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Synthesis of a Composite Based on Humic Acid Tuned to Sorbed Copper Ion

We obtained modified humic acid-based cross-linked composite pre-tuned to the sorbed copper ion. The composite synthesis had three stages. At first, we obtained prepolymerization complex using humic acids isolated from Shubarkol deposit oxidized coals and multi-walled carbon nanotubes (MWCNTs) with template (CuSO4). We used ultrasonic activation for uniform dispersion of multi-walled carbon nanotubes. Second stage comprised copolymerization in the presence of amine and cross-linker; here the prepolymerization composite complex with the template was fixed in certain nodes of polymer network. At the third stage, acid hydrolysis destroyed the bonds of the template with the composite macromolecules, the template was removed, and imprints complementary to the template in shape, size, and functionality were formed and retained "molecular memory". Such tuning forms adsorption centers in the polymer network of the composite, which can repeatedly and highly specifically interact with the template, and highly selectively extract target molecules from solution, leading to significant increase in sorbent capacity. The reaction was controlled by direct and back titration, and added amine, which was determined using Elementar Unicube elemental analyzer. The crosslinked composite can be used CC a selective sorbent tuned to a specific metal ion.

Keywords: natural polymer, multi-walled carbon nanotubes, composite, template, tuning, sorption, functionalization, ultrasound.

Introduction

Currently, natural polymer sorbents with molecular imprints due to their recognition ability to selectively sorb ions from mixtures have become one of the topical topics for researchers. Natural polymeric sorbents with high selectivity, which recognize target molecules or ions, attract special attention [1–3]. However, due to their inherent significant drawback, namely a slow sorption rate, such polymer sorbents have not yet received wide practical application, although their scope of application is extremely wide [4–7].

In the literature, a relatively small number of studies have been devoted to the methods of obtaining, mechanism and kinetics of ion sorption by natural polymer sorbents with molecular imprints [8–16].

It should be noted that humic acids (HA) are increasingly being used as sorbents for purification man-made environments from heavy metals. The presence of a variety of oxygen-containing functional groups in combination with aromatic, heterocyclic and other structural fragments enables humic acids for almost any kind of interactions, namely ionic, redox, donor-acceptor and sorption ones. Numerous studies have proved that HA can bind almost all types of ecotoxicants, including transition metal ions [17–21].

Previously, we [22] investigated methods for obtaining aminohumic sorbents pre-tuned to an ion using the Molecular Imprinting method. The proposed method gives opportunity to obtain products for selective binding of target metals. However, the use of the obtained products in technological processes is hampered by changes in the molecular structure of sorbents under the influence of chemical factors. In this regard, it is of interest to increase the chemical stability and mechanical strength of HA by modifying them with other reagents.

The aim of this work is the synthesis of modified polymer sorbents based on humic acids, with the introduction of multi-walled carbon nanotubes (MWCNTs) pre-tuned to copper ion and investigation of their properties.

Experimental

Materials used were humic acids isolated from oxidized coals of the Shubarkol deposit with the following characteristics, %: humidity (W^a) — 12.1±0.3, ash content (A^a) — 22.0±0.2, carbon (C^g) — 36.30±0.2, hydrogen (H^g) — 3.73±0.1, nitrogen (N^g) — 0.70±0.1, sulfur (S^g) — 1.02±0.1, oxygen (O^g) — 58.30±0.5, (Σ(COOH+OH)) — 5.0 mg-eq·g^{-1}; multi-walled carbon nanotubes (MWCNTs, "Taunit" series); hexameth-

ylenetetramine was used as an amine; formaldehyde was used as a crosslinking agent; $CuSO_4$ was used as a template.

The object of the study was a cross-linked composite based on humic acid with incorporated MWCNTs and amine tuned to the copper ions sorption.

Synthesis of composite (HA: MWCNTs: M: Amine) was carried out in three stages in an aqueous-alkaline medium at a ratio of HA: MWCNTs: Amine = 2:0.1:1, pH=8 according to the method developed by us earlier [22]. The content of copper ions introduced during tuning was 4 mg-eq per gram of composite.

