https://doi.org/10.58805/ct.V.1(32)-3

COMPARATIVE STUDY OF THE PURIFICATION OF FULVIC ACID OBTAINED FROM AMMONIUM HUMATE USING CARBON SORBENTS

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Received: 29 June 2026
Accepted: 16 September 2026
Published: 30 September 2026
Citation: M.K. Kazankapova, et al. « COMPARATIVE STUDY OF THE PURIFICATION OF FULVIC ACID OBTAINED FROM AMMONIUM HUMATE USING CARBON SORBENTS ». Chemical Technology, vol. 1, no. 32, Sept. 2026, doi: https://doi.org/10.58805/ct.V.1(32)-3
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This study investigates the purification of fulvic acid obtained from humic substances derived from oxidized brown coal using carbon sorbents derived from Kazakhstani coals. Fulvic acid was obtained by acidification of ammonium humate with a 5% nitric acid solution, followed by purification using sorbents produced from Shubarkol and Shoptykol coals, coconut activated carbon, KU-2-8 cation-exchange resin, and membrane dialysis. Ion chromatographic analysis showed that the combined purification process effectively reduced the concentrations of major inorganic ions. Nitrate and potassium removal exceeded 97% for all investigated sorbents, with the highest removal efficiencies being obtained using the Shubarkol sorbent (99.33% and 99.67%, respectively). Shoptykol showed the highest removal efficiency for Mg^{2+} (89.16%), whereas coconut activated carbon provided the highest removal efficiencies for SO_4^{2-} (67.72%) and Ca^{2+} (85.02%). The FA concentration after purification remained at 100–103 mg/L compared with 120 mg/L in the initial sample, corresponding to a retention of approximately 83–86% of the initial FA concentration. FTIR and ^1H NMR analyses indicated changes in the relative contributions of oxygen-containing, aliphatic, and aromatic structural fragments after purification. The results demonstrate that the combination of carbon sorption, KU-2-8 cation exchange, and membrane dialysis is an effective approach for reducing inorganic impurities while preserving the main fulvic acid fraction. Among the investigated sorbents, Shubarkol and Shoptykol demonstrated promising performance for the purification of fulvic acid obtained from ammonium humate.

Keywords: humic substances, fulvic acid, adsorption, membrane purification, inorganic ion removal, dialysis.

АММОНИЙ ГУМАТЫНАН АЛЫНҒАН ФУЛЬВОҚЫШҚЫЛДЫ КӨМІРТЕКТІ СОРБЕНТТЕРДІ ПАЙДАЛАНА ОТЫРЫП ТАЗАРТУДЫ САЛЫСТЫРМАЛЫ ЗЕРТТЕУ

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Жұмыс Қазақстан көмірлері негізінде дайындалған көміртекті сорбенттерді пайдалана отырып, тотыққан қоңыр көмірден алынған гуминді заттардан бөлінген фульвоқышқылын тазартуға арналған. Фульвоқышқылы аммоний

гуматын 5%-дық азот қышқылы ерітіндісімен қышқылдандыру арқылы алынып, кейіннен Шұбаркөл және Шөптікөл кен орындарының көмірлерінен алынған сорбенттер, кокос белсендірілген көмірі, КУ-2-8 катионалмастырғыш шайыры және мембраналық диализ көмегімен тазартылды. Иондық хроматографиялық талдау кешенді тазарту үдерісінің негізгі бейорганикалық иондардың концентрациясын тиімді төмендеткенін көрсетті. Барлық зерттелген сорбенттер үшін нитрат және калий иондарын жою дәрежесі 97%-дан жоғары болды, бұл ретте ең жоғары тазарту тиімділігі «Шұбаркөл» сорбентін қолдану кезінде байқалды және сәйкесінше 99,33% және 99,67%-ды құрады. «Шөптікөл» сорбенті Mg^{2+} иондарын ең жоғары дәрежеде жоюды көрсетті (89,16%), ал кокос негізіндегі белсендірілген көмір SO_4^{2-} (67,72%) және Ca^{2+} (85,02%) иондарын жою бойынша ең жоғары көрсеткіштерді қамтамасыз етті. Тазартудан кейінгі фульвоқышқылдардың концентрациясы бастапқы үлгідегі 120 мг/л мәнімен салыстырғанда 100–103 мг/л деңгейінде сақталды, бұл бастапқы фульвоқышқылдардың шамамен 83–86%-ының сақталғанын көрсетеді. FTIR және ^{1}H NMR талдаулары тазартудан кейін құрамында оттегі бар, алифатты және ароматты құрылымдық фрагменттердің салыстырмалы үлесінің өзгергенін көрсетті. Алынған нәтижелер көміртекті материалдардағы сорбцияны, КУ-2-8 ионалмастырғыш шайырындағы ион алмасуды және мембраналық диализді үйлестіру бейорганикалық қоспалардың мөлшерін төмендету және фульвоқышқылдардың негізгі фракциясын сақтау тұрғысынан тиімді тәсіл болып табылатынын көрсетті. Зерттелген сорбенттердің ішінде «Шұбаркөл» және «Шөптікөл» көмірлері негізіндегі материалдар аммоний гуматынан алынған фульвоқышқылдарды тазартуда жақсы нәтижелер көрсетті.

