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Article

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Synthesis and Study of the Properties of a Composite Material Based on Sulfohumic Acid and Multi-Walled Carbon Nanotubes

A composite sorption material based on sulfohumic acid (SHA) and multi-walled carbon nanotubes (MWCNTs) was synthesized. The composite was obtained via ultrasonic-enhanced coprecipitation, which ensures the efficient incorporation of nanotubes into the sulfohumic matrix. The structural and physicochemical properties of the initial SHA and the SHA:MWCNTs composite were studied using elemental analysis, conductometric titration, infrared spectroscopy, thermogravimetric analysis, and electron microscopy. The introduction of MWCNTs was shown to alter the surface morphology, increase roughness, and form a more developed porous structure. Thermogravimetric analysis indicates increased thermal stability of the composite material. The sorption properties of the synthesized composite with respect to Cu^{2+} ions from aqueous solutions were also studied. It was established that the SHA:MWCNTs composite possesses higher sorption capacity compared to the original SHA. Analysis of sorption isotherms revealed that the process is predominantly described by the Langmuir model, while satisfactory agreement with the Freundlich model indicates the energetic heterogeneity of the sorbent surface. These results demonstrate the potential of the SHA:MWCNTs composite as an effective sorption material for removing heavy metal ions from aqueous solutions.

Keywords: natural polymer, composite, sulfohumic acid, multi-walled carbon nanotubes, modification, ultrasound, sorbent, sorption

Introduction

Water pollution with heavy metals remains a serious global problem. Researchers are devoting considerable attention to the development of effective sorption materials for the extraction of heavy metal ions from aqueous solutions [1–4]. One promising area is the creation of composite sorbents incorporating carbon nanomaterials with a developed surface area and unique physicochemical properties [5–7].

Among the various types of carbon nanomaterials, multi-walled carbon nanotubes (MWCNTs) are of particular interest. These structures are cylindrical nanomaterials formed by several concentric graphene layers. MWCNTs are characterized by a high specific surface area, significant mechanical strength, chemical and thermal stability, and a developed π-bond electron system. Due to these properties, carbon nanotubes can effectively participate in the adsorption of various organic and inorganic compounds [8–11].

However, the use of native carbon nanotubes in sorption systems has several limitations. The surface of unmodified nanotubes contains a relatively small number of functional groups capable of interacting with metal ions. Furthermore, nanotubes are prone to aggregation due to strong van der Waals interactions between graphene layers, which leads to a decrease in the available specific surface area and a reduction in sorption efficiency [12–14].

To improve the sorption properties of carbon nanotubes, methods of chemical modification and the formation of composite materials combining nanostructured carbon with functionally active organic compounds are widely used [9, 15, 16]. One of the most promising areas is the creation of hybrid systems based on carbon nanotubes and natural organic substances, in particular humic compounds [17, 18].

Humic acids (HA) are natural, high-molecular-weight organic substances with a complex structure, formed during the humification of organic residues. Their macromolecules include condensed aromatic fragments linked by aliphatic chains of varying degrees of branching. The structure of humic acids contains a wide range of functional groups, the most common of which are carboxyl (–COOH), phenolic hydroxyl

(–OH), carbonyl, and quinone groups. The presence of these functional centers determines the pronounced physicochemical properties of humic substances, including ion-exchange capacity, sorption activity, hydrophilicity, and the ability to complex with metal ions [19–25].

Due to the combination of hydrophobic aromatic fragments and hydrophilic functional groups, humic acids are capable of adsorbing on various surfaces and exhibiting the properties of natural surfactants. Moreover, their sorption properties can be significantly improved through chemical modification aimed at increasing the number of functional groups and ionogenic centers in the macromolecule structure [23–25].

One effective method for modifying humic acids is sulfonation, which results in the formation of sulfohumic acids. The introduction of sulfo groups ($-SO_3H$) into the structure of the humic matrix increases the content of ionogenic centers and enhances the cation-exchange capacity of the material. The resulting sulfated derivatives are characterized by more pronounced surface-active and sorption properties and can be considered promising organic ion-exchange materials. Given the low solubility of sulfohumic acids, their synthesis is of practical interest for the creation of solid-phase sorbents [26–30].

Despite the significant sorption potential of humic and sulfohumic acids, their use in individual form has certain limitations. The main disadvantages include relatively low mechanical strength, a tendency to partially dissolve in alkaline environments, and difficulties in separating the sorbent from aqueous solutions after the sorption process. Therefore, a relevant area of research is the development of composite materials in which humic substances are immobilized on the surface of various inorganic or carbon matrices [31].

In such composite systems, carbon nanotubes act as a structural framework with a high specific surface area and a developed porous structure. Humic components, in turn, provide the functional groups involved in the binding of metal ions. Interactions between humic molecules and the nanotube surface can occur through π–π interactions between the aromatic fragments of the humic structures and the graphene layers of the nanotubes, as well as through hydrogen bonds and electrostatic interactions [17, 32–34].

The creation of composite materials based on sulfohumic acid and multi-walled carbon nanotubes is of particular interest, as this combination combines the advantages of both components. Carbon nanotubes provide a high specific surface area, structural stability, and mechanical strength to the composite, while sulfohumic acid forms a layer of polyfunctional organic groups on the nanotube surface that can effectively interact with metal ions.

The presence of carboxyl, phenolic, and sulfonic functional groups in the composite structure creates a developed system of active sites capable of binding copper cations through complexation, ion exchange, and electrostatic interactions. The carbon nanostructure also increases the accessibility of active sites and prevents the aggregation of organic components, which can lead to increased efficiency of sorption processes.

