ХИМИЯЛЫҚ ТЕХНОЛОГИЯ
ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ
CHEMICAL TECHNOLOGY

DOI 10.51885/1561-4212_2024_2_96
IRSTI 31.21.01

B.S. Tantybayeva[1], **B.S. Saurbayeva**[2], **R.A. Ramazanova**[2], **M.K. Zhamanbayeva**[2], **Z.S. Dautova**[1], **Zh.S. Abisheva**[3], **G.K. Tazhkenova**[4], **Ye.N. Ivashchenko**[2]
[1]S. Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan
E-mail: bati_54@mail.ru
E-mail: dautowa@mail.ru
[2]D. Serikbayev East Kazakhstan Technical university, Ust-Kamenogorsk, Kazakhstan
*E-mail: saurbaeva71@mail.ru**
E-mail: raigul_77_33@mail.ru
E-mail: manogk@mail.ru
E-mail: elenaiva69@mail.ru
[3]Nazarbayev Intellectual schools, Ust Kamenogorsk, Kazakhstan
E-mail:zhanar_a_2010@mail.ru
[4]Eurasian National University named after L.N. Gumilyov, Astana, Kazakhstan
E-mail: gaukhar-1970@mail.ru

PREPARATION OF A COMPLEX COMPOUND OF HUMIC ACID WITH GLYCINE

ГУМИН ҚЫШҚЫЛЫНЫҢ ГЛИЦИНМЕН КҮРДЕЛІ ҚОСЫЛЫСЫН АЛУ

ПОЛУЧЕНИЕ КОМПЛЕКСНОГО СОЕДИНЕНИЯ ГУМИНОВОЙ КИСЛОТЫ С ГЛИЦИНОМ

Annotation. *Our study focuses on obtaining and studying the properties of a complex consisting of humic acids and glycine. Through the analysis of quantitative data and theoretical approaches, we investigated the formation of complexes between humic substances and glycine, while also considering the current research status in the field of humic acid complexation. Furthermore, we utilized mathematical planning to determine the optimal conditions for activating brown coal from the Kenderlyk deposit using hydrochloric acid. The resulting complex of humic acids with glycine demonstrates promising applications in agriculture and can be effectively employed as a conventional plant fertilizer.*

Keywords: *complex, organics, humic, glycine, properties.*

Аңдатпа. *Жұмыс глицинмен гумин қышқылдары кешенінің қасиеттерін зерттеу және қосылысын алудан тұрады. Жұмыс барысында глицинмен гуминді заттардың кешендерін алуды сипаттайтын сандық мәліметтер, оларды анықтаудың теориялық тәсілдері талданды. Гумин қышқылдарын кешендеу саласындағы зерттеулердің қазіргі жағдайы қарастырылды. Математикалық жоспарлау әдісін қолдана отырып, Кендірлік кен орнының қоңыр көмірін тұз қышқылымен белсендіру шарттары анықталды. Алынған глицинмен гумин қышқылдарының кешені ауыл шаруашылығында қолдануға мүмкіндік береді. Сондай-ақ, оны классикалық өсімдік тыңайтқышы ретінде пайдалануға болады.*

Түйін сөздер: *кешен, органика, гумин, глицин, қасиеттер.*

Аннотация. *Наша работа заключается в получении и изучении свойств комплекса гуминовых кислот с глицином. В ходе работы проанализированы количественные данные, характеризующие получение комплексов гуминовых веществ с глицином, теоретические подходы к их определению. Рассмотрено современное состояние исследований в области комплексообразования гу.миновых кислот.*

С применением метода математического планирования были определены условия активации бурого угля Кендырлыкского месторождения соляной кислотой. Полученный комплекс гуминовых кислот с глицином имеет перспективу для использования в сельском хозяйстве. А также его можно использовать в качестве классического удобрения растений.

Ключевые слова: *комплекс, органика, гумин, глицин, свойства.*

Introduction. Humic compounds (HC) are organic matters located in soil, natural bodies of water and deposits formed by putrefaction of plants and natural residues. They cpmprise 50-90% of the total amouont of the organic matters accumulated in the ocean. They also contain macro- and microelements,e.g. zink,calcium, iron, magnesium, iodin, boron,sulphur, molibdenum, etc. Humic acids are part of HC.

Humic acids (HAs) are natural high molecularorganic compounds included in peat, soil and lignite. They differ from other HC fractions (fulvic acids and humins) in that they are soluble in alcaline conditions, partially soluble in water and insoluble in acidic conditions. Due to their amphiphilic properties HAs form micelle-like structures in neutral and acidic conditions used in agriculture for the purification of wastewater from heavy metals, and also in medicine and pharmaceuticals [1].

