OBTAINING DERIVATIVES OF HUMIC SUBSTANCES FROM OXIDIZED COAL AND STUDY OF PHYSICO-CHEMICAL AND ADSORPTION PROPERTIES

Abstract. In the work, a chemical analysis of humic substances based on oxidized coal of the Maikuben basin (Kazakhstan) is carried out. Humic acids were obtained on the basis of potassium humates by acidification with a 20% acid solution to pH = 3–4.5. The optimal conditions for obtaining nitrohumic acids from oxidized coals are: the duration of the process is 3 hours, the ratio of S:L = 1:5, the content of nitric acid is 64%, sulfuric acid is 96% and the composition of the nitrating mixture is 1:1 (g/g). Ammonium derivatives were obtained in the presence of a 3% aqueous solution of ammonia using mechanical activation and ultrasonic treatment. The samples obtained were tested as an adsorbent for water purification from heavy metals. Humic acids and amnonhumate showed the highest degrees of purification for zinc (99.0-100.0%) and cadmium (80.0-96.7%), and nitrohumic acid showed a high adsorption capacity for heavy metals like copper - 100.0 % and lead 82.9%. This is due to the fact that when interacting with heavy metals, humic acids and their derivatives (amino and nitro) form chelate complexes due to carboxyl, phenolic, nitro and amino groups. As a result of the study, the possibility of using them as non-toxic available sorbents for the purification of heavy metals in aqueous media has been shown.

Key words: oxidized coal, humic acid, nitrogumic acid, amino humate, adsorbent, heavy metals.

Humic substances (HS) are a macrocomponent of organic matter in soil and water ecosystems, as well as solid fossil fuels. The use of brown and oxidized bituminous coals for the production of humic fertilizers and plant growth stimulants is one of the promising directions in coal chemistry. For humic acids (HA) coals are characterized by a general type of composition and structure. However, depending on the initial composition of coal, the method of extraction and storage, the indicators of their composition and structure may vary. The physiological activity of HA is largely due to the content of quinoid groups and phenolic hydroxides [1].

The presence in the macromolecules of oxidized carbons and humic acids of an aromatic framework, highly substituted by functional groups such as carboxyl, phenolic, quinoid, carbonyl and others, determines their ability to enter into an ion exchange reaction and the possibility of using them as sorbing substances [2].

To increase the efficiency of humic preparations in sorption processes, their directed functionalization seems to be promising, in particular, by introducing nitro-, amino- and other groups into their composition. Interest in such sorbents is caused by the combination of ion-exchange properties with respect to alkali and alkaline earth metals and the possibility of complexation with transition metals. A significant contribution to the complexation is made by nitrogen atoms, which, in contrast to oxygen atoms, have a higher polarizability and are more prone to the formation of donor-acceptor bonds with metal ions [3].

Nitrohumic acids have received considerable attention as potential soil amendments for nitrogen fertilizers and many other applications, such as plant biostimulants and chelating agents for metals [4–7].
as they are characterized by high sorption and complexing properties. They are usually produced by basic coal mining that has been oxidized with nitric acid.

Aromatic nitrilation, discovered by Mitscherlich in 1834, is a typical electrophilic substitution reaction. The electrophile is the nitronium cation \( \text{NO}_2^+ \). The nitronium ion has a linear structure, the nitrogen atom is in the sp\(^2\) state, and oxygen is in the sp\(^2\) hybridization state [8].

Humic substances (HS), in addition to being a source of C and N for microorganisms and plants, are important in the chemical and physical properties of the soil, mainly due to their high complexing ability with respect to metal ions, which is a consequence of the presence of oxygen-containing functional groups in their structure associated with their high specific surface [9, 10].

It is known that the coals of humic acids are weakly acidic cation exchangers. When nitrogen atoms are more prone to donor-acceptor bonds with metal ions than oxygen atoms are introduced into these carbons, the latter become more complex and polyampholytic [11].

Methods for introducing nitro and amino groups into the composition of coals or humic acids (HS) are their direct nitrilation or amination.

The aim of the work is to obtain nitro-, amino-humic substances from oxidized coal of the “Maikuben” basin and to study their physicochemical and adsorption properties.

The raw material used was brown coal from the Maikuben deposit, pre-crushed to a particle size of less than 0.1 mm and having the following characteristics (wt%): \( A^d = 25.8 \); \( W^d = 9.3 \); \( I^d = 46.6 \); \( S^d = 0.71 \). The yield of free humic acids was on the analytical state - 87%.