The proposed composite differs from previously described sorbents based on humic acids and carbon nanotubes in that the humic matrix undergoes preliminary chemical functionalization by sulfonation, resulting in the formation of sulfated humic acid (SHA) with an increased density of oxygen-containing functional groups, including sulfone groups ($-SO_3H$). The sulfonation stage leads to targeted chemical modification of the humic matrix, accompanied by changes in the distribution of active sites, acid-base characteristics, and complexing properties of the material. This fundamentally distinguishes the developed composite from previously described sorbents.

The role of MWCNTs in the developed composite is not limited to mechanical filling alone. MWCNTs form a developed structural framework that promotes a more uniform distribution of SHA, reduces the degree of aggregation of sulfohumic macromolecules, and forms a hierarchically organized sorption structure with increased accessibility of active sites.

Thus, the scientific novelty of this work lies in the development of a new type of functionalized composite based on SHA and MWCNTs, which utilizes the synergistic effect of chemical functionalization and nanostructured reinforcement. This ensures a change in the structural and chemical organization of the sorbent and increased accessibility of functional groups compared to previously described humic nanocomposites.

Experimental

Materials and Methods

Natural polymers — humic acids (HA), isolated from oxidized coal waste from the Shubarkol deposit (Karaganda, Kazakhstan), were used as feedstock for the synthesis of composite materials [17]. Chemical modification of HA by sulfonation allowed the synthesis of their sulfonated derivatives — sulfohumic acids (SHA).

Multi-walled carbon nanotubes (MWCNTs) from Sigma Aldrich (USA, 412988-2G) were used as a composite modifier. They have the following characteristics: as-produced cathode deposit > 75 % MWCNTs basis, OD×L 7–15 nm × 0.5–10 µm. Concentrated sulfuric acid was used as the sulfonating agent. Distilled water was used to prepare solutions. Analytical-grade NaOH (0.1 M) and HCl (0.1 M) solutions were used to adjust the pH.

The functional composition of the composite materials was studied using infrared spectroscopy (FTIR). Spectra were recorded in the 400–4000 cm^{-1} range using an *FSM-1201* spectrometer (Infraspec Company, St. Petersburg, Russia). Samples were prepared using the standard potassium bromide (KBr) pressing method. The resulting spectral data were processed and approximated using *Fityk 1.3.1* software, which allowed for the isolation and identification of characteristic absorption bands corresponding to the functional groups of the composites.

The quantitative content of oxygen-containing functional groups in the composite materials was determined conductometrically using an *Anion-4100* laboratory conductometer (Infraspak-Analit, Novosibirsk, Russia). The progress of the sulfonation reaction was monitored by monitoring the functional composition of the resulting products. The total content of oxygen-containing functional groups, including carboxyl, phenolic, and sulfo groups ($\Sigma COOH+OH+SO_3H$), was determined by conductometric titration. The total concentration of functional groups was calculated based on the volume of titrant consumed to the equivalence point, taking into account its molar concentration and the mass of the test sample. The amount of introduced sulfo groups was calculated as the difference between the total content of oxygen-containing functional groups in the sulfonated product and the initial sulfohumic acid. The obtained values are expressed as mg-eq/g. Each determination was performed in three parallel experiments, after which the average values were calculated. The relative standard deviation of the results did not exceed 3–5 %.

The surface morphology of the composite materials was characterized using a *MIRA 3* scanning electron microscopy system (Tescan Orsay Holding, Brno-Kohoutovice, Czech Republic), equipped with detectors recording various signals. The resulting SEM images were used to analyze the surface morphological features.

The thermal stability of the composites was studied using differential thermal analysis (DTA) combined with thermogravimetric analysis on a *STA 6000* (Perkin Elmer, USA) synchronous thermal analyzer. Measurements were performed in the temperature range from room temperature to 900 °C under a nitrogen atmosphere, at a heating rate of 10 °C/min.

Experimental Procedure

Sulfonation of Humic Acids

A two-necked flask was charged with 100 ml of H_2SO_4 solution of varying concentrations (25, 52, and 96 %) at a 1:1 ratio of the initial components, HA:H_2SO_4. The reaction mixture was cooled to –2 °C, after which 10 g of humic acid was gradually added with continuous stirring over 40 minutes. Stirring was continued for 3 hours at room temperature (23 °C). The reaction mixture was then heated in a water bath to boiling point and maintained at this temperature for 3 hours. Upon completion of the reaction, the mixture was cooled, 500 ml of distilled water was added, and stirring was continued for another 2 hours at room temperature. The solid phase was separated from the liquid by centrifugation, after which the precipitate was thoroughly washed with copious amounts of distilled water.

Synthesis of Composite Materials Based on Humic Acids and MWCNTs

Composite materials based on sulfohumic acids (SHA) and multi-walled carbon nanotubes (MWCNTs) were synthesized via ultrasound-enhanced coprecipitation. First, a 0.25 g sample of MWCNTs was dispersed in 50 ml of distilled water. Dispersion was performed using an *IL 100-6/2* ultrasonic unit equipped with an ultrasonic generator with a magnetostrictive transducer operating at a frequency of 22 kHz and a cylindrical waveguide. The resulting MWCNTs dispersion was slowly introduced into an aqueous solution of sulfohumic acid containing 2 g of SHA with constant stirring. During mixing, the pH of the reaction system was maintained at approximately 9. After the components were completely added, the resulting suspension was further ultrasonicated for 15, 30, and 60 min to enhance interfacial interactions between the components. The reaction mixture was then stirred at 60 °C for 6 hours, which facilitated the formation of the composite structure. Upon completion, the system was acidified with an HCl solution to a pH of 2.0–2.5, resulting in the precipitation of the composite material. The resulting precipitate was separated by filtration, washed with distilled water until neutral (pH 7.0), and dried at 60 °C to constant weight. The yield of the resulting composite materials was 50–60 %.