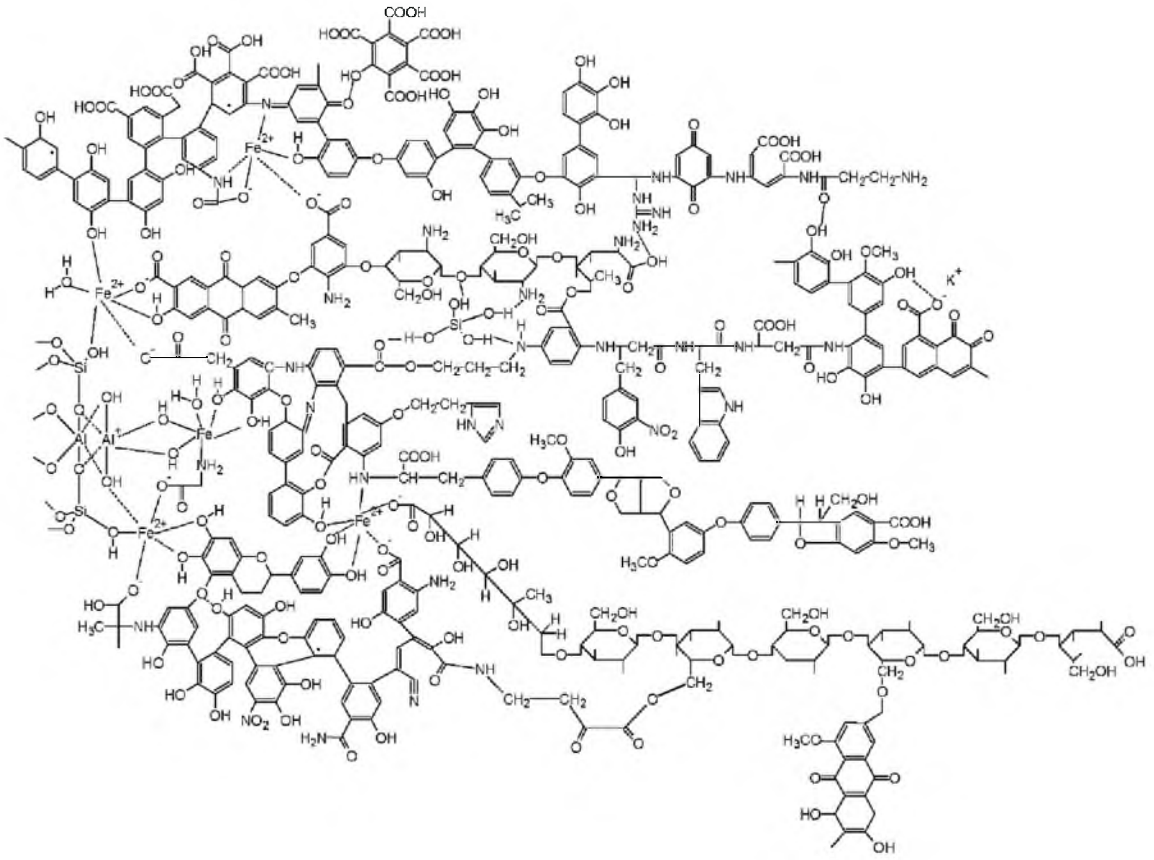

Figure 1. HA hypothetic fragment

HA chemical composition can change depending on its origin, age, climatic conditions and biologic conditions. Therefore, its exact composition is impossible to determine. HA molecular mass is in the range from 2 to 1300 kDa. HAs contain many functional groups as shown in Figure 1, which are mainly composed of phenolic, carboxylic, hydroxoalken, quinone and ester functional groups, but can also contain sugar and peptide parts. However, phenolic and carboxylic groups prevail in HA structures. The huge structure of the HA molecule consists of hydrophylic parts of OH-groups and of hydrophobic parts of aliphatic chains and aromatic rings [2].

Literature Review. HAs contain many functional groups as shown in Figure 1. They are mainly composed of phenolic, carboxylic, phenolic, enolic, quinone and ester functional groups, but can also contain sugar and peptide parts.