Ultrasonic dispersion of MWCNTs was carried out on an IL-100-6/2 ultrasonic disperser with a vertical cylindrical waveguide, with a radiation frequency of 22 kHz.

The stability investigation of the "tuned" sorbents to acid hydrolysis was carried out as follows: the metal-containing composite was filled with 1 N HCl solution, heated to 50 °C and kept for 30 minutes. Then the mixture of "tuned" sorbents was filtered, repeatedly washed with distilled water to a neutral medium and the absence of Cl⁻ ions in the washing waters, and dried to a constant mass.

The structure of the obtained composites was also confirmed by IR spectroscopy data taken on the device IR Fourier spectrometer FSM-1201 in KBr tablets. The range of wave numbers was 4000–400 cm^{-1}, the error in determining the wave numbers did not exceed 2 cm^{-1}. Mathematical processing was carried out using the program for curve fitting and data analysis Fityk 1.3.1.

Experiments on static adsorption of copper ions were carried out to study the sorption capacity of cross-linked composites after "tuning". The binding capacity of the "tuned" cross-linked composites was estimated by the value of the static exchange capacity (SEC, mg-eq·g^{-1}). For comparative analysis, cross-linked composites were prepared simultaneously under identical conditions, but without "tuning".

The content of oxygen-containing groups in the composite was determined by direct and reverse conductometric titration using laboratory conductometer Anion 4100 (Russia). The measurements were carried out sequentially on three samples of the composite; the average value of three experiments was taken as the final value. The measurement error was ±0.2 %.

Elemental analysis for the content of carbon, hydrogen, nitrogen, sulfur and oxygen was carried out on the Elementar Unicube elemental analyzer.

The stability of the composites was studied by differential thermal analysis (DTA) using a Perkin Elmer STA 6000 synchronous thermogravimetric differential analyzer in the measurement range: T_m up to 800 °C in nitrogen atmosphere, υ=10°/min.

Results and Discussion

At the first stage, a pre-polymerization complex based on humic acid was obtained, with the introduction of a nanofiller (MWCNTs) and a molecular template (M). At the same time, a stable pre-polymerization complex (HA:MWCNTs:M) between humic acid, MWCNTs and template molecules was formed. Due to the formation of such a pre-polymerization complex, polymer molecules are arranged and fixed in a certain way around the template molecule.

The difference between MWCNTs and other nanofillers is their smooth surface, which leads to the stretching of the macromolecules of the matrix polymer on this surface and the formation of a densely packed polymer matrix-MWCNTs interfacial layer. However, it should be noted that carbon nanomolecules are packed in tight bundles and tend to form conglomerates that prevent their uniform distribution in the matrix and thus do not allow achieving the desired efficiency when modifying the polymer.

An effective way to overcome this problem is ultrasonic treatment (UST). Ultrasound is the most accessible and powerful factor influencing the properties, structure, velocity and direction of reactions. Under the influence of ultrasound, the processes of oxidation and reduction are enhanced, heterogeneous reactions on the surface of MWCNTs are significantly accelerated, which is due to an increase in their porosity and surface activity.

The introduction of the filler into the HA was carried out using ultrasound. In the course of the study, the influence of the duration of UST and temperature on the process of functionalization of MWCNTs was studied. The results of the study are shown in Table 1.

Functionalization of MWCNTs under the influence of ultrasound

Sample	Time period for ultrasonic treatment, min	Temperature, °C	Yield, %	Σ(COOH), mg-eq$\cdot$g^{-1}
MWCNTs (original)	–	–	–	1.4
MWCNTs	15	25	84	1.8
		50	68	1.6
		70	84	1.8
	30	25	88	1.4
		50	72	1.6
		70	80	1.2
	60	25	80	1.6
		50	72	1.8
		70	80	1.2
	120	25	84	1.6
		50	76	1.8
		70	80	1.0

The data in Table 1 show that minimal exposure to UST and room temperature is sufficient to increase the number of reaction centers of MWCNTs. Prolonged exposure to UST leads to a decrease in the amount of oxygen-containing groups. For further research, we used MWCNTs, ultrasound-activated at a temperature of 25 °C for 15 minutes.