Study of the Adsorption Properties of Composites

Sorption experiments were conducted in static mode. A 1.0 g sample of the composite was placed in a flat-bottomed flask with a ground-glass stopper, after which 100 ml of aqueous copper sulfate solutions with initial concentrations ranging from 10 to 150 mmol/L were added to each flask. The resulting systems were stirred for 24 hours on a *PE-6410* laboratory shaker (St. Petersburg, Russia) until sorption equilibrium was reached. Afterward, the sorbent was separated from the solution by filtration. The residual concentration of Cu^{2+} ions in the filtrate was determined using iCAP6500 inductively coupled plasma atomic emission spectrometry (*SPECTRO ARCOS EOP SPECTRO* Analytical instruments GmbH, Germany).

The sorption capacity of the composite with respect to the Cu^{2+} ion was calculated based on the difference in their concentrations in the solution before and after sorption:

$$A = \frac{(C_0 - C_{eq})\cdot V}{m},$$

where A — the sorption capacity of the composite (mmol/g); C_0 — the initial concentration of Cu^{2+} ions in the solution before sorption (mmol/L); C_{eq} — the equilibrium concentration of Cu^{2+} ions in the solution after sorption (mmol/L); V — the volume of the analyzed solution (L); m — the mass of the composite (g).

The elemental composition of the resulting composite materials was determined by elemental analysis (C, H, O) using an *Elementar Unicube* automated analyzer (Elementar Analysensysteme GmbH, Germany). At least three parallel measurements were performed for each sample, from which the average mass fractions of the corresponding elements were calculated.

Results and Discussion

Humic acids were sulfonated using concentrated sulfuric acid at varying concentrations. The progress of the sulfonation reaction was monitored by monitoring the functional composition of the resulting products. The results are presented in Table 1.

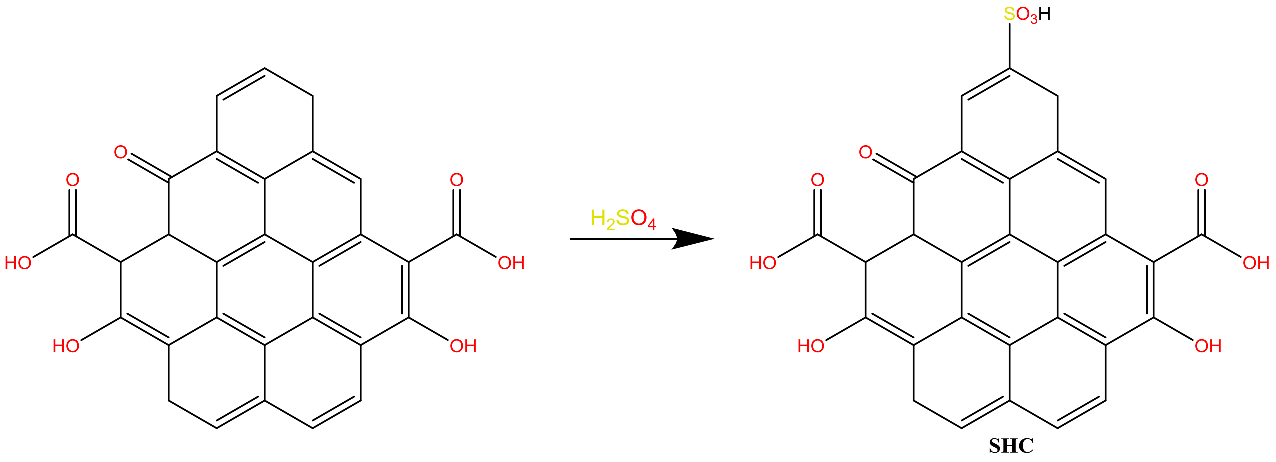
Table 1

Sulfonation of humic acids

Sample	H_2SO_4 concentration, %	$\sum$COOH+OH+SO_3H, mg-eq/g	Yield, %
HA	–	4.5±0.2	80
SHA	25	4.9±0.2	75
SHA	52	5.8±0.2	70
SHA	96	6.5±0.2	66

The study results showed that increasing the sulfuric acid concentration in the reaction system leads to an increase in the total amount of oxygen-containing functional groups in the product. Thus, when using 25 % H_2SO_4, the total content of oxygen-containing functional groups reached 4.9 mg-eq/g, and the yield of SHA was 75 %. Increasing the acid concentration to 52 % resulted in a further increase in oxygen-containing functional groups to 5.8 mg-eq/g. The highest content of oxygen-containing functional groups was achieved using 96 % H_2SO_4, where the total content of oxygen-containing functional groups increased to 6.5 mg-eq/g. However, this was accompanied by a decrease in product yield to 66 %, which is likely due to partial destruction of the humic matrix under high acidity conditions.