The significance of humic substances (HS) in the complex formation and transportation of metals in aquatic systems is comprehensively recognized and extensively studied. They constitute the major part of an organic matter in the natural environment with a typical organic carbon concentration from 0.1 to 1 000 mg/l. Multy-functionality anddiversity of structures allow these compounds to enter ionic, molecular and electronic oxidation and reduction processes. Like ionic polyelectrolytes, humic substances react with cations, anions, neutral molecules, radionuclide compounds, and other pollutants. For example, HS form compounds with heavy metals, as well as pesticide adducts, thus significantly affecting the mobility of these substances in the environment. For this reason, they can substantially increase the heavy metal content in natural water. Even small HS concentration can considerably influence free and total metal concentration in soil and groundwater.

Carboxyl, hydrixyl, and carbonyl groups in combination with aromatic structures in HS provide the HAs ability to enter ionic and donor-acceptor interactions, form hydrogen bindings, and take an active part in sorption processes (Table 1) [3].

Table 1. Role of HS Functional Groups [4]

Structural Groups	Interaction Mode
– COOH	Ion exchange
CAr–OH	Complex formation
> C=O	Oxidation and Reduction
C_6H_6	Donor-Acceptor
– CH_n	Hydrophobic Interactions

The main HAs properties such as solubility, pH-dependence, interaction with hydrophobic groups and metal chelation are related to their structure. Table 2 summarizes the HA functional effects employed in different spheres and their interaction with the structural properties of HAs [5].

Table 2. Relation of functional effects with HA structural properties and their technological utilization [6]

HA Technological Utilization	Functional effect	Structural properties
1	2	3
Purifying contamination	Chelate heavy metals Dissolve hydrophobic contaminants	Deprotonation OH/OOH Amphiphilic nature
Agriculture	Fertilizing and growing plants Bactericidal activity Fungicidity	OH/OOH deprotonation and production of reactive oxygen species (ROS) Production of reactive oxygen species (ROS) Production of reactive oxygen species (ROS)

End of table 2

1	2	3
Medicine	Antiviral properties Antiphlogistic properties Antimutagenic properties Wound therapy Cancer therapy Prion therapy	OH/OOH deprotonation OH/OOH deprotonation OOH prevalence Production of reactive oxygen species (ROS) Production of reactive oxygen species (ROS) OH/OOH deprotonation
Pharmaceutics and cosmetology	UV protection Antioxidant capacity Medication solvent	UV absorption OOH prevalence Amphiphilic nature

Proteins are a special class of polyelecrtolytes that can also interact with HS. Howerver, there is little research on HS interaction with proteins. Nevertheless, HS binding with proteins can be particularly relevant for fertilization [7,14].

The role of pathogenous proteins such as insecticidal protein toxins, pharmaceutical proteins (produces by transgenic plants) and infectious (prion) proteins involved into transmissive spongiform encephalopathy causing such diseases as BSE (Bovine spongiform encephalopathy) and Creutzfeldt-Jakob that could be found in soil and on the surface of the water [8]. HS interaction with protein can result in modifying protein structure and, consequently, to changes in protein biological activity.

Peat like other solid fuels has humic acids mostly bound with relatively low activity [9]. Their reaction centers are blocked, and different physical and chemical activation methods are used to unlock HC data centers, such as hydration, acid and alkaline hydrolysis, physical processing, etc. For example, alkaline activation of humic acids is based on their ability to dissolve in hydroxides which is the basis for most HC separation methods. Treatment of peat with NaOH solution results in the formation of soluble humates Na [10]:

$$\mathrm{Hum(COOH)_n + nNaOH \rightarrow Hum(COONa)_n + nH_2O} \qquad (1)$$

However, scientists' opinions on methods of extraction and purification of HAs from broun coal diverge due to different composition and properties of these compounds, in particular their solubility in alkaline solutions, regardless of their general type of structure. Humic compounds differ not only in the form of metal humates (K, Na, Ca, Mg, Cu, Fe, etc.) and in the nature and strength of the bond, but also in the organic mass of the compound organic and mineral part of the coal (C, P, S) [11].

Materials and methods of research. Production of humid acids. Effect of hydrochlorid acid on the coal activation process.

The conditions of activation of brown coal from Kendyrlyk deposit by hydrochloric acid were revealed by mathematical planning. The process was carried out at ratios S:L (Solid:Liquid)=1:8, the experiment planning matrix is given in Table 1. It can be concluded that the coefficients of linear effect of temperature and concentration are significant in the brown coal processing with hydrochloric acid. In our case, we changed only the concentration.

