Humic composites - sorbents for analysis of river water quality

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Abstract The current state of the problem shows that climate change is accompanied by a certain impact on the basic parameters of human life, among which a special place is occupied by the problem of water resources, their quality, quantity, possibilities of consumption, purification and others. In this regard, much attention is paid to assessing the quality of consumed water, since its use is determined by a number of factors, including: irrational use, pollution (chemical/biological), uneven distribution. A rather complex environmental situation has formed in the Kyrgyz Republic, associated with an increase in the level of man-made pressure on the environment. This influence, in turn, is accompanied by the emergence of new problems of protection and reproduction of geo- and biological resources. To analyze the quality of river water samples of the Alamedin River (spring and autumn samples) were selected, followed by purification with modified humic materials in the form of humic composites containing hybrid nanoparticles of iron oxide and rare earth metals. The purpose of the work is to study the influence of sorption modes on modified humic composites when analyzing water samples from the Alamedin River.
Keywords: river water, raw materials, water treatment, humic acids, hybrid nanocomposites, polymeric nanosorbents

1 Introduction

A rather complex environmental situation has formed in the Kyrgyz Republic, associated with an increase in the level of man-made pressure on the environment [1]. This influence, in turn, is accompanied by the emergence of new problems of protection and reproduction of geo- and biological resources. These resources include: raw materials, biodiversity, soil, water and others. It should be noted that the problem of protection and environmental safety of these resources, as well as issues of their rational consumption, are relevant not only for the Kyrgyz Republic. This is also due to the fact that on the territory of our country there are a sufficient number of man-made zones that affect the parameters of the distribution zones of these resources and pose a great danger to people’s livelihoods [2-3]. A special place among the resources of mountainous areas is occupied by river waters, which play a significant role in the transport of nutrients and pollutants, affecting other areas of the overall ecosystem. Each of these functions plays a specific role, which is characterized on the one hand by the speed of

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delivery of nutrients, and on the other by ensuring the dilution and decomposition of pollutants. In general, the main pollution of river water is most often located along river beds and includes domestic, industrial and agricultural sources [4].

To analyze the quality of river water samples of the Alamedin River (spring and autumn samples) were selected, followed by purification with modified humic materials in the form of humic composites containing hybrid nanoparticles of iron oxide and rare earth metals [5-8].

The purpose of the work is to study the influence of sorption modes on modified humic composites when analyzing water samples from the Alamedin River.

2. Materials and Methods

The objects of the study were humic composite sorbents obtained on the basis of humic acids isolated from oxidized brown coal from the Kyzyl-Kiya deposit [9-11].

Within the framework of this goal, the following research objectives were identified:

1. analysis of water samples from the Alamedin River by the method of ion exchange sorption (static mode) using composite sorbents containing hybrid nanoparticles;
2. analysis of water samples from the Alamedin River by the method of ion exchange sorption (dynamic mode) using composite sorbents containing hybrid nanoparticles.

A series of analyzes were carried out on organoleptic indicators and qualitative reactions to cations dissolved in these water samples.

Methodology: 2-3 drops of a solution of magnesium salt were added to the test tube, and 1-2 drops of solutions of NH_4C1, ammonia and Na_2HPO_4 were added. The solution becomes cloudy and white flakes form - suspensions of NH_4MgPO_4.

3-4 drops of an iron salt solution were added to the test tube and 3-4 drops of NaOH solution were added. The solution became cloudy and red-brown flakes of iron (III) hydroxide appeared.

3. drops of a solution of cobalt (II) chloride were added to the test tube and an aqueous solution of alkali was slowly added drop by drop, with continuous stirring of the mixture, until a blue precipitate of CoOHCl formed, which, with further addition of alkali, transformed into a pink precipitate of $Co(OH)_2$, which after some time turns black due to oxidation to $Co(OH)_3$.

To carry out the sorption regimes, a sorbent containing hybrid nanoparticles of transition and rare earth metals was used [12, 13].

All water samples were previously analyzed for the presence of dissolved metal ions. For this purpose, analytical research approaches (qualitative and quantitative analysis) were used.