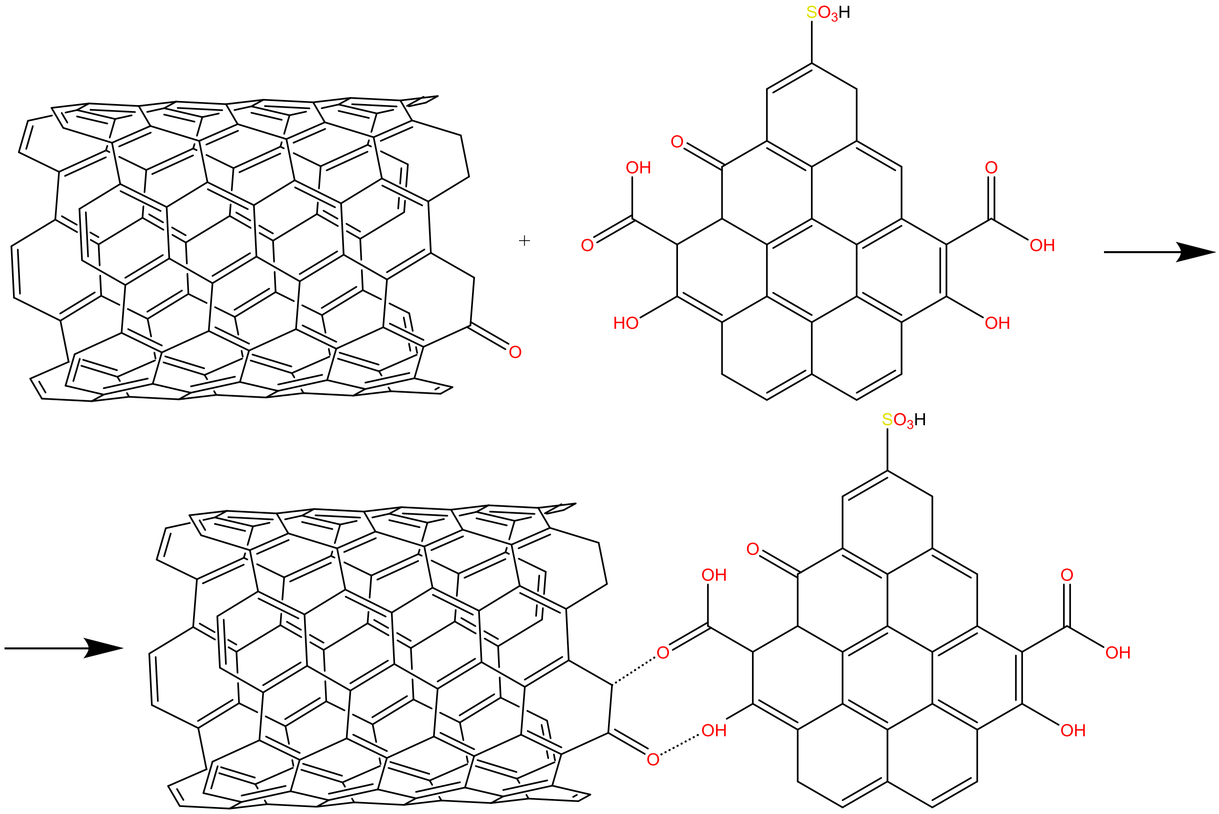
Thus, it has been established that increasing the sulfuric acid concentration in the reaction system promotes an increase in the content of oxygen-containing functional groups in the humic acid structure. The sulfonation process occurs via the mechanism of electrophilic aromatic substitution in the aromatic fragments of the humic macromolecule. In concentrated sulfuric acid, an active sulfonating agent (HSO_3^+) is formed, which acts as an electrophile and attacks the aromatic rings of the humic acid. This results in the formation of an intermediate σ-complex, followed by proton detachment and reduction of the aromatic system, forming a sulfo group (–SO_3H) in the macromolecule structure (Scheme 1).



Scheme 1. Sulfonation process in the aromatic fragments of the humic macromolecule

To obtain a composite material based on the synthesized SHC, it was further modified with multi-walled carbon nanotubes (MWCNTs) from Sigma-Aldrich (USA, 412988-2G). The formation of a composite material based on SHA and MWCNTs occurs through a complex of non-covalent interactions between the functional groups of the sulfohumin matrix and the surface of the carbon nanostructures. SHA contains aromatic fragments and oxygen-containing functional groups (–COOH, –OH, >C=O), as well as sulfonic groups (–SO_3H), capable of participating in intermolecular interactions.

The primary mechanism for SHC attachment to the MWCNTs surface is π–π stacking between the aromatic structures of the sulfohumin matrix and the graphene-like layers of the nanotubes. Additionally, the composite is stabilized due to the formation of hydrogen bonds and electrostatic interactions between the functional groups of the SHA and defective oxygen-containing centers on the surface of the MWCNTs (Scheme 2).



Scheme 2. SHC attachment to the multi-walled carbon nanotubes (MWCNTs) surface

The structural and functional characteristics of the synthesized composite material were confirmed by elemental analysis, conductometric titration, infrared spectroscopy (IR), thermogravimetric analysis (TGA), and electron microscopy.

Table 2

Elemental composition and functional characteristics of SHA and composite

Sample	C, mass. %	H, mass. %	O, mass. %	S, mass. %	Σ(COOH+OH+SO_3H), mg-eq/g	Yield, %
SHA	57.3±0.2	4.5±0.1	36.2±0.2	2.0±0.2	6.5±0.2	66
SHA:MWCNTs	61.5±0.2	4.1±0.1	32.6±0.2	1.8±0.2	5.6±0.2	75

Table 2 presents the results of elemental analysis, the total content of oxygen-containing functional groups Σ(COOH+OH+SO_3H), and the yields of the initial SHA and the synthesized composite material, allowing us to evaluate changes in the material's functional composition during the modification process.