Table 3. Effect of temperature and Solid-Liquid concentration on HA output

Specimens	T, °C	Solid:Liquid(S-L)	Output, %
Non-activated	25	–	26
HCl activation	25	1:5	50.6
HCl activation	25	1:8	51.3

The infrared spectrum of hydrolic acid activated coal differs from that of the original sample, indicating a structural modification of the coal by the action of HCl.

For example, the intensity of absorption bands in the range of 3450-3360 cm^{-1} corresponding to phenolic hydroxylames bound by intermolecular hydrogen bonds increases under the acid. Due to the overlap of peaks of valence oscillations of CH_3–, CH_2–, CH-groups of aliphatic carboxylic acids, wide bands are observed in the range of 2920-2810 cm^{-1}. Absorption bands in the range of 1720-1680 cm^{-1}, related to C=On carboxylic acid bonds are increasing [12].

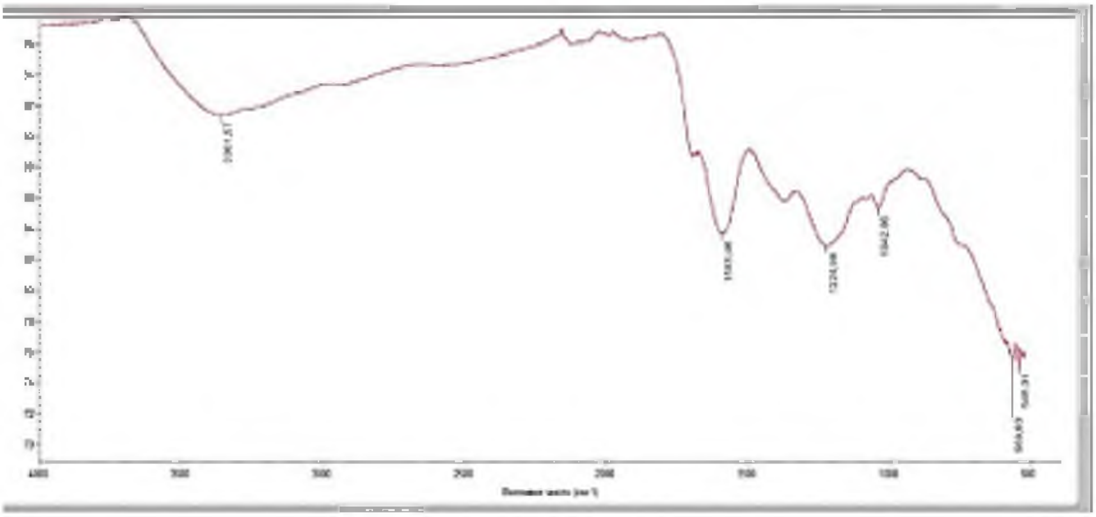

Figure 2. Humic acid produced by hydroxide method (HCl, S:L=1:8)

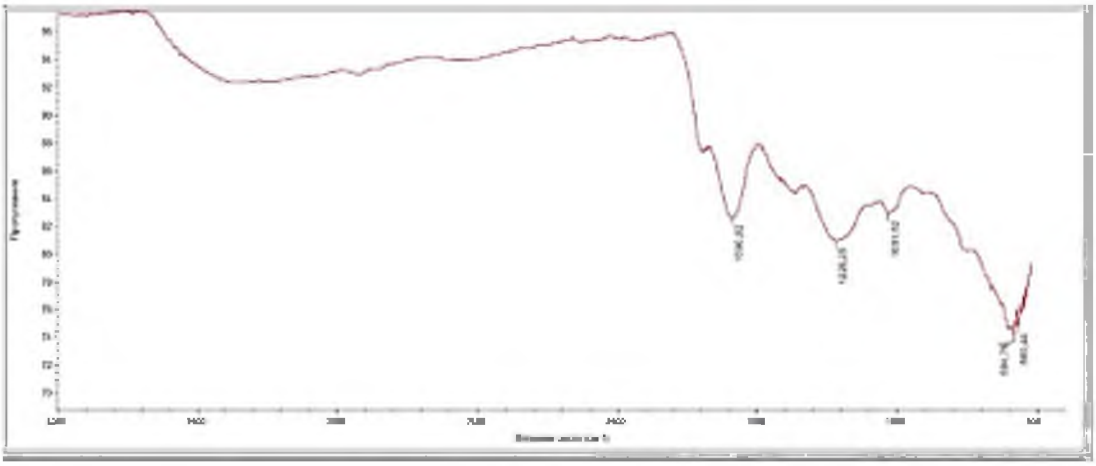

Figure 3. Humic acid produced by pyrophosphate method (HCl, S:L=1:8, t=ambient)