At the second stage, the synthesis of a crosslinked composite preconfigured for sorption by a local arrangement of macromolecule sites was carried out by copolymerization of the pre-polymerization complex (HA:MWCNTs:M) with an amine and a crosslinking agent.

The essence of two stages consists in the interaction of the modified polymer and the sorbed ion under conditions when the links of macromolecules still have sufficient mobility, with subsequent fixation of the resulting conformations optimal for sorption, which in turn should lead to a significant improvement in the sorption characteristics of the composite.

At the third stage, a molecular template was removed from the polymer mesh. The stability of the "tuned" sorbents to acid hydrolysis was studied by treating the composite with a hydrochloric acid solution with further filtration, repeated washing and drying. The reaction in the composite was controlled by the attached amine, which was determined using the Elementar Unicube elemental analyzer, as well as by direct and reverse conductometric titration. The composition of the obtained composites was confirmed by the data of X-ray phase analysis. The results of the study are presented in Table 2.

Characteristics of synthesized composites

Composite	C^g, %	H^g, %	N^g, %	S^g, %	O^g, %	Yield, %	Σ(COOH+OH) mg-eq$\cdot$g^{-1}
before hydrolysis							
HA	36.30±0.2	3.73±0.1	0.70±0.1	1.02±0.1	58.30±0.5	75.01	5.0
HA:MWCNTs:M:A	44.50±0.2	3.90±0.1	1.08±0.1	0.91±0.1	49.61±0.5	79.40	4.5
after hydrolysis							
HA:MWCNTs:A	44.61±0.2	3.99±0.1	1.13±0.1	0.97±0.1	49.30±0.5	75.40	5.8

The increase in the sum of oxygen-containing groups in the samples subjected to acid hydrolysis (Table 2) confirmed our assumption about the possible breaking of the coordination bonds of copper ions with the functional groups of the composite. This assumption was also confirmed by the data of IR spectroscopy (Figure 1).
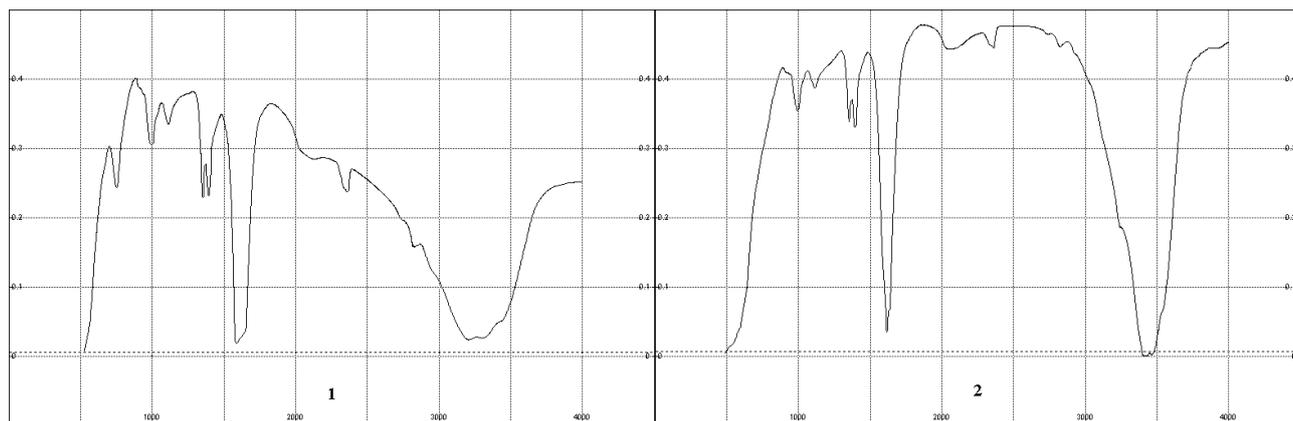
1 — HA:MWCNTs:M:A (before hydrolysis); *2* — HA:MWCNTs:A (after hydrolysis)