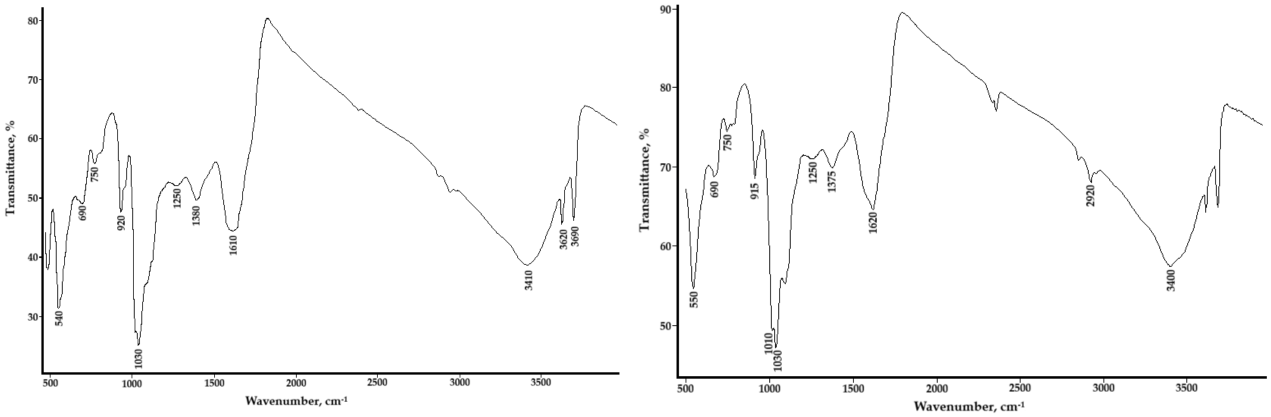
According to the elemental analysis data, the initial SHA contains 57.3 wt.% carbon, 4.5 wt.% hydrogen, 36.2 wt.% oxygen, and 2.0 wt.% sulfur. The high oxygen content is due to the presence of oxygen-containing functional groups, primarily carboxyl and phenolic ones, the total content of which is Σ(COOH+OH) = 6.5 mmol/g. The yield of the product in the production of sulfohumic acid is 66 %.

The introduction of multiwalled carbon nanotubes leads to a change in the elemental composition of the composite. For the SHA:MWCNTs sample, an increase in the carbon mass fraction to 61.5 % and a simultaneous decrease in the oxygen content to 32.6 % are observed, which is due to the introduction of a carbon nanofiller characterized by a high carbon content. The hydrogen content decreases to 4.1 %, and the sulfur content to 1.8 %.

The total content of oxygen-containing functional groups Σ(COOH+OH) for the composite is 5.6 mmol/g. This slight decrease in this value compared to the original SHA is due to the dilution of the humic matrix with carbon nanotubes. At the same time, the yield of the composite material increases to 75 %.

The obtained results indicate the formation of a composite structure in which the humic matrix, containing oxygen-containing functional groups, is combined with a carbon nanofiller. This combination can contribute to the improvement of the physicochemical and sorption properties of the synthesized material.

The composition of the SHA and the composite based on it was confirmed by IR spectroscopy (Fig. 1).



a *b*

Figure 1. IR spectra of SHA (*a*) and SHA:MWCNTs composite (*b*)

The IR spectrum of SHA exhibits a broad, intense absorption band in the 3200–3400 cm^{-1} region, corresponding to the stretching vibrations of the hydroxyl groups –OH associated with the phenolic and carboxyl fragments of the sulfohumin structure. The bands in the 2920–2850 cm^{-1} region are attributed to the stretching vibrations of the aliphatic fragments –CH_2 and –CH_3. The absorption band near 1610 cm^{-1} is primarily due to the stretching vibrations of the aromatic C=C bonds in the condensed aromatic fragments of the sulfohumin matrix, with possible overlap with the asymmetric vibrations of the carboxylate groups –COO^-. The absorption band at 1380 cm^{-1} corresponds to the symmetric stretching vibrations of the –COO^- carboxylate groups and may be partially related to the deformation vibrations of the –CH_3 aliphatic groups.

The presence of sulfonic acid groups is confirmed by absorption bands at 1220–1250 cm^{-1} and 1030–1040 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of the S=O bonds of the –SO_3H functional group. In this region, overlapping bands due to the vibrations of the C–O and S–O bonds of the oxygen-containing functional groups of the sulfohumic matrix is possible.

The spectrum of the SHA:MWCNTs composite retains the main characteristic bands of SHA, but exhibits changes in their intensity and slight shifts in the absorption maxima. In particular, a decrease in the band intensity in the 3200–3400 cm^{-1} region is noted, which may indicate a redistribution of the hydrogen bond system due to the interaction of the functional groups of the SHA with the surface of the carbon nanotubes. The change in the band intensity in the 1600 cm^{-1} region is due to the contribution of the sp^2-hybridized graphite-like structure of the MWCNTs. However, the absorption bands of the carboxyl and sulfonic acid groups are retained, indicating the preservation of the active functional centers of the sulfohumic matrix.

Thus, analysis of the IR spectra confirms the formation of a composite material in which MWCNTs are integrated into the sulfohumic matrix primarily through hydrogen bonds and π–π interactions, while maintaining the main functional groups.

Figure 2 shows the TG of the initial SHA and the SHA:MWCNTs composite in the temperature range from room temperature to 1000 °C.