The intensity of the C=C bands of aromatic groups at 1620-1590 cm^{-1} increases under the action of hydrochloric acid due to the influence of oxygen bonds of carboxyl groups. The bands at 1420-1380 cm-1 are characteristic for valence vibrations of C-O bonds of the peripheral part,while the absorption bands in the range of 1340-1250 cm^{-1} belong to deformation vibrations of OH-groups, which intensity increases under the action of hydrochloric acid. The absorption bands at 1100-1020 cm^{-1} belong to the deformation vibrations of –CH -groups of heterocyclic aromatic compounds, which also become more intense due to acid activation [13, 15].

Table 4. Characteristic of IR spectra of brown coal (BC) and hydrochloric acid-activated coal (BC-2)

Absorption	Frequency, cm^{-1}	
	BC	BC-2
ν (OH)	3450-3380 (w.)	3440-3360 (m.)
ν (CH_3, CH_2, CH)	2920-2810 (m.)	2900-2820 (s.)
ν (C=O)	1720-1680 (w.)	1720-1680 (s.)
ν (C=C)	1620-1590 (m.)	1620-1590 (s.)
ν (CO)	1420-1320 (m.)	1420-1310 s.)
ν (OH)	1340-1250 (w.)	1340-1250 (s.)
ν (CH)	1100-1020 (m.)	1100-1000 (s.)

*Footnote s. - strong, m. - medium, w. - weak bands.

Thus, the data of elemental, functional and IR spectral analysis proves that the intraction of lignite with hydrolic acid results in coal structural modification, leading to an increase in the humic acid output.

Results and discussion. The obtained HAs were studied by infrared spectroscopy (Figure 2) and spectrophotometry (Figure 3). Also, the HA complex with glycine was investigated with spectrophotometry (Figure 4).

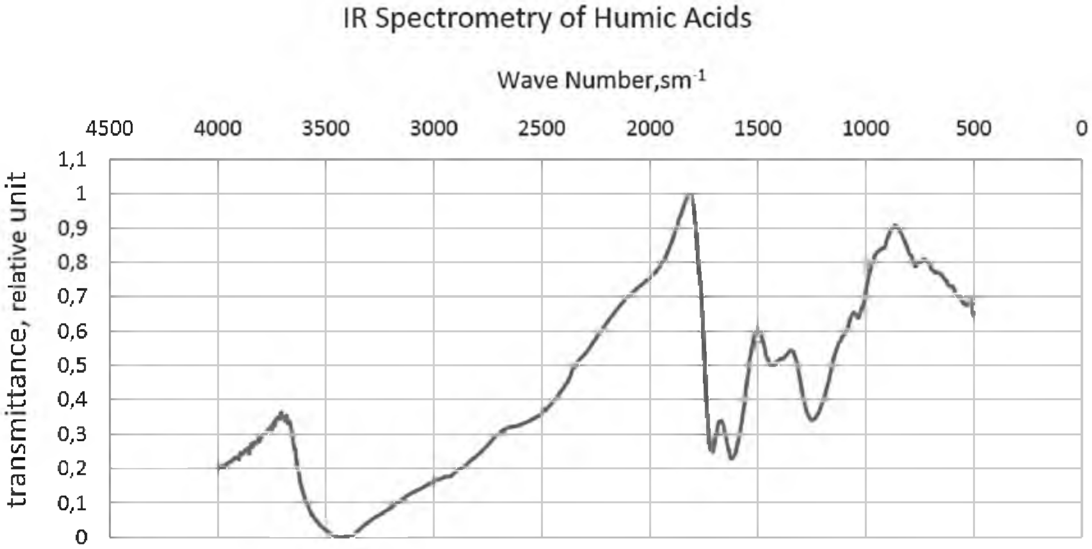

Figure 4. IR spectrometry of HAs

We can draw the following conclusions from the graph:

– The peak at 3,400-3,200 cm^{-1} indicates at OH-group and intramolecular hydrogen bindings in HA structure.

– The peaks at 1700 and 1600 cm^{-1} show that there are C=O bonds in the HA structure.

– Considering the top points, there are COOH groups in the HA structure.

– A peak of 1,240 cm^{-1} indicates at amine groups in the HA structure.