Түйін сөздер: гуминді заттар, фульвоқышқылы, адсорбция, мембраналық тазарту, бейорганикалық иондарды жою, диализ.

СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ ОЧИСТКИ ФУЛЬВОКИСЛОТЫ, ПОЛУЧЕННОЙ ИЗ ГУМАТА АММОНИЯ, С ИСПОЛЬЗОВАНИЕМ УГЛЕРОДНЫХ СОРБЕНТОВ

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Работа посвящена очистке фульвокислот, выделенных из гуминовых веществ, полученных из окисленного бурого угля, с использованием углеродных сорбентов на основе углей Казахстана. Фульвокислоту получали путем подкисления гумата аммония 5%-ным раствором азотной кислоты с последующей очисткой с применением сорбентов из углей месторождений Шубарколь, Шоптыколь и кокосового активированного угля, катионообменной смолы КУ-2-8 и мембранного диализа. Ионно-хроматографический анализ показал, что комплексный процесс очистки эффективно снижает концентрации основных неорганических ионов. Для всех исследованных сорбентов степень удаления нитрат- и калий-ионов превышала 97%, при этом наибольшая эффективность очистки была достигнута при использовании сорбента «Шубарколь» и составила 99,33% и 99,67% соответственно. Сорбент «Шоптыколь» продемонстрировал наибольшую степень удаления ионов Mg^{2+} (89,16%), тогда как активированный уголь из кокосового сырья обеспечил наиболее высокую степень удаления ионов SO_4^{2-} (67,72%) и Ca^{2+} (85,02%). Концентрация фульвокислот после очистки сохранялась на уровне 100–103 мг/л по сравнению со 120 мг/л в исходном образце, что соответствует сохранению примерно 83–86% исходного содержания фульвокислот. Анализ методом FTIR и ^{1}H NMR продемонстрировал изменения в относительном содержании кислородсодержащих, алифатических и ароматических структурных фрагментов после очистки. Полученные результаты свидетельствуют о том, что сочетание сорбции на углеродных материалах, ионного обмена на смоле КУ-2-8 и мембранного диализа является эффективным подходом к снижению содержания неорганических примесей при сохранении основной фракции фульвокислот. Среди исследованных сорбентов материалы «Шубарколь» и «Шоптыколь» показали хорошие результаты при очистке фульвокислот, полученных из гумата аммония.

Ключевые слова: гуминовые вещества, фульвокислота, адсорбция, мембранная очистка, удаление неорганических ионов, диализ.

Introduction. The molecular structure and origin of humic substances have been widely studied over the past two centuries. Humic and fulvic acids are formed during the decomposition and transformation of natural organic matter under various environmental conditions. Humic and fulvic acids can be extracted from natural sources in a variety of ways. As a rule, FA and HA are extracted from natural humic raw materials by successive alkalization and acidification. Thus, alkalization extracts humic and fulvic acids together, and acidification helps separate humic acids from fulvic acids. Next, the raw products are washed with water to remove salts formed as a result of the acid-base reaction. Isolation of FAs in high yields is difficult because they are soluble in both acidic and basic environments. In addition, acidic solutions of fulvic acids contain undesirable substances derived from other acid-soluble particles or sources of humic substances. Sources of humic substances may also contain radioactive compounds associated with fulvic acids, raising further concerns about large-scale use of FAs. Moreover, FA and HA molecules have almost identical polar functional groups, which complicates their separation and purification. Therefore, the purification of fulvic acids is becoming increasingly important for their potential use in the pharmaceutical and industrial sectors. Many methods have been discovered for the isolation and purification of fulvic acids; however, it is difficult to obtain pure FAs due to low extraction yields, environmental instability, and complex and labor-intensive purification procedures [1-3].

Fulvic acids are defined as the colored fraction of humus remaining in solution after separation of humic acids, soluble in dilute acid and alkali, or soluble in water at any pH value [4]. Fulvic acid can bind metal ions through complexation, forming chelate-like complexes. Fulvic acid can participate in redox processes and exhibits buffering capacity due to the presence of ionizable functional groups.

H umic and fulvic acids are complex mixtures of naturally occurring substances that are commonly isolated from natural raw materials. However, the purity of the isolated fulvic acid is very low. The isolation and purification of highly pure fulvic acid are often expensive processes [5-7].

Fulvic acids have attracted considerable attention due to their diverse physicochemical and biological properties and their potential applications in the pharmaceutical, agricultural, cosmetic, and industrial sectors. However, the isolation and purification of fulvic acids remain challenging because of the complexity of humic-derived mixtures and the presence of inorganic and low-molecular-weight impurities [8, 9].