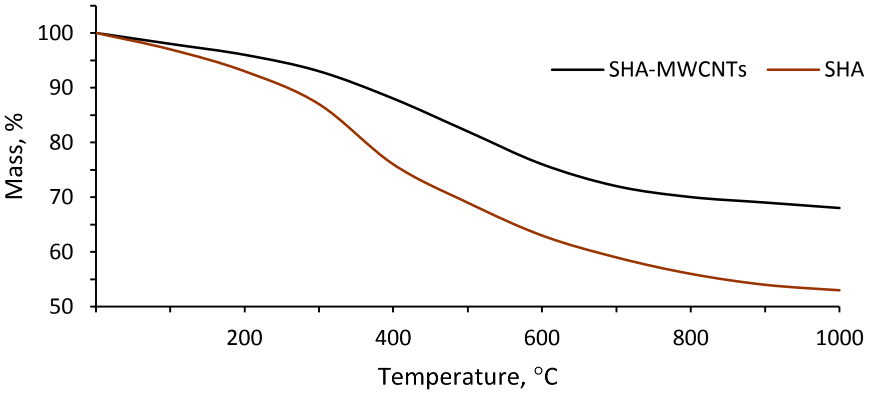


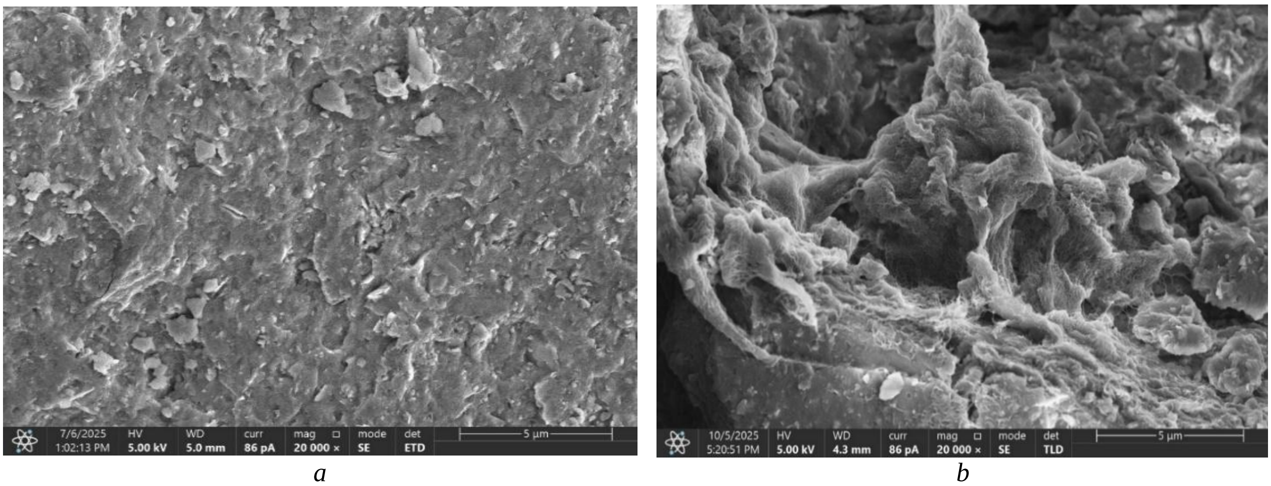
Figure 2. Thermogravimetric curves of samples SHA and SHA:MWCNTs

In the initial temperature range (up to 150–200 °C), both samples exhibit minor weight loss due to the removal of physically adsorbed water and volatile compounds retained within the material structure. In the temperature range of approximately 200–450 °C, a more intense weight loss is observed due to the thermal decomposition of oxygen-containing functional groups (carboxyl, phenolic, and sulfonic groups), as well as partial destruction of the organic sulfohumic acid matrix. For the original SHA, this process is more intense, resulting in a sharper weight loss compared to the composite.

In the range of 450–700 °C, the degradation of aromatic and aliphatic fragments of the organic structure of sulfohumic acid continues. In this temperature range, the contribution of decomposition processes is significantly greater for the original SHA, whereas for the SHA : MWCNTs composite, the weight loss is more gradual. With a further increase in temperature to 1000 °C, the residual mass of the composite (approximately 69 %) remains significantly higher than that of the initial SHA (up to 53 %). This higher residual mass is due to the presence of thermally stable multiwalled carbon nanotubes (MWCNTs), which exhibit high thermal stability.

Thus, the results of thermogravimetric analysis indicate that modification of sulfohumic acid with MWCNTs leads to increased thermal stability of the composite.

Figure 3 shows scanning electron micrographs of the surface of the initial SHA and the SHA : MWCNTs composite. The images were taken at a magnification of ×20,000, an accelerating voltage of 5 kV, and a working distance of 5 mm; the scale bar is 5 μm. Scanning electron microscopy revealed significant differences in the surface morphology of the SHA and the SHA : MWCNTs composite.



a *b*

Figure 3. Surface morphology of SHA (*a*) and SHA:MWCNTs (*b*)

The surface of the SHA (Fig. 3*a*) is characterized by pronounced morphological heterogeneity and an amorphous structure with developed roughness. The particles form dense, irregularly shaped aggregates with an uneven relief. Fragments of various shapes and sizes are observed on the surface, forming a microstructure represented by individual lamellar formations. This morphology is characteristic of humic substances and is due to the tendency of macromolecular fragments to aggregate and form associated structures. The presence of a rough microrelief can contribute to an increase in the number of accessible active sites, including functional groups ($–SO_3H$, –COOH, and –OH), which play an important role in sorption interactions with metal ions.

Unlike the original SHA, the surface of the SHA : MWCNTs composite (Fig. 3*b*) is characterized by a more developed and structurally organized morphology. The composite structure clearly displays elongated filiform structures corresponding to MWCNTs, distributed throughout the sulfohumic matrix. The nanotubes are partially incorporated into the sulfohumic phase, forming areas of intertwined fragments and forming a unique spatial framework. This distribution indicates the effective fixation of MWCNTs on the surface of the SHA. The introduction of MWCNTs significantly modifies the surface texture, resulting in increased roughness, the formation of additional interparticle voids, and the development of a more pronounced porous structure. This morphology indicates partial decompression of the original sulfohumic matrix and the formation of a more open spatial structure in the composite. The presence of carbon nanotubes prevents dense aggregation of humic macromolecules and promotes the formation of a spatially developed network structure.