The sorption of HA ions and magnetically active nanohybrid composites based on humic acids was carried out in three modes.

Model 1. A primary solution containing ions dissolved in water samples from the Alamedin River in a volume of 50 ml was poured into a volumetric flask, into which a sorbent with different ratios of components (0.1 - 1.5 g) was added. The system with the sorbent was left for 2 days, during which the change in pH of the solution was checked (until an equilibrium value was reached). Then the sedimentary part was titrated and the water was analyzed for the content of metal ions after sorption. Calculations were made according to the formula:

$$A_i = \frac{(C_o - C_{samp}) \cdot V_{samp}}{1000} \qquad (1)$$

Model 2. When carrying out sorption under dynamic conditions, water samples from the Alamedin River were mixed with sorbent (1.5 g) in a storage reactor, and then through connecting tubes they entered the receiver, where the sorbent settled on a special grid, and the liquid entered flasks for analysis. The speed and time of passage of the water flow were regulated by applying special keys - regulators.

Model 3. In this case, carrying out sorption under dynamic conditions of a water sample from the Alamedin River included the preparation of a sorption matrix - a filter, which contained a hybrid humic composite sorbent (1.5 g). The speed and time of passage of the water flow were also regulated by applying special keys - regulators. After the sorption process, the ions in the filtrate were analyzed. To do this, a filter assembled from several cotton-paper layers with a humic sorbent inside was placed in the column on a special substrate. The test liquid was passed through at a rate of 3-5 drops per second; if necessary, the flow rate can be slowed down using a compression valve. After passing through the filter, the liquid was collected in a special receiver (a series of test tubes can be used). Calculations were made using the formulas:

$$A = \frac{(C_o - C_{samp}) \cdot V_{samp}}{1000} \qquad (2)$$

$$DOE = \frac{A_1 + A_2 + A_i}{m} \qquad (3)$$

Where,
A - is the amount of sorbed ion
C – solution concentration
DOE – dynamic exchange capacity
m – amount of methylene blue in the column

3. Results and Discussion

Since the objects of the study were water samples from the Alamedin River, selected at different times of the year (spring and autumn sampling), and humic composite sorbents obtained on the basis of humic acids isolated from oxidized brown coal from the Kyzyl-Kiya deposit, for this type of experiment we selected several modes.

Each mode included the preparation of the sorbent for the sorption process, depending on the conditions.

Preliminarily, 2 samples were determined for the selected water samples of the Alamedin River: autumn - AI (November) and spring - AII (April).

The next stage was a series of analyzes on the organoleptic characteristics of these samples.

For this purpose, an initial assessment was carried out in laboratory conditions through the determination of organoleptic indicators (color, smell, smell when changing T°, taste). Since organoleptic indicators are used to characterize the quality of the water used, human senses, such as vision, taste, touch, and smell, are used for their analysis. Therefore, organoleptic assessment of water quality can be presented as a strict, necessary and basic procedure that is included in the sanitary and chemical control of water. Most often, this type of analysis uses a special test scale of tables, which allows us to talk about the systematicity and correctness of the research conducted.

1. Study of the color of water samples from the Alamedin River.

This measurement method involves conducting a comparative study of the color intensity of water with a standard, which is expressed in degrees on the platinum-cobalt scale. Color comparison shows the intensity of color associated with the concentration of solutes in a given sample. The color indicator of water may be due to the presence of dissolved humic substances or heavy metal compounds. In general, the overall color of water samples will be determined by several factors: since water samples from a natural source are selected for analysis, their color will also depend on geological conditions, aquifers, the nature of the soil, as well as the time of year at which the samples were selected. For general characteristics, the color of natural waters was chosen, which ranges from a few to thousands of degrees (Table 1).

Table 1. Color for different water samples [14]

Chromaticity	Units of measurement, degrees platinum-cobalt scale
Very small	25
Small	25 - 50
Average	50 - 80
High	80 - 120
Very High	120 and more

It should be noted that when analyzing color, they also distinguish between “true color,” which includes dissolved substances, and “apparent” color, which can be described due to the presence of colloidal and suspended particles in the analyzed water, the ratios between which are largely determined by the pH value.