Recently, carbon-based sorbents have attracted significant attention due to their high surface area, tunable porosity, and strong adsorption properties. In particular, sorbents derived from coal and carbon-rich natural materials demonstrate excellent efficiency in removing organic impurities from complex mixtures. Their surface functional groups and porous structure make them promising materials for the selective purification of fulvic acids from humic-derived solutions. Therefore, the use of carbon sorbents based on Kazakhstan coals represents a promising approach to improve the purity and quality of fulvic acid products while maintaining environmentally friendly and cost-effective processing conditions [10-14].

Previous studies of our research group have focused on the isolation and purification of fulvic acid obtained from oxidized brown coal. In the earlier study reported at HIT-2022, the ionic composition of fulvic acid obtained from Maikuben oxidized brown coal was investigated at an earlier stage of purification using carbon sorbents based on Shubarkol and Shoptykol coals [15]. A subsequent study presented at HIT-2024 further examined the extraction and purification of fulvic acid from Sarykol oxidized brown coal using the Forsyth approach, including adsorption, ion-exchange purification and dialysis [16]. The 2024 study published in Vestnik KazUTB investigated fulvic acid obtained from potassium humate prepared from Maikuben oxidized brown coal and characterized the purified samples using acid-base titration, ion chromatography, FTIR and NMR spectroscopy [17]. Another study published in 2025 examined the physicochemical properties of fulvic acid solutions after purification [18].

The present study differs from these previous investigations in the starting humate and experimental dataset. In the present work, fulvic acid obtained from ammonium humate is comparatively purified using Shubarkol, Shoptykol and coconut carbon sorbents followed by KU-2-8 ion-exchange treatment and membrane dialysis. Particular attention is given to the changes in ionic composition and functional-group characteristics after the complete purification sequence.

The aim of this study was to comparatively evaluate the purification of fulvic acid obtained from ammonium humate using carbon sorbents derived from Shubarkol and Shoptykol coals and coconut activated carbon, followed by KU-2-8 cation-exchange treatment and membrane dialysis, with particular emphasis on

changes in ionic composition and functional-group characteristics.

Materials and methods. The following reagents and equipment were used: 0.1 N HCl, 0.1 N NaOH, 5% HNO_3, acetone, KU-2-8 cation exchanger, ammonium humate, distilled water, laboratory centrifuge TsN-12, laboratory stirrer IKA RH «basic 2», rotary evaporator RV 3 IKA, ion chromatograph «Dionex» ICS 6000, FT-IR spectrometer Nicolet iS10, JEOL ECA-500 MHz NMR spectrometer.

Oxidized lignite from the Sarykol deposit was used as the raw material for humate production. The particle-size distribution was characterized by D10 = 2.95 μm, D50 = 63.8 μm, and D90 = 452 μm, with the following characteristics, expressed on a dry basis (wt%): A^d (ash content) 66.09; W^r (total moisture) 5.73; V^d (volatile matter) 17.78 and elements: S 0.71; C 21.01; H 1.68; N 2.09, Na 0.61, Al 0.89, K 0.58, Ca 0.31, Ti 0.22, Fe 1.11, Zr 0.08. The X-ray diffraction phase composition of the sample allowed to distinguish halloysite ($Al_2Si_2O_5(OH)_4$), silica (SiO_2), and albite ($NaAlSi_3O_8$).

The preparation of ammonium humate from oxidized coal by an electrophysical process consisted of several stages. First, crushed oxidized Sarykol coal was subjected to intensive oxidation and dispersion in atmospheric oxygen using an RPA at 50 °C. The coal particles were reduced to an ultrafine state and homogenized in the presence of a 3% aqueous ammonia solution for 20 min. After treatment in the RPA, the resulting mass was transferred to extraction tanks and held for 1 h. The aged solution was subsequently subjected to ultrasonic dispersion for 25 min [19].

Shubarkol and Shoptykol coal-based adsorbents (Kazakhstan) and coconut activated carbon Extrasorb GAC (India) were used for the purification of fulvic acid. To obtain fulvic acid, the ammonium humate solution was mixed with a 5% aqueous nitric acid solution and acidified to pH 1–2. The mixture was stirred for 30 min and then centrifuged at 3000 rpm for 30 min to separate humic acids from the fulvic acid fraction. During centrifugation, humic acids precipitated at the bottom, while fulvic acids remained in the aqueous phase. The resulting fulvic acid solution was then subjected to the purification procedure.

Experimental reproducibility and purification conditions. The purification experiments were performed in three independent replicates. In each experiment, 100 mL of the fulvic acid solution was passed through 5.0 g of carbon sorbent (Shubarkol, Shoptykol, or coconut activated carbon), corresponding to a sorbent-to-solution ratio of 50 g/L. The adsorption purification was carried out for 60 min at room temperature under continuous contact with the carbon sorbent.

Following the carbon adsorption stage, the resulting fulvic acid solution was subjected to cation-exchange purification using KU-2-8 cation-exchange resin. Approximately 10 g of KU-2-8 resin was used for 100 mL of solution. The ion-exchange purification was carried out at a flow rate of approximately 1 mL/min for 60 min.