Thus, modification of SHA with multi-walled carbon nanotubes results in the formation of a heterogeneous composite microstructure with a more developed surface area and an increased number of accessible active sites. The formation of such a structure can contribute to improved sorption properties of the material, making the SHA : MWCNTs composite a promising sorbent for the extraction of metal ions and organic compounds from aqueous solutions.

In this study, Cu^{2+} ions were chosen as a model ion due to their high environmental significance and widespread occurrence in industrial wastewater, as well as their pronounced ability to complex with oxygen-containing functional groups of humic substances. Furthermore, Cu^{2+} is often used as a model ion in studies of the sorption mechanisms of functionalized carbon-containing and humic materials, allowing for a reliable comparison of the obtained results with literature data. The study was limited to the Cu^{2+} model system for a more detailed analysis of the mechanisms of interaction between metal ions and the functional groups of the composite. Figure 4 shows the dependence of sorption capacity Q (mmol/g) on the equilibrium sorbate concentration C (mmol/L) for sulfohumic acid (SHA) and the SHA : MWCNTs composite.

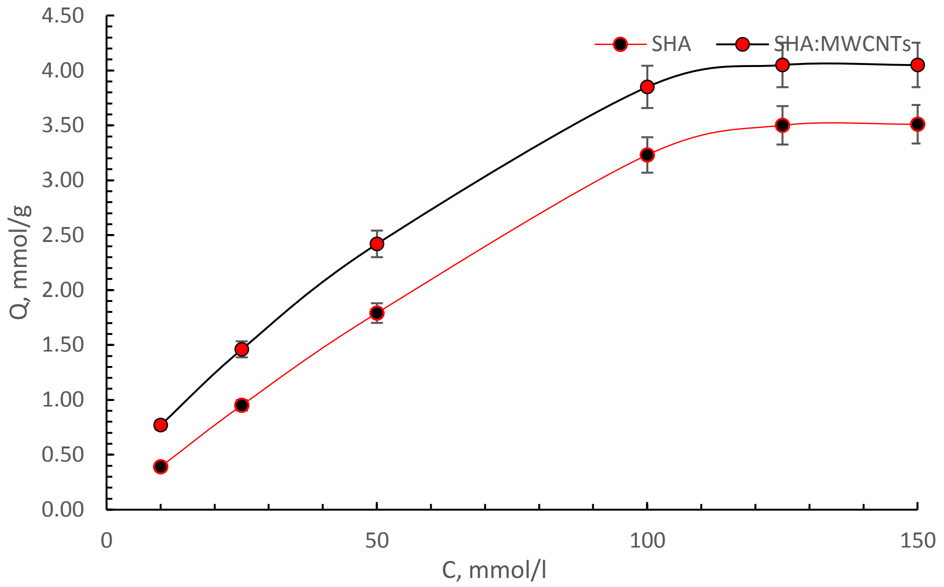


Figure 4. Sorption isotherms of Cu^{2+} ions in SHA and SHA : MWCNTs

With increasing sorbate concentration in the solution, a monotonic increase in sorption capacity is observed for both samples. At low concentrations (10–50 mmol/L), sorption capacity increases most rapidly, indicating the presence of a significant number of accessible active sites on the sorbent surface. As the solution concentration increases, the increase in sorption capacity gradually slows, and at concentrations of approximately 120–150 mmol/L, the curves reach a plateau, indicating gradual saturation of the sorption sites and the attainment of the maximum sorption capacity. The SHA : MWCNTs composite exhibits higher sorption capacity values compared to the original SHA across the entire concentration range studied. The maximum sorption capacity for the composite is approximately 4.0 mmol/g, while for SHA it is 3.5 mmol/g. The increase in sorption capacity from 3.5 to 4.0 mmol/g may seem modest when considering only absolute values. However, it should be noted that for humic sorbents, even a relatively small increase in sorption capacity is significant, since it is achieved without the use of expensive methods of deep chemical functionalization, aggressive reagents, or complex multi-stage synthesis procedures. The increase in sorption capacity is accompanied by an improvement in the structural organization of the composite, increased accessibility of functional groups, and a decrease in the degree of aggregation of the sulfohumic matrix due to the introduction of MWCNTs, which contributes to more efficient interaction of the sorbent's active centers with metal ions.

Table 3 shows the coefficients of the linear approximation of the equation $y = kx + b$, as well as the calculated parameters of the Langmuir and Freundlich isotherms for sulfohumic acid (SHA) and the SHA : MWCNTs composite.

Table 3

Parameters of the Cu^{2+} sorption isotherms on SHA and SHA : MWCNTs calculated using the Langmuir and Freundlich models

Langmuir isotherm parameters					
Sample	*k*	*b*	Maximum specific adsorption A_∞, mmol/g	Adsorption equilibrium constant K_L, L/mmol	*r*
SHA	0.2038	6.7031	4.9058	0.0304	0.9808
SHA : MWCNTs	0.1688	5.0822	5.9238	0.0322	0.9915
Freundlich isotherm parameters					
Sample	*k*	*b*	K_F	*n*	*r*
SHA	0.5651	–0.5297	1.9923	1.7695	0.9815
SHA : MWCNTs	0.5648	–0.4315	1.7527	1.7706	0.9881

High correlation coefficients for the Langmuir model ($r = 0.9808$ for SHA and $r = 0.9915$ for SHA : MWCNTs) demonstrate good agreement with the experimental data of this model and indicate a predominantly monomolecular nature of sorption on a limited number of active sites on the sorbent surface.