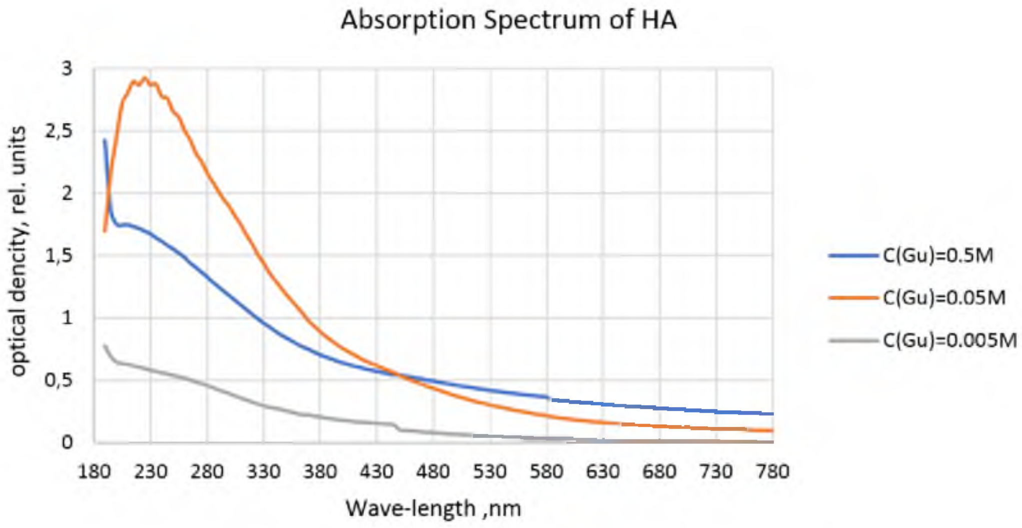

Figure 5. Humic Acid Absorption Spectrum

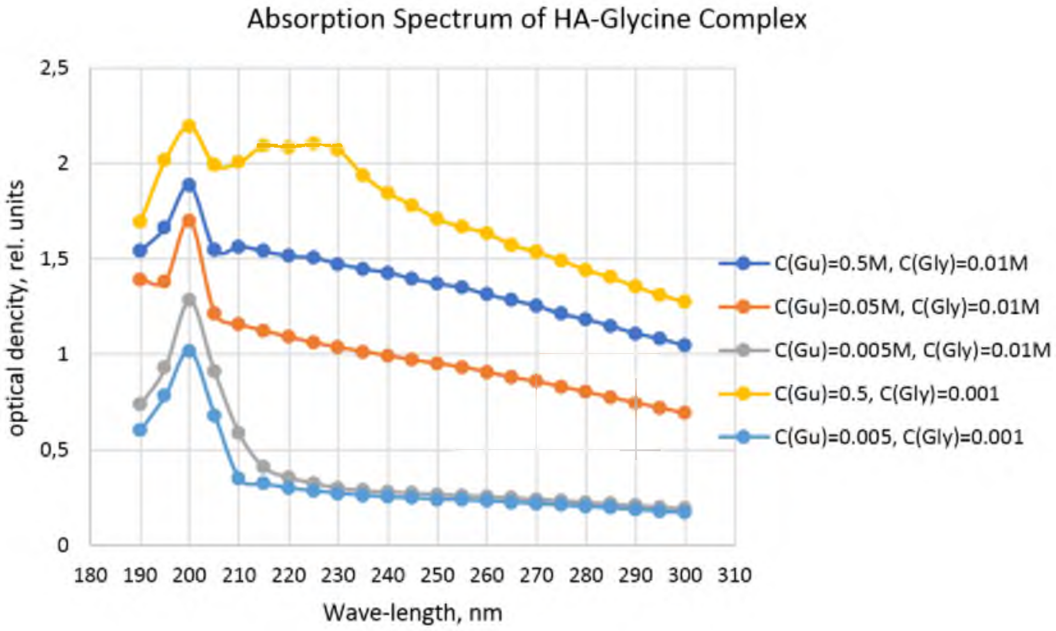

Figure 6. Absorption Spectrum of HA-Glycine Complex

The obtained peaks of 230 nm (Figure 6) and 200 nm (Figure 5) prove the formation of a complex between HAs and glycine.

Conclusion. Humic acids were extracted from the lignit of the Kendyrlyk deposit by activation of lignit with hydrochloric acid by pyrophosphate method.

Infrared spectroscopy of HAs and spectral-photometry of HA and the HA complex with glycine were carried out after their poducing. Having used the above-mentioned measurements, we proved the formation of the HA complex with glycine by the method of continuous change and molar ratio.