The final purification stage was performed by membrane dialysis. The fulvic acid solution obtained after carbon adsorption and cation-exchange purification was placed in a dialysis membrane and dialyzed against distilled water for 24 h. The dialysis medium was replaced every 4–6 h to maintain the concentration gradient and facilitate the removal of residual inorganic ions and low-molecular-weight impurities.

All analytical measurements were performed in three replicates. The results are expressed as mean ± standard deviation (SD).

Results and discussion. The Shubarkol and Shoptykol sorbents were produced by the Institute of Coal Chemistry and Technology LLP. Their technical and physicochemical characteristics are presented in Table 1.

Table 1 – Characteristics of the coal-based adsorbents from the «Shubarkol» (1) and «Shoptykol» (2) deposits

№;	W^r_t,%	A^r,%	V^d, %	V_{Σ}; (water), cm^3/g	ρ_{bulk}, g/cm^3	$pH_{aqueous\ extract}$	$A_{m.o.}$, mg/g	$A_{m.b.}$, mg/g	A_{iodine}; %	S_{BET}; m^2/g
1	28.52	11.25	12.20	0.58	0.68	9.00	21.0	185.0	40.64	1130.613
2	26.49	24.91	14.94	1.1	0.60	9.18	66.5	210.0	34.29	926.67

Characteristics of coconut activated carbon Extrasorb GAC (12x40) are presented in Table 2.

Content of functional groups of the initial fulvic acid, mmol/g: carboxyl – 0.018; phenolic – 0.571; total

acidity – 0.589. The contents of the functional groups after purification are presented in Table 3. Compared with the initial FA sample, the content of carboxyl groups after purification increased by 5–9 times, while the contents of phenolic groups and total acidity decreased by approximately 3–4 and 1.7–2.4 times, respectively (Table 3).

Table 2 – Characteristics of coconut activated carbon Extrasorb GAC (12x40)

Characteristic	Value
Appearance	black irregular granules
Particle size, mm	
less than 0.425	not more than 3 %
0.425-1.7	not less than 94 %
more than 1.7	not more than 3 %
Adsorption activity for iodine, mg/g	not less than 1000
Total pore volume in water, cm^3/g	0.81
Sorption capacity for methylene blue, mg/g	not less than 240
Abrasion, %	not more than 2
Humidity, %	not more than 5
Ash content, %	not more than 3
Bulk density, g/l	485

Table 3 – Functional groups of samples

№	Name	Carboxyl group, mmol/g	Phenolic group, mmol/g	Total acidity, mmol/g
1	Initial FA before purification	0.018	0.571	0.589
2	FA after purification with coconut activated carbon	0.136	0.157	0.293
3	FA after purification with coconut activated carbon and cation exchanger KU-2-8	0.157	0.148	0.305
4	FA after treatment with coconut activated carbon, cation exchanger KU-2-8 and membrane dialysis	0.161	0.181	0.342
5	FA after purification with the sorbent Shoptykol	0.106	0.180	0.286
6	FA after purification with the Shoptykol sorbent and the KU-2-8 cation exchanger	0.118	0.163	0.281
7	FA after treatment with Shoptykol sorbent, cation exchanger KU-2-8 and membrane dialysis	0.125	0.162	0.287
8	FA after purification with the sorbent Shubarkol	0.089	0.156	0.245
9	FA after purification with the Shubarkol sorbent and the KU-2-8 cation exchanger	0.094	0.193	0.287
10	FA after treatment with Shubarkol sorbent, cation exchanger KU-2-8 and membrane dialysis	0.120	0.187	0.307

The results show an increase in the carboxyl-group content after the purification steps, accompanied by a decrease in the phenolic-group content and total acidity. Table 4 shows the pH changes at each stage of fulvic acid purification.

After passing the fulvic acid solution through the KU-2-8 cation exchanger during the second purification

stage, the pH decreased. This decrease may be associated with the release of H^+ ions during cation exchange. At the final purification stage, membrane dialysis resulted in an increase in pH, which indicates the removal of ionic impurities and other low-molecular-weight components from the fulvic acid solution through diffusion into the distilled water.

Fulvic acid obtained with 5% nitric acid and ammonium humate was analyzed for the ionic composition of fulvic acid after the sorbent, after the cation exchanger and after membrane purification (dialysis) on a Dionex ICS-6000 ion chromatograph in the Nazarbayev University laboratory. Samples were filtered using a syringe filter (pore size 0.20 μm). The samples were diluted 100-fold with deionized water with a resistivity of 18.2 MΩ·cm because the concentrations of the analyzed substances were high.

Table 4 – Changes in pH at each stage of fulvic acid purification

№;	Name	pH after sorbent	pH after cation exchanger KU-2-8	pH after membrane dialysis
1	FA after Shubarkol sorbent, cation exchanger KU-2-8 and membrane dialysis	0.89	0.47	2.33
2	FA after Shoptykol sorbent, cation exchanger KU-2-8 and membrane dialysis	1.09	0.27	2.08
3	FA after coconut activated carbon, cation exchanger KU-2-8 and membrane dialysis	0.83	0.28	2.75

The concentrations of inorganic ions in the fulvic acid solutions before and after the complete purification procedure are presented in Table 5. The purification efficiency was calculated using the equation:

$$Removal \quad efficiency(\%) = \frac{C_0 - C_f}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of the corresponding ion and C_f is its concentration after purification. The calculated values characterize the decrease in the concentration of inorganic ions in the fulvic acid solution.