Figure 1. IR spectra of synthesized composites

In Figure 1, we can observe the appearance of a peak at 741 cm^{-1} for the HA:MWCNTs:M:A composite (before hydrolysis), which refers to the stretching vibrations of the Cu–O bond. The absence of similar absorption bands in the composite after hydrolysis indicates a change in the structure of chemical bonds and the removal of copper from the crosslinked composite during hydrolysis. The appearance of a pronounced band at 3400 cm^{-1} in the HA:MWCNTs:A composite (after hydrolysis), which can be attributed to vibrations of OH-groups bound by intermolecular hydrogen bonds, also indicates the destruction of oxygen bonds with copper and the formation of hydroxyl groups in their place.

The interaction strength of the obtained composites was studied by differential thermal analysis (DTA). The thermogravimetric curve of the composites before and after hydrolysis showed a low-temperature weight loss. The main weight loss began in the temperature range of 448-564 °C. Thus, the main mass loss for the composite before hydrolysis (15 wt.%) began in the temperature range of 456-564 °C, and after hydrolysis (19.10 wt.%) at 448-556 °C. The total weight loss of the samples was estimated at about 32 wt.%.

The sorption properties of cross-linked composites obtained with and without "tuning" to the copper ion were studied. A study of the sorption properties of a composite pre-tuned to copper ions showed that after acid hydrolysis its capacity sharply increased compared to a similar composite cross-linked without "tuning". The effect of improving the sorption properties for Cu^{2+} for the HA: MWCNTs: A composite was equal to 4.1 mg-eq g^{-1}, and for the composite cross-linked without "tuning" it was equal to 2.2 mg-eq g^{-1}. This once again confirmed the assumption about the efficiency of the cross-linked composite selectively tuned to the adsorbed ion.

Conclusions

Thus, the synthesis of a cross-linked composite based on humic acid with the introduction of MWCNTs and a molecular template was carried out using the Molecular Imprinting method under ultrasonic dispersion conditions, followed by copolycondensation with amine and formaldehyde tuned to the sorbed copper ion. One of the important properties of MWCNTs, which determines the possibility of their use in new technologies, is associated with their high sorption characteristics and chemical stability. Since MWCNTs are a surface structure, their entire mass is enclosed in the layers surface; therefore, they have an anomalously high specific surface area, which, in turn, determines the features of their sorption characteristics and high strength. The introduction of nitrogen atoms into the composition of humic acids, which are more prone to the formation of donor-acceptor bonds with metal ions compared to oxygen atoms, will increase both the complexing properties of HA and at the same time impart polyampholyte properties to HA. Ultrasound contributes to the increase and regulation of their porous structure, changing the chemical nature of the surface. The structure of the resulting composites was proven by modern physicochemical methods. The reaction was monitored by the added amine, using an elemental analyzer, and by the content of oxygen-containing groups determined by conductometric titration. With the introduction of a tuned cross-linked composite of MWCNTs and amine, the content of carbon increased by 8.20 % and nitrogen by 0.38 %, and the sum of oxygen-containing groups was equal to 4.5 mg-eq g^{-1}. The study of the sorption properties of the preliminarily "tuned" crosslinked composite to copper ions suggested the formation of cavities (imprints) in the "tuned" crosslinked composite, which were capable of interacting with target template molecules and increasing the

capacity of the sorbent by a factor of two compared to the same composite stitched without tuning. The static exchange capacity for the "tuned" composite was 4.1 mg-eq g^{-1}, which made it possible to double the capacity of the sorbent compared to the same composite cross-linked without "tuning".