The moisture, ash content and volatility of the samples were determined on a “Thermolyst Eltra” thermogravimetric analyzer (according to ASTM D7582-12). The total pore volume, bulk density, pH of the aqueous extract, adsorption activity for methyl orange and methylene blue were determined in accordance with the procedures [12, 13]. The adsorption characteristics of the sorbents (specific surface area) were studied by the Brunauer-Emmett-Teller (BET) method, measurements were carried out on a KATATON Sorbtometer M. Chemical analysis and surface morphology were studied by energy dispersive X-ray spectroscopy using an SEM instrument (Quanta 3D 200i) with an EDAX energy dispersive analysis attachment. The IR spectrum of the samples was recorded on a Nicolet iS 10 FT-IR spectrometer.

Humic substances are obtained from oxidized brown coal, purified and determined in accordance with the recommendations of the International Humic Substances Society (IHSS). Humic acids were obtained on the basis of potassium humates, by acidifying them with a 20% acid solution to \( \text{pH} = 3 - 4.5 \), as a result of the reaction, humic acids precipitated in the form of amorphous brown sediments.

Nitro-humic acids were obtained according to the method described in [2], where coal was treated with 64% nitric acid and 96% sulfuric acid in a ratio of 1: 1 (g / g) in a cooled flask. The ratio S:L was 1: 5. The coal nitrilation method using a nitrating mixture is the most effective. Sulfuric acid has a catalytic effect and reduces the oxidative effect of nitric acid. The nitrating mixture was added to the moistened charcoal in small portions with vigorous stirring and cooling. The process was carried out at a temperature not higher than 40-50 °C to suppress oxidative reactions, the duration of the experiment was 3 hours. The precipitate was separated from the filtrate, washed several times with water, and dried. The nitrocarbon yield was 85%. Nitrohumic acid was obtained from nitrocarbon by alkaline treatment (3% KOH, microwave treatment for 6-7 min, power 1000 W) and subsequent precipitation with 5% acid solution.

The nitrating agent is nitronium ions, which are formed during the decomposition of concentrated nitric acid:

\[
2\text{HNO}_3 \rightarrow \text{NO}_2^- + \text{NO}_3^- + \text{H}_2\text{O}
\]

or in the interaction of sulfuric and nitric acid:

\[
\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2\text{HSO}_4^-
\]

Nitration of coals occurs similarly to aromatic hydrocarbons by the mechanism of electrophilic substitution for the aromatic nucleus of carbon macromolecules and leads to the formation of nitrohumic acids [1].
To obtain aminogumic substances, oxidized coal was crushed to 2.95-452 microns. Then, in a rotary-pulsating apparatus (RPA), it was subjected to intensive oxidation and dispersion of coal particles with atmospheric oxygen, the mixture was heated to 50 °C and brought to an ultrafine state and a homogenized mass in the presence of a 3% aqueous ammonia solution for 20 minutes. After RPA, the finished mass was fed into the extraction vessel for holding the solution for 1 hour. The aged solution was fed to the synthesis module for ultrasonic dispersion, where it was subjected to ultrasonic dispersion at a certain frequency. The ultrasonic treatment time was 25 minutes.

To carry out research on the removal of heavy metals using humic substances, a model solution of heavy metals (copper, zinc, lead, cadmium) was prepared from state standard samples (SSS). In a conical flask (250 ml), a weighed portion of the sorbent (0.5 g) was stirred with a model solution (50 ml, pH = 5.26) and stirred in a shaker at room temperature (25°C) at a stirring speed of 200 rpm for 3 hours. After the process, humic substances with heavy metals were extracted from the solution by filtration. The solution filtered from the adsorbent was analyzed for the content of heavy metals on a Ta-lab voltammetric analyzer.

The chemical composition and physicochemical characteristics of the obtained humic substances are shown in tables 1-3.

Table 1 - Chemical composition of humic substances

<table>
<thead>
<tr>
<th>№</th>
<th>Denomination</th>
<th>Content of elements, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Humic acids</td>
<td>19.47</td>
</tr>
<tr>
<td>2</td>
<td>Nitrohumic acids</td>
<td>50.51</td>
</tr>
<tr>
<td>3</td>
<td>Aminohumate</td>
<td>56.09</td>
</tr>
</tbody>
</table>
According to the data obtained, it should be noted that the potassium content (38.06%) in comparison with the initial humic acid decreases to 0.70% and 0.65% in the derivatives of nitrogumic and aminohumic acids, respectively, which may be due to the replacement of potassium ions by amino and nitro groups.