Table 5 – Concentrations and removal efficiencies of inorganic ions in fulvic acid samples

Name	Concentration (C), ppm							
	Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Initial FA before purification	35.4473	71.4420	23821.9014	57.0635	14.1041	1520.9613	7.8783	50.6674
FA after Shubarkol sorbent, cation exchanger KU-2-8 and membrane dialysis								
FA after purification	14.8971	33.5257	159.5939	10.2114	3.1870	5.0733	1.1816	9.9496
Removal efficiency (%)	57.97	53.07	99.33	82.11	77.40	99.67	85.00	80.36
FA after Shoptykol sorbent, cation exchanger KU-2-8 and membrane dialysis								
FA after purification	17.1516	25.2961	240.1812	13.9942	7.6091	13.0994	0.8539	11.2097
Removal efficiency (%)	51.61	64.59	98.99	75.48	46.05	99.14	89.16	77.88
FA after coconut activated carbon, cation exchanger KU-2-8 and membrane dialysis								
FA after purification	34.1742	23.0595	577.3391	23.5595	13.8716	18.8476	1.4937	7.5924
Removal efficiency (%)	3.59	67.72	97.58	58.71	1.65	98.76	81.04	85.02
Commercial fulvic acid product “Golden Elixir” (Bashkortostan)								
FA	12.3768	55295.4308	-	321.1675	17.2597	16734.6703	1.4400	14.8665

A comparison of the three sorbents shows that all investigated purification systems were highly effective in reducing nitrate and potassium ions, with removal efficiencies exceeding 97% in all cases. The highest nitrate and potassium removal efficiencies were obtained using the Shubarkol sorbent, reaching 99.33% and 99.67%, respectively. Shoptykol demonstrated the highest removal efficiency for Mg^{2+} (89.16%) among the investigated sorbents, whereas coconut activated carbon showed the highest removal efficiencies for Ca^{2+}

(85.02%) and SO_4^{2-} (67.72%). At the same time, the lowest removal efficiencies for Cl^- (3.59%) and NH_4^+ (1.65%) were observed for coconut activated carbon. These differences indicate that the physicochemical and porous characteristics of the sorbents may influence their affinity toward individual inorganic ions.

For comparison, the ionic composition of the commercial fulvic acid product "Golden Elixir" from Bashkortostan was also analyzed. The commercial sample contained substantially higher concentrations of SO_4^{2-} and K^+ (55,295.43 and 16,734.67 ppm, respectively) than the purified laboratory samples. The concentrations of SO_4^{2-} in the Shubarkol-, Shoptykol- and coconut-purified samples were 33.53, 25.30 and 23.06 ppm, respectively, while the corresponding K^+ concentrations were 5.07, 13.10 and 18.85 ppm. These results indicate substantially lower residual concentrations of SO_4^{2-} and K^+ in the laboratory-purified samples compared with the commercial sample. However, direct conclusions regarding the overall purity or production technology of the commercial product cannot be made solely on the basis of ionic composition, because commercial and laboratory samples may differ in formulation, concentration and manufacturing process.

Overall, the obtained results demonstrate that the combined purification sequence consisting of carbon sorption, KU-2-8 cation exchange and membrane dialysis effectively reduces the concentrations of major inorganic ions present in the fulvic acid solutions. Among the tested sorbents, Shubarkol showed the highest removal efficiencies for NO_3^- and K^+, while Shoptykol and coconut activated carbon demonstrated higher removal efficiencies for selected ions, particularly Mg^{2+}, SO_4^{2-} and Ca^{2+}. Therefore, Shubarkol and Shoptykol carbon sorbents can be considered promising materials for further investigation of coal-derived fulvic acid purification.

The IR spectrum of the original fulvic acid obtained from ammonium humate is shown in Fig. 1 (1). No pronounced C=O stretching band was observed in the spectrum. Therefore, the contribution of carbonyl-containing groups appears to be relatively low in the initial sample. A broad band at 3230 cm^{-1} can be attributed to O–H stretching vibrations associated with hydrogen bonding. The bands at 1410 and 1338 cm^{-1} may be associated with a combination of O–H bending, CH_2 and CH_3 deformation, C–H bending in alkenes, C–N stretching in carboxamide groups, and symmetric stretching vibrations of the $–COO^-$ group. The absence of a pronounced asymmetric $–COO^-$ stretching band in the 1650–1550 cm^{-1} region should also be noted. The band at 872 cm^{-1} may be assigned to out-of-plane deformation vibrations of C–H groups in substituted aromatic structures.