The calculated values of the maximum sorption capacity A_∞ indicate that the SHA : MWCNTs composite has a higher sorption capacity (5.9238 mmol/g) compared to the original SHA (4.9058 mmol/g). The increase in the maximum sorption capacity is due to the introduction of multi-walled carbon nanotubes, which contribute to an increase in the specific surface area of the composite and the formation of additional active sorption sites. The adsorption equilibrium constant K_L for SHA is 0.0304 L/mmol, while for the SHA : MWCNTs composite it is 0.0332 L/mmol. The obtained values characterize the affinity of the sorbate for the surface of the studied materials and confirm the effective interaction of the sorbents with the adsorbed molecules.

The correlation coefficients obtained by approximating the experimental data with the Freundlich equation ($r = 0.9815$ for SHA and $r = 0.9881$ for SHA : MWCNTs) also indicate a good fit to this model. This indicates a certain heterogeneity in the sorption surface of the studied materials, caused by the presence of various functional groups and structural defects.

The Freundlich constant K_F, which characterizes the sorption capacity of the material, is 1.9673 for SHA, while for the SHA : MWCNTs composite it is 1.7527. The parameter n, which reflects the intensity of the sorption process, has values of 1.7695 for SHA and 1.7706 for SHA : MWCNTs. Values of $n > 1$ indicate favorable sorption and indicate high affinity of the sorbate for the sorbent surface.

Comparison of isotherm parameters shows that the sorption process on the surface of SHA and the SHA : MWCNTs composite can be satisfactorily described by both the Langmuir and Freundlich models, as evidenced by high correlation coefficients ($r = 0.9815$–0.9881). However, slightly higher r values obtained for the Langmuir equation indicate a better fit of the experimental data with this model. This indicates that sorption predominantly occurs via the mechanism of monomolecular filling of active sites on the sorbent surface.

At the same time, the satisfactory description of the experimental data by the Freundlich model indicates the presence of energetic heterogeneity on the sorbent surface due to the presence of various functional groups (–COOH, –OH, and $–SO_3H$), as well as structural heterogeneities in the composite material.

Thus, an analysis of the parameters of both models shows that sorption predominantly occurs via the mechanism of monomolecular filling of active sites (the Langmuir model). However, the sorbent surface is characterized by a certain amount of energetic heterogeneity, which is also reflected in the satisfactory description of the process by the Freundlich model. Modification of sulfohumic acid with multiwalled carbon nanotubes leads to an increase in the ultimate sorption capacity and improved sorption characteristics of the composite material.

To assess the reusability of the synthesized SHA : MWCNTs composite, we further studied its regeneration after adsorption of Zn^{2+} ions from a model solution. Regeneration was performed by acid hydrolysis using a 0.1 N HCl solution at 50–60 °C for 30 min. After treatment, the composite was separated by filtration and washed with distilled water until Cl^- ions were completely removed. Regeneration was performed after each adsorption cycle. The Zn^{2+} concentration in the solution was determined by atomic emission spectrometry, and the amount of adsorbed ions was calculated from the difference in concentrations before and after sorption, normalized to the mass of the sorbent.

It was found that after the first regeneration cycle, the composite retained approximately 60 % of its initial adsorption capacity, while after the second cycle, this value decreased to 40 % of the initial value. The obtained results indicate a gradual decrease in the material's sorption activity with repeated regeneration, which is likely due to partial changes in the composite's structure and functional groups under acid hydrolysis conditions.

Thus, the conducted studies confirm the feasibility of regeneration and reuse of the SHA : MWCNTs composite. However, it was found that with an increasing number of regeneration cycles, a decrease in the material's sorption activity is observed. Under the studied conditions, acceptable adsorption efficiency is maintained with no more than two regeneration cycles.

Conclusions

As a result of the study, a composite material based on SHA and MWCNTs was synthesized. The composite was obtained by ultrasonic-enhanced co-precipitation, which ensured the effective incorporation of carbon nanotubes into the structure of the sulfohumic matrix. A comprehensive study of the synthesized composite using elemental analysis, conductometric titration, infrared spectroscopy, thermogravimetric analysis, and electron microscopy confirmed changes in the structural and functional characteristics of the material after modification. It was found that the introduction of MWCNTs leads to the formation of a more developed and disordered surface morphology, increased roughness, and the formation of additional interparticle voids, which contributes to the increased availability of active sorption sites. The results of thermogravimetric analysis showed that modification of SHA with carbon nanotubes leads to increased thermal stability of the composite material. A study of the sorption properties showed that the SHA : MWCNTs composite is characterized by higher sorption capacity compared to the original SHA. The maximum sorption capacity increases from 4.9058 mmol/g for SHA to 5.9238 mmol/g for the composite. Analysis of the sorption isotherms showed that the adsorption process is predominantly described by the Langmuir model, indicating a monomolecular occupation of the active sites on the sorbent surface. At the same time, satisfactory agreement between the experimental data and the Freundlich model indicates the presence of energetic heterogeneity on the surface due to the presence of various functional groups and structural features of the composite material.

Thus, the use of ultrasonic-enhanced coprecipitation enables the efficient formation of composite materials based on SHA and MWCNTs with improved structural, thermal, and sorption properties. The obtained results demonstrate the potential of the SHA : MWCNTs composite as an effective sorbent for the extraction of metal ions from aqueous solutions.

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Conflicts of Interest

The authors declare no conflict of interest.

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