Table 2 - Content of functional groups of humic substances

<table>
<thead>
<tr>
<th>№</th>
<th>Denomination</th>
<th>Carboxyl groups, meq / g</th>
<th>Total acidity, meq / g</th>
<th>Phenolic group, meq / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Humic acids</td>
<td>1.18</td>
<td>1.60</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>Nitrohumic acids</td>
<td>0.60</td>
<td>1.64</td>
<td>1.04</td>
</tr>
<tr>
<td>3</td>
<td>Aminohumate</td>
<td>0.12</td>
<td>0.73</td>
<td>0.61</td>
</tr>
</tbody>
</table>

The data in table 2 show a 50 % decrease in carboxyl groups from the original form of humic acid in the derivatives of humic acids. The nitro and amino groups increase the reactivity of other substituents on the aromatic ring. It should be noted that in aromatic acids nitration often occurs the substitution of the carboxyl group for nitro and amino groups.

Table 3 - Physical and chemical characteristics of the obtained humic substances

<table>
<thead>
<tr>
<th>№</th>
<th>Denomination</th>
<th>W&lt;sub&gt;n&lt;/sub&gt;, %</th>
<th>A&lt;sub&gt;n&lt;/sub&gt;, %</th>
<th>V&lt;sub&gt;d&lt;/sub&gt;, %</th>
<th>S&lt;sub&gt;bgr&lt;/sub&gt;, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
<th>p&lt;sub&gt;0吸&lt;/sub&gt;, g/cm&lt;sup&gt;3&lt;/sup&gt;</th>
<th>V&lt;sub&gt;b&lt;/sub&gt; by water, cm&lt;sup&gt;3&lt;/sup&gt;/g</th>
<th>pH</th>
<th>A&lt;sub&gt;H&lt;/sub&gt;, mg/g</th>
<th>A&lt;sub&gt;N&lt;/sub&gt;, mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Humic acids</td>
<td>13.32</td>
<td>25.73</td>
<td>62.25</td>
<td>0.42</td>
<td>0.95</td>
<td>-</td>
<td>4.09</td>
<td>28.0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Nitrohumic acids</td>
<td>5.52</td>
<td>57.87</td>
<td>67.93</td>
<td>5.637</td>
<td>0.882</td>
<td>0.43</td>
<td>6.60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Aminohumate</td>
<td>3.41</td>
<td>74.13</td>
<td>56.77</td>
<td>3.940</td>
<td>0.857</td>
<td>0.17</td>
<td>10.07</td>
<td>45.5</td>
<td>112.5</td>
</tr>
</tbody>
</table>

Figure 1 shows the IR spectrum of humic acid, peaks were found in the region of 2918 cm<sup>-1</sup>, which can be associated with CH stretching vibration of alkyl chains, which can also be a broad signal N - H/O - H. Peak at about 1701 cm<sup>-1</sup> typical for the stretching vibration of C = O carbonyl groups of ketones (including quinones), carboxylic acids and / or amides. The band of deformed stretching vibrations in the region of 1650-1520 cm<sup>-1</sup> also indicates the presence of a strong N-H group. The peak in the 1100-1000 cm<sup>-1</sup> range is responsible for the strong elongation of the C-O group.

![Figure 1 - IR spectrum of humic acid](attachment:image.png)
In Figure 2, the absorption bands in the range of wavenumbers 3700-3300 cm$^{-1}$ refer to weak stretching vibrations of O – H bonds, probably due to the presence of moisture in this compound. In the region of 2923 cm$^{-1}$ to be associated with C-H stretching vibration of alkyl chains. A peak at about 1700 cm$^{-1}$, typical of the C = O stretching vibration of carbonyl groups of ketones (including quinones), carboxylic acids and / or amides, confirms that these units are present in humic acid. The peak in the 1100-1000 cm$^{-1}$ range is responsible for the strong elongation of the C-O group. The wide range of peak variation from 800-650 cm$^{-1}$ can be explained by the tensile C-H vibration. Peak 920-830 cm$^{-1}$ for nitroparaffin compounds, 1560-1500 cm$^{-1}$ for aryl groups.

Figure 3 shows a peak at 2993 cm$^{-1}$, which is responsible for the presence of aromatic stress assigned to C-H. There is also a slight shift of the band at 1576 cm$^{-1}$, which also indicates the presence of a strong N – H group. The peak at 1560 cm$^{-1}$ is characterized by asymmetric and 1363 cm$^{-1}$ symmetric tensile vibration of aromatic tertiary amines. The peak in the 1100-1000 cm$^{-1}$ range is responsible for the strong elongation of the C-O group.