References

1. B.A. Melo, F.L. Motta, M.H. Santana. Humic acids: Structural properties and multiple functionalities for novel technological developments // Materials Science and Engineering: C. – 2016. – № 62. – P. 967-974. https://doi.org/10.1016/j.msec.2015.12.001
2. Nikitina I.M. Razrabotka sposoba polucheniya reagenta na osnove torfa dlya snizheniya soderzhaniya tyazhely`kh metallov v stochny`kh vodakh gorny`kh predpriyatij: speczial`nost` 25.00.36 «Geoe`kologiya»: dissertacziya na soiskanie uchenoj stepeni kandidata pedagogicheskikh nauk // Naczional`ny`j issledovatel`skij tekhnologicheskij universitet «MISIS». – Moskva, 2015. – 124 s.
3. 3.Perminova I.V. Guminovy`e veshhestva - vy`zov khimikam XXI veka // Khimiya i zhizn` – XXI vek. – 2008. – № 1. – S. 50-55.
4. Li, Y., Tan, W. F., Wang, M. X., Liu, F., Weng, L. P., Norde, W., & Koopal, L. K. Influence of lysozyme complexation with purified Aldrich humic acid on lysozyme activity // European Journal of Soil Science. 2012. Vol. 63. №5. P. 550–557. https://doi.org/10.1111/j.1365-2389.2012.01459.x
5. Tan, W., Koopal, L., Weng, L., van Riemsdijk, W., & Norde, W. Humic acid protein complexation // Geochimica Et Cosmochimica Acta. 2008. Vol. 72. – № 8. – P. 2090-2099. https://doi.org/10.1016/j.gca.2008.02.009
6. Lebedev S.V., Osipova E.A. Change in the amount of heavy metals in wheat under the action of various forms of iron with humic acids // Fundamental research. 2014. № 11. P. 2438-2442. https://fundamental-research.ru/ru/article/view?id=35962
7. Lebedev S.V., Osipova E.A., Arkushenko E.A., ZHeneev S.A.Izmenenie kolichestva medi, cinka i marganca v pshenice pod dejstviem razlichnyh form zheleza s guminovymi kislotami // Aktual'nye problemy gumanitarnyh i estestvennyh nauk. 2014. – № 12-1. – S. 31-35.
8. Nekrasova O.A., Dergacheva M.I. Soderzhanie mikroelementov v chernozemah obyknovennyh i ih guminovyh kislotah (na primere YUzhnogo Urala) // Vestnik Tomskogo gosudarstvennogo universiteta. Biologiya. 2011. № 4 (16). – S. 7-16.
9. Platonov V.A., Hadarcev A.A. Fridzon K.YA., CHunosov S.N. Himicheskij sostav i biologicheskaya aktivnost' sapropelya oz. Glubokoe (Tatarstan) // Vestnik novyh medicinskih tekhnologij. – 2014. – № 3. – S. 199-204.
10. Stepanova, Pisareva: Guminovye veshchestva pochvy. Rol' guminovyh veshchestv v rastenievodstve, zhivotnovodstve, medicine. Uch.pos. Izdatel'stvo: Lan' 2022 g, – 460 s.
11. Fedotov G.N., SHuba S.A., Fedotova M.F., Stepanov A.L., Streleckij R.A. Pochvennye drozhzhi i ih rol' v prorastanii semyan. Pochvovedenie, 2017, №5, S.592-602.
12. Orlov, D.S. Praktikum po himii gumusa / D.S. Orlov, L. A. Grishina. – M.: Izd-vo MGU, 1981. – 272 s.
13. Saurbaeva B.S., Ivashchenko E.N., Ramazanova R.A., Tantybaeva B.S., Bolatқan D.Q., Akimbaeva N.O. Poluchenie modificirovannogo sorbenta iz guminovyh veshchestv burogo uglya Kendyrlykskogo mestorozhdeniya // Vestnik VKTU, 2023. – № 1. – S 204-212 DOI 10.51885/1561-4212_2023_1_204
14. Avvakumova N.P., Krivopalova M.A., Glubokova M.N., Katunina Ye.Ye., Zhdanova A.V. Guminovyye veshchestva kak regulyatory ekologicheskogo gomeostaza. Izvestiya Samarskogo nauchnogo tsentra Rossiyskoy akademii nauk, №2(2) 2016 S 267-271
15. Lishtvan I.I., Kaputskiy F.N., Yanuta Yu.G., Abramets A.M., Monich G.S., Navosha Yu.Yu., Strigutskiy V.P., Glukhova N.S., Aleynikova V.N. Guminovyye kisloty spektral'nyy analiz i struktura fraktsiy, Vestnik BGU. Ser. 2. – 2012. – № 1.

