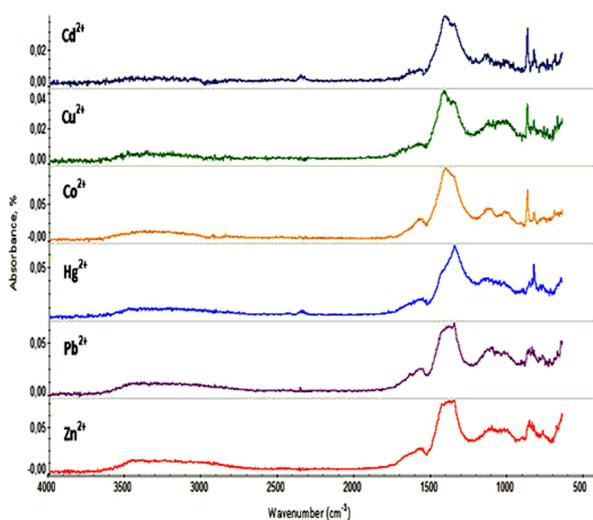


Fig. 4. IR spectrum of humic substances after interaction with metal ions

cally does not lead to a significant increase in the extraction of metal ions.

Fig. 4 shows the IR spectra of humic substances after interaction with heavy metal ions (concentration of humic substances is 5 mg/l).

#### Conclusions.

1. Ukrainian brown coal of the Oleksandriia geological-industrial district contains a large amount (about 80 %) of humic acid, which is the basis for obtaining effective water-soluble sorbents.

2. It is proved that humic substances obtained from brown coal of Ukraine allow binding up to 99 % of heavy metal ions in complexes.

3. The most optimal concentration of humic substances in terms of their concentration and selectivity of heavy metal ions extraction is 5 mg/l.

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## Використання вугілля України

### для отримання водорозчинних сорбентів

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**Мета.** Розробка методу використання солей гумінових кислот, отриманих із бурого вугілля України, для сорбції іонів важких металів і їх вилучення за допомогою ультрафільтраційних мембран.

**Методика.** Розроблено унікальне лабораторне устаткування для визначення сорбційної здатності гумінових речовин концентрацією від 0 до 20 мг/л по відношенню до іонів важких металів ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ) концентрацією 5 мг/л. Задля оцінки якості бурого вугілля, гумінових речовин і розчину гумінових речовин з іонами важких металів використовували результати технічного та елементного аналізів, а також інфрачервоної та оптико-емісійної спектроскопії.

**Результати.** Українське буре вугілля Олександрійського геолого-промислового району містить велику кількість (близько 80 %) гумінової кислоти, що є основою для отримання ефективних водорозчинних сорбентів. Доведено, що гумінові речовини виділені з бурого вугілля України, дозволяють пов'язувати до 99 % іонів важких металів у комплекси. Найбільш оптимальною концентрацією гумінових речовин з точки зору їх концентрації й селективності вилучення іонів важких металів є 5 мг/л.

**Наукова новизна.** Доведена можливість практичного використання гумінових речовин, отриманих із бурого вугілля України, для сорбції іонів важких металів. В якості ультрафільтраційних мембран використовували мембрани UF-20-PAN, що є пористими полімерними плівками на основі поліакрілонітрилу з розміром пор 20 мкм, площа робочої поверхні мембрани –  $28,26 \times 10^{-4} \text{ м}^2$ .

**Практична значимість.** Упровадження розробленої технології дозволить, по-перше, відновити практичне використання великих покладів бурого вугілля України, а по-друге, запровадити глибоке очищення промислових і стічних вод.

**Ключові слова:** буре вугілля, сорбція, іони важких металів, мембрана, гумінові речовини, інфрачервона спектроскопія

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