The IR spectrum of fulvic acid purified using the Shubarkol sorbent is shown in Fig. 1 (2). The spectrum is generally similar to that of the initial fulvic acid, but a distinct C=O stretching band appears at 1716 cm^{-1}, which may be associated with carbonyl groups of carboxylic acids, ketones, or related structures. A band at 1635 cm^{-1} can be attributed to C=C stretching vibrations. Broad absorption in the 3000–3650 cm^{-1} region corresponds to O–H stretching vibrations of different hydroxyl groups. The bands at 1338 and 1417 cm^{-1} may be associated with CH_2 and CH_3 bending vibrations, C–H bending in alkenes, and C–O stretching vibrations.

The IR spectrum of fulvic acid purified using the Shoptykol sorbent is shown in Fig. 1 (3). The spectrum is similar to that obtained after purification with the Shubarkol sorbent; however, the bands at 1716 and 1616 cm^{-1}, corresponding to C=O and C=C stretching vibrations, respectively, are less intense. A broadening of the bands around 1400 cm^{-1}, accompanied by decreased intensity, and in the 1312–1350 cm^{-1} region is also observed. These bands may be associated with CH_2 and CH_3 bending vibrations, C–H bending in alkenes, and C–O stretching vibrations. The band at 1149 cm^{-1} may be attributed to C–O–C stretching vibrations.

The IR spectrum of fulvic acid purified using the coconut activated carbon is shown in Fig. 1 (4). Only a weak broad O–H absorption band is observed in the 3000–3500 cm^{-1} region. Bands at approximately 1700 and 1600 cm^{-1} can be attributed to C=O and C=C stretching vibrations, respectively. The bands in the 1339–1457 cm^{-1} region may be associated with CH_2 and CH_3 bending vibrations, C–H bending in alkenes, and C–O stretching vibrations. The IR spectrum of the commercial fulvic acid product «Golden Elixir» from Bashkortostan shows a broad O–H stretching band in the 3000–3650 cm^{-1} region, associated with hydrogen-bonded hydroxyl groups.

The band at 1713 cm^{-1} may be attributed to C=O stretching vibrations of carboxylic acids, ketones, and related carbonyl-containing structures. The absorption bands in the 1600–1700 cm^{-1} region may include contributions from aromatic C=C stretching and other overlapping vibrations. The bands in the 1390–1100 cm^{-1} region may be associated with CH_2 and CH_3 bending vibrations, C–H bending in alkenes,

symmetric stretching vibrations of –COO^- groups, and C–O stretching vibrations. The band at 1038 cm^{-1} may be attributed to C–O stretching vibrations in polysaccharide or polysaccharide-like structures. The band at 885 cm^{-1} may correspond to out-of-plane C–H deformation vibrations in substituted aromatic structures, while the band at 575 cm^{-1} may be associated with out-of-plane bending vibrations of aromatic –(CH)n– groups.