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З.М. Молдахметов, А.М. Ғазалиев, А.Х. Жакина, Е.П. Василец, О.В. Арнт

Сорбцияланған мыс ионына бапталған, гумин қышқылы негізіндегі композиттің синтезделуі

Модификацияланған гумин қышқылының негізінде алдын ала сорбцияланатын мыс ионына бапталған тігілген композит алынды. Композит синтезі үш кезеңде жүзеге асырылды. Бірінші кезеңде, Шұбаркөл кен орнының тотыққан көмірінен бөлінген гумин қышқылдары мен шаблоны (CuSO₄) бар көпқабырғалы көміртекті нанотүтікшелер (ККНТ) арасындағы өзара әрекеттесуі арқылы полимеризация алдындағы кешені алынды. ККНТ біркелкі диспергирлеу үшін ультрадыбыстық белсендіру жүргізілді. Екінші кезеңде, амин және айқас байланыстырушы агентінің қатысуымен сополимеризация жүзеге асырылды, онда шаблоны бар композиттің полимеризацияға дейінгі кешені полимер торының белгілі бір позицияларына бекітілді. Үшінші кезеңде, қышқылдық гидролиз процесінде шаблонның композиттік макромолекулаларымен байланыстары бұзылады, шаблон жойылып, пішіні, өлшемі және функционалдығы бойынша шаблонға қосымша болып табылатын іздер түзіледі және олардың «молекулярлық жадысын» сақтайды. Осындай баптау нәтижесінде композиттің полимерлік торында шаблонмен қайталанатын жоғары спецификалық өзара әрекеттесуге және ерітіндіден мақсатты молекулаларды жоғары селективті алынуына қабілетті адсорбциялық орталықтар түзіледі, бұл сорбенттің сыйымдылығының айтарлықтай артуына әкеледі. Реакция тікелей және кері титрлеу арқылы, сондай-ақ қосылған амин бойынша бақыланды, ол Elementar Unicube анализаторының көмегімен анықталды. Рентгендік фазалық талдаудың көмегімен алынған композиттердің құрамы дәлелденді. Айқас байланысқан композитті белгілі бір мыс ионына бапталған селективті сорбент ретінде пайдалануға болады.

Кілт сөздері: табиғи полимер, ККНТ, композит, шаблон, баптау, сорбция, функционализация, ультрадыбыс.

З.М. Мулдахметов, А.М. Газалиев, А.Х. Жакина, Е.П. Василец, О.В. Арнт

Синтез композита на основе природного полимера, настроенного на сорбируемый ион меди

На основе модифицированной гуминовой кислоты получен сшитый композит, предварительно настроенный на сорбируемый ион меди. Синтез композита осуществлен в три этапа. На первом этапе получен предполимеризационный комплекс взаимодействием между гуминовыми кислотами, выделенными из окисленных углей Шубаркольского месторождения, и многостенными углеродными нанотрубками (МУНТ) с шаблоном (CuSO4). Для равномерного диспергирования многостенных углеродных нанотрубок проведена ультразвуковая активация. На втором этапе в присутствии амина и сшивающего агента осуществлена сополимеризация, при которой предполимеризационный комплекс композита с шаблоном фиксируется в определенных позиции полимерной сетки. На третьем этапе в процессе кислотного гидролиза происходит разрушение связей шаблона с макромолекулами композита, удаление шаблона и образование отпечатков, комплементарных шаблонным по форме, размеру и функциональности и сохраняющие «молекулярную память» о них. В результате такой настройки в полимерной сетке композита формируются адсорбционные центры, способные к повторному высокоспецифичному взаимодействию с шаблоном и к высокоселективному извлечению молекул-мишеней из раствора, что приводит к значительному увеличению емкости сорбента. Контроль реакции осуществляли методом прямого и обратного титрования, а также по присоединенному амину, который

определяли с использованием элементного анализатора Elementar Unicube. С помощью рентгенофазового анализа доказан состав полученных композитов. Сшитый композит может найти применение в качестве селективного сорбента, настроенного на определенный ион металла.

Ключевые слова: природный полимер, МУНТ, композит, шаблон, настройка, сорбция, функционализация, ультразвук.

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