The particle size of the amino humate was determined using the Mastersizer 3000. The frequency results are shown in Figure 4. The particle size of the amino humate was 10% - 0.687 μm, 50% - 7.21 μm, 90% - 296 μm.
The obtained HS were tested for water purification from heavy metals. Analysis of the data obtained showed that after water purification, the values of all heavy metals decrease (table 4).

<table>
<thead>
<tr>
<th>Heavy metals, mg/l</th>
<th>C_{0} (Me), mg/l</th>
<th>C_{residual} (Me), mg/l</th>
<th>Purification degree,%</th>
<th>C_{residual} (Me), mg/l</th>
<th>Purification degree,%</th>
<th>C_{residual} (Me), mg/l</th>
<th>Purification degree,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>0.10±0.01</td>
<td>0.0010±0.0004</td>
<td>99.00</td>
<td>0.052±0.009</td>
<td>48.00</td>
<td>Item not found</td>
<td>100.00</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.10±0.01</td>
<td>0.0033±0.0003</td>
<td>96.70</td>
<td>0.10±0.03</td>
<td>-</td>
<td>0.020±0.005</td>
<td>80.00</td>
</tr>
<tr>
<td>Lead</td>
<td>0.10±0.01</td>
<td>0.0216±0.0005</td>
<td>78.40</td>
<td>0.015±0.004</td>
<td>85.00</td>
<td>0.036±0.009</td>
<td>64.00</td>
</tr>
<tr>
<td>Copper</td>
<td>0.10±0.01</td>
<td>0.0171±0.0003</td>
<td>82.90</td>
<td>Item not found</td>
<td>100.00</td>
<td>0.1±0.01</td>
<td>-</td>
</tr>
</tbody>
</table>

As a result of sorption, the obtained humic substances removed most of the heavy metals from the solution and showed a high degree of purification. Humic acids and aminohumate showed the highest degrees of purification for zinc (99.0-100.0%) and cadmium (80.0-96.7%), and nitrohumic acid showed a high adsorption capacity for heavy metals like copper - 100.0 % and lead 82.9%. This is due to the fact that when interacting with heavy metals, humic acids and their derivatives (aminoh and nitro) form chelate complexes due to carboxyl, phenolic, nitro and amino groups.

Thus, nitro- and amino-humic substances were obtained from the oxidized coal of the Maikuben deposit by nitration and amination. Their physicochemical and adsorption properties have been studied. As a result of the study, the possibility of using them as non-toxic available sorbents for the purification of heavy metals in aqueous media has been shown.

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ТОППЫҚАН КОМІРДІҢ ЖАТТУЫҢДЫСЫҢ АЛУ ЖОНЕ ФИЗИКА-ХИМИЯЛЫҚ АДОСБЕРІНІҢ ҚАСІТЕТІНІҢ ЗЕРТТІГІ

Аннотация. Жұмысқа Майкобе басылған (Қазақстан) топықтан қомир жетілдінде алынған гуминді заттарға химиялық таңдау жұрғызалығы. Гумин қышқылдарының қақырысы 20% қышқылды өртіндісімен pH = 3-4,5 дейін қышқылдықтарды аркылы алынды. Топықтан қомирден нитрогумин қышқылдары алынған адам тартарының: үлкенің ұзынғылығы — 3 сант., қызметі қысықты 1,5, азот қышқылдарының концентрациясы 64%, күкір қышқылы 96% және нитрат кәрі қышқылдық құрылымды 1:1 (т/т). Нитрат қосылысы қызметі аркылы қомирді нитраттау өңдеісі тәуелді болып саналады. Қуыққы қышқылдың катализитикалық қасыр екеуе және эзеді азот қышқылының тозуы есеп етіледі.

Комирліңің ароматикалық компоненттерінің саны қомирдің макромолекула-сыйлық ароматикалық адрсыз бойынша электродағы адамдарға механизмін есеп етеді және нитрогумин қышқылдары нысанда болады. Нитрат қосылысы қызметі аркылы қомирді тозу және есеп етілген құрылымды қозғалысы қамтамасыз етеді.