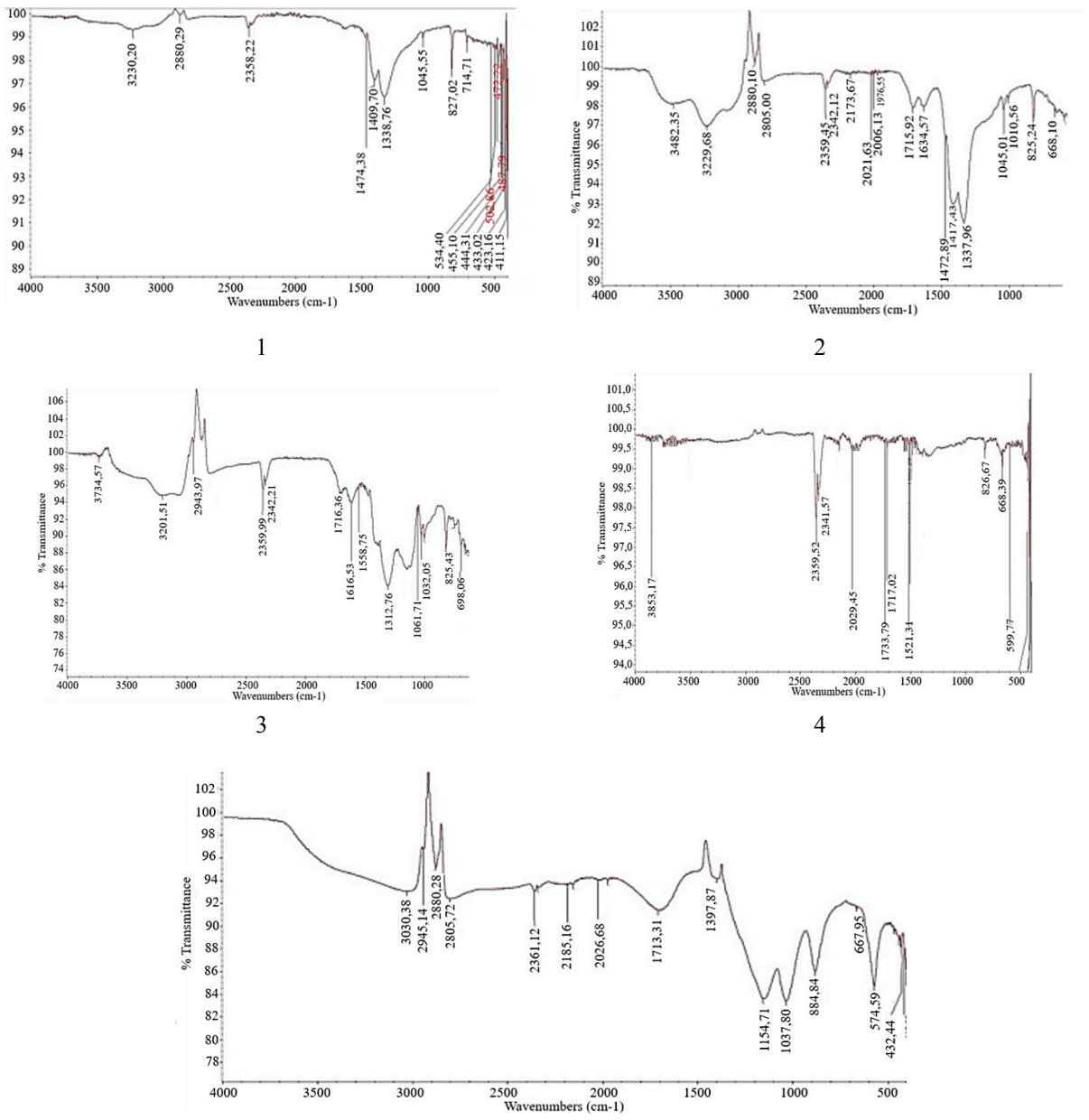

Fig. 1 - FTIR spectra of fulvic acid obtained from ammonium humate: 1 – initial sample; 2 – after purification with Shubarkol sorbent; 3 – after purification with Shoptykol sorbent; 4 – after purification with coconut activated carbon; 5 – commercial fulvic acid product «Golden Elixir» (Bashkortostan).

The ^{1}H NMR spectrum of the initial fulvic acid obtained from ammonium humate was analyzed to identify the main proton environments associated with aliphatic, oxygenated and aromatic structural fragments. NMR analysis of fulvic acid was performed using a JEOL ECA-500 MHz NMR spectrometer. In the ammonium salt sample, intense resonances of aromatic and heteroaromatic protons (6.96-7.18 ppm) are observed in the initial sample (Fig. 2), while resonances in the aliphatic region of the spectrum are significantly less intense, suggesting a relatively high contribution of aromatic and heteroaromatic proton environments. The

use of the Shubarkol sorbent leads to a decrease in the content of polyaromatic groups compared with aliphatic and other functional substituents, and the spectrum contains signals attributable to terminal saturated hydrocarbon groups (0.81-1.52 ppm), aliphatic protons in the α-position to aromatic, alkenyl and carbonyl groups (1.94-2.22 ppm), aliphatic protons in ester groups and in the α-position relative to OH and OR groups, as well as aliphatic OH protons (2.81-3.62 ppm). In the sample after treatment with the Shoptykol sorbent, a similar picture is observed, although the intensity of the signals of aliphatic protons in ester groups and in the α-position to the OH and OR groups, as well as aliphatic OH protons (approximately 3.00-4.00 ppm) is significantly lower compared to the sample after treatment with Shubarkol sorbent. A similar pattern is also observed in the sample treated with coconut activated carbon.

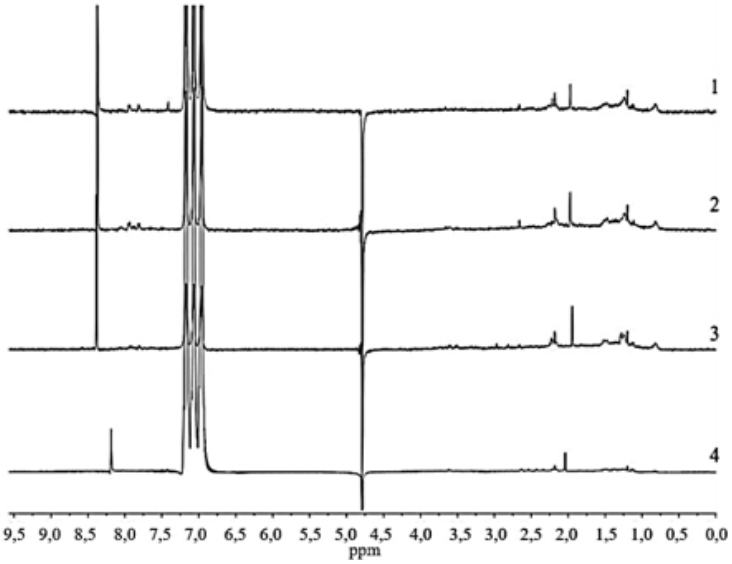

Fig. 2 - Comparison of the H NMR spectra of fulvic acid obtained from ammonium humate: 1 - initial sample 2 - after purification with Shubarkol sorbent 3 - after purification with Shoptykol sorbent 4 - after purification with coconut activated carbon

Compared with the previously described samples, the commercial “Golden Elixir” sample showed (Fig. 3) a higher ratio of aliphatic and O–H signals to aromatic and heteroaromatic signals, particularly in the 3.00–4.00 ppm region.