Список литературы

1. B.A. Melo, F.L. Motta, M.H. Santana. Humic acids: Structural properties and multiple functionalities for novel technological developments // Materials Science and Engineering: C. - 2016. - № 62. – C. 967-974. https://doi.org/10.1016/j.msec.2015.12.001
2. Никитина И.М. Разработка способа получения реагента на основе торфа для снижения содержания тяжелых металлов в сточных водах горных предприятий: специальность 25.00.36 «Геоэкология»: диссертация на соискание ученой степени кандидата педагогических наук // Национальный исследовательский технологический университет «МИСИС». – Москва, 2015. – 124 с.
3. Перминова И.В. Гуминовые вещества – вызов химикам XXI века // Химия и жизнь – XXI век. – 2008. – № 1. – С. 50-55.
4. Li, Y., Tan, W. F., Wang, M. X., Liu, F., Weng, L. P., Norde, W., & Koopal, L. K. Influence of lysozyme complexation with purified Aldrich humic acid on lysozyme activity // European Journal of Soil Science. 2012. Vol. 63. №5. P. 550–557. https://doi.org/10.1111/j.1365-2389.2012.01459.x
5. Tan, W., Koopal, L., Weng, L., van Riemsdijk, W., & Norde, W. Humic acid protein complexation // Geochimica Et Cosmochimica Acta. – 2008. – Vol. 72. – № 8. – P. 2090-2099. https://doi.org/10.1016/j.gca.2008.02.009
6. Лебедев С.В., Осипова Е.А. Изменение количества тяжелых металлов в пшенице под действием различных форм железа с гуминовыми кислотами // Фундаментальные исследования. – 2014. – № 11. – С. 2438-2442. https://fundamental-research.ru/ru/article/view?id=35962
7. Лебедев С.В., Осипова Е.А., Аркушенко Е.А., Женеев С.А.Изменение количества меди, цинка и марганца в пшенице под действием различных форм железа с гуминовыми кислотами // Актуальные проблемы гуманитарных и естественных наук. – 2014. – № 12-1. – С. 31-35.
8. Некрасова О.А., Дергачева М.И. Содержание микроэлементов в черноземах обыкновенных и их гуминовых кислотах (на примере Южного Урала) // Вестник Томского государственного университета. Биология. 2011. – № 4 (16). – С. 7-16.
9. Платонов В.А., Хадарцев А.А. Фридзон К.Я., Чуносов С.Н. Химический состав и биологическая активность сапропеля оз. Глубокое (Татарстан) // Вестник новых медицинских технологий. –2014. – № 3. – С. 199-204.
10. Степанова, Писарева: Гуминовые вещества почвы. Роль гуминовых веществ в растениеводстве, животноводстве, медицине. Уч.пос. Издательство: Лань 2022 г, 460 стр
11. Федотов Г.Н., Шуба С.А., Федотова М.Ф., Степанов А.Л., Стрелецкий Р.А. Почвенные дрожжи и их роль в прорастании семян. Почвоведение, 2017. – № 5. – С. 592-602.
12. Орлов, Д.С. Практикум по химии гумуса / Д.С. Орлов, Л.А. Гришина. – М.: Изд-во МГУ, 1981. – 272 с
13. Саурбаева Б.С., Иващенко Е.Н., Рамазанова Р.А., Тантыбаева Б.С., Болатқан Д.Қ., Акимбаева Н.О. Получение модифицированного сорбента из гуминовых веществ бурого угля Кендырлыкского месторождения // Вестник ВКТУ. 2023.№1 С 204-212 DOI 10.51885/1561-4212_2023_1_204
14. Аввакумова Н.П., Кривопалова М.А., Глубокова М.Н., Катунина Е.Е., Жданова А.В. Гуминовые вещества как регуляторы экологического гомеостаза. Известия Самарского научного центра Российской академии наук, №2(2). – 2016. – С. 267-271.
15. Лиштван И.И., Капуцкий Ф.Н., Янута Ю.Г., Абрамец А.М., Монич Г.С., Навоша Ю.Ю., Стригуцкий В.П., Глухова Н.С., Алейникова В.Н. Гуминовые кислоты спектральный анализ и структура фракций, Вестник БГУ. – Сер. 2. – 2012. – № 1.