Процесстер реакцияларының әсерінде 80-90 °С астынан температурада жұрғызылған, қасиеті өзгертілген құрылымды 3 сәттің пропага жылғайды. Процесс төзімділігінің басында 40-50 °С астынан температура жұрғызылған, және қасиеті өзгерту құрылымды 3 сәттің ортасы 3. Адамдар қоғамдық қызметін аркылы алынған қоғамдық құрылымды алып қалады.

Аминогумин қышқылдардың өңдеу қасырлары қашықтығы және электродың құрылымдары тәуелді болады, азырыңың қасыры 3 сәт тозу және есеп етілген құрылымды қазына жатады.

Сорбция қолданылған алынған гуминді заттарға есеп етілген, азырыңың құрылымды алып қалады.

Туын сөз: топықтан қомир, қызылқы, нитрогумин қышқылдары, аминогумин, адыр, абордерт, адыр металдар.

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ПОЛУЧЕНИЕ ПРОИЗВОДНЫХ ГУМИНОВЫХ ВЕЩЕСТВ ИЗ ОКСИЛЕННОГО УГЛЯ И ИЗУЧЕНИЕ ФИЗИКО-ХИМИЧЕСКИХ И АДОСБЕРНЫХ СВОЙСТВ

Аннотация. В работе представлены результаты химического анализа гуминовых веществ на основе оксиленного угля Майкобе бассейна (Казахстан). Гуминовые кислоты были получены на основе гуматов калия путем подкисления 20%-ным раствором кислоты до pH = 3-4,5. Оптимальными условиями для получения нитрогуминовых кислот из оксиленных углей являются: продолжительность процесса 3 часа, соотношение Т:Ж=1,5, концентрация ацетатной кислоты 64%, серной кислоты 96% и состав нитрогуминов смеси 1:1 (т/т). Метод нитрования угля со использованием нитрующего средства является наиболее эффективной. Серная кислота оказывает каталитическое влияние и уменьшает окислительное действие ацетатной кислоты. Нитрование углей происходит подобно ароматическим углеводородам по механизму электрофильного замещения по ароматическому ядру макромолекул углей и приводит к образованию нитрогуминовых кислот. Нитрующую смесь прибавляли к углю в последующем до небольшими порциями при интенсивном перемешивании и охлаждении. Процесс проводился при температуре не выше 40-50 °С для подавления окислительных реакций, продолжительность опыт составляла 3 часа. Осадок отделяли от фильтрата, промывали многократно водой и сушили. Выход нитрогуминов составил 85%.
Nitrigenousy kislotu polucheni iz nitrugumnoj celioloi obrabotki (3 % KOH, obrabotka v mikrovlnnoi plachi ot 6-7 min, mozhnost 1000 W) i posleduyushchee osakihenie 5 % razrashenii kisloty.

Aminogumonovye provodimostnye byli polucheni v pristignii 3 % vodnogo rastvora aminkvi s primenieniem metanaloytsii i ultrazvukovoi obrabotki. Dla polucheni aminogumonovych veshchestv okisleniy yugul byl izmenen do 2,95-4,52 mil. Dalnee v rotoryno-pulzacionnom apparate (RPA) podvergalis intensivnem okisleniyu i dispergirovaniu chasticy ugli kislorod vozduha, smessi nitrugumnoj i 50C i dovodilas' do ultradzykstvennoi sotsnosti yugul, izmeneniya nitrugumnoj kisloty v pristignii 3 % vodnogo rastvora amfikvi v 20 min. Posle RPA gotovaya massa podvalaia v emkosti ekstraktsii dlya vydereki rastvora v inna tsiance. Vydereki rastvora podvalaia v modul sinitza dlya ultradzykstvennoi dispergirovaniya, podelas' vozdejstviem ultradzykstvennym dispergirovaniem, opredeleniya gostostei. Vremia ultradzykstvennoi obrabotki sostava 25 min. Dla rabota i ispolzovaniya po ochistke i perenemnoi rastvora ultrazvukovoj dispergirovaniy, podvalaia vozdejstviem ultradzykstvennym dispergirovaniem, opredeleniya gostostei.

V rezultate ispolzovaniya po ochistke i perenemnoi rastvora ultrazvukovoj dispergirovaniy, podvalaia vozdejstviem ultradzykstvennym dispergirovaniem, opredeleniya gostostei. V rezultate ispolzovaniya po ochistke i perenemnoi rastvora ultrazvukovoj dispergirovaniy, podvalaia vozdejstviem ultradzykstvennym dispergirovaniem, opredeleniya gostostei.

Key words: okisleniy yugul, nitrugumonovye, amfikvi, amfikvy, adsorben, tijekhymy metally.

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