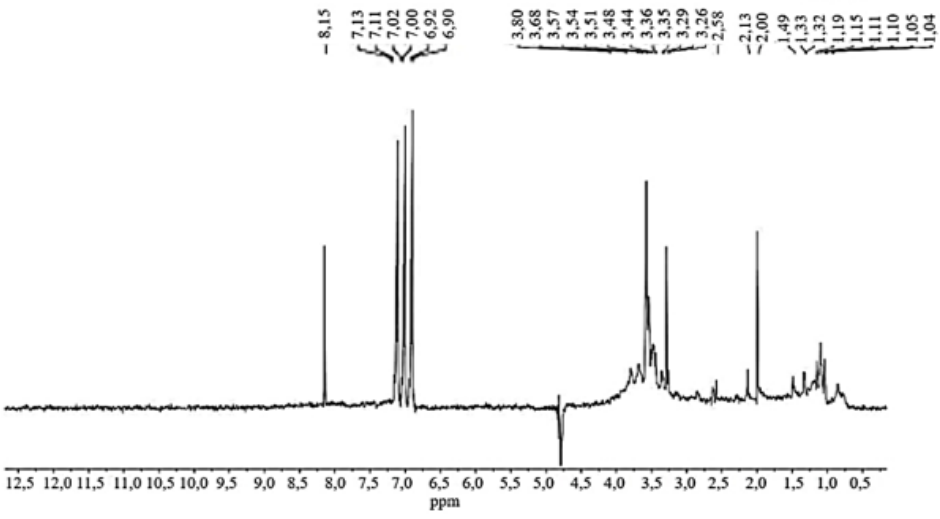

Fig. 3 - H NMR spectra of fulvic acid «Golden Elixir» (Bashkortostan)

Titration curves for the isolated fulvic acid samples were constructed based on pH-metric measurements,

and the pK values were determined using the appropriate equations. Table 6 presents the pK values of fulvic acid purified using different sorbents.

Table 6 – pK values and fulvic acid concentrations

№;	Name	pK values	Concentration, mg/l
1	Initial FA before purification	7.58	120
2	FA after Shubarkol sorbent, cation exchanger KU-2-8 and membrane dialysis	7.97	100
3	FA after Shoptykol sorbent, cation exchanger KU-2-8 and membrane dialysis	6.77	103
4	FA after coconut activated carbon, cation exchanger KU-2-8 and membrane dialysis	12.49	101

The obtained titration data indicate that the purification procedure affected the acid–base properties of the fulvic acid samples. The initial FA showed a pK value of 7.58, while after sequential purification with carbon sorbents, KU-2-8 cation-exchange resin, and membrane dialysis, the pK values were 7.97, 6.77, and 12.49 for Shubarkol, Shoptykol, and coconut activated carbon, respectively. These differences may be related to changes in the relative contribution of ionizable functional groups and the removal of inorganic ions and low-molecular-weight compounds during purification.

The initial FA concentration was 120 mg/L, while the purified samples contained 100, 103, and 101 mg/L for Shubarkol, Shoptykol, and coconut activated carbon, respectively. Thus, approximately 83–86% of the initial FA concentration was retained after purification, indicating relatively low losses of the target fraction. The similar final concentrations demonstrate comparable purification performance of the investigated sorbents, while their different pK values indicate differences in the acid–base characteristics of the resulting FA fractions.

Spectral analysis showed characteristic absorption maxima at 360, 450, 610, and 800 nm in the 320–1000 nm range. These spectral features reflect the chromophoric structures of fulvic substances and provide additional evidence of changes in their chemical characteristics following purification.

Conclusion. A comparative purification study of fulvic acid obtained from ammonium humate was performed using Shubarkol, Shoptykol, and coconut activated carbon, followed by KU-2-8 cation exchange and membrane dialysis. The results demonstrated that the combined purification procedure substantially reduced the concentrations of major inorganic ions while retaining 83–86% of the initial fulvic acid concentration.

Shubarkol showed the highest removal efficiencies for NO_3^- and K^+, reaching 99.33% and 99.67%, respectively. Shoptykol demonstrated the highest removal of Mg^{2+} (89.16%), whereas coconut activated carbon showed the highest removal of SO_4^{2-} (67.72%) and Ca^{2+} (85.02%). FTIR and ^1H NMR analyses indicated changes in the relative contributions of functional groups and structural fragments. The pK values also changed after purification, indicating differences in the acid–base characteristics of the resulting FA fractions.

Overall, the combination of carbon adsorption, KU-2-8 cation-exchange treatment, and membrane dialysis can be considered an effective approach for the purification of fulvic acid obtained from ammonium humate. Shubarkol and Shoptykol sorbents demonstrated particularly promising performance and can be considered for further development and optimization of FA purification processes.

Acknowledgement. *This research has been funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. BR34637102 "Development and implementation of technology for the integrated transformation of coal and coal waste, aimed at ensuring sustainable development and improving environmental safety").*

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