To analyze color, some samples of water from the Alamedin River were considered: AI and AII. The use of a chromaticity table showed that these samples can be characterized as waters with a high chromaticity of 80 to 120 degrees, according to the platinum-cobalt scale. Which is due to the time of taking water samples from the river (November, April). If we use the classification of “true” or “apparent” color, then these two samples (AI and AII) can be classified as “apparent” water samples.

It should be noted that the high color value of water samples characterizes the weak organoleptic properties of water.

Since this method was the visual part of the study, the photometric method was used to compare the data obtained. To do this, we prepared a series of solutions from a mixture of $K_2Cr_2O_7$ and $CoSO_4$ salts of different concentrations to construct a calibration curve. As a result of determining experimental points for two water samples, it was revealed that the color value in the waters of these samples does not correspond to the minimum value required for water used for drinking purposes. Thus, for drinking purposes, water is used in which the maximum permissible color value should be 35 degrees on the platinum-cobalt scale. However, for samples AI and AII this value ranged from 80 to 120 degrees, which means it cannot be used for drinking purposes.

2. Study of the odor of water samples from the Alamedin River.

Since organoleptic indicators include the determination of odor, in our work we studied the intensity of this indicator in two samples of water from the Alamedin River (AI and AII), using a special scale. According to this table - scale, smell, as one of the organoleptic indicators of water, is characterized by intensity, which is assessed on a 5-point scale. In the work, the samples studied for this indicator for the water sample of the Alamedin River (AI) are characterized by a very strong odor, which makes the water unsuitable for drinking, i.e. the basic value corresponds to 5 points. Whereas for drinking water, an odor of no more than 2 points is allowed. It should be noted that for water samples from the Alamedin River (AII) - spring sample, the smell corresponds to I or II value, which allows settlements located along the river bed to sometimes use its water for drinking.

3. Study of taste and taste of water samples from the Alamedin River.

A general analysis of the taste of water can be carried out only for drinking natural water, if there is no suspicion of its contamination. This classification includes 4 taste criteria: salty, sour, bitter, sweet (in addition, the classification also includes different tastes: salty, bitter, metallic, chlorine). This parameter, like others, is assessed on a special scale-table. The samples studied for this indicator for two water samples from the Alamedin River (AI and AII) are characterized by a very strong odor, which makes the water unsuitable for drinking. Therefore, this criterion can be classified as the fifth group.

4. Study of turbidity of water samples from the Alamedin River.

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For the work, the turbidity of water samples (AI and AII) of the Alamedin River was determined visually by the degree of turbidity of a column 10-12 centimeters high in a turbidity test tube. And they were described using the following criteria: transparent; slightly opalescent; opalescent; slightly cloudy; cloudy very cloudy, according to Interstate standard (Fig. 1).

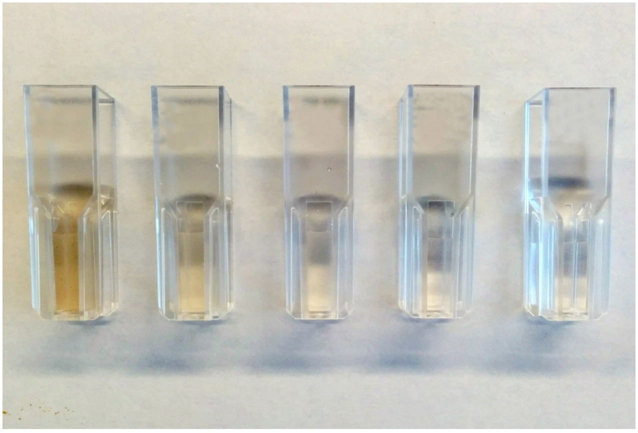

Fig.1. Water samples for visual determination of water turbidity [15]

The turbidity of the Alamedin River water samples (AI and AII) can be characterized as turbid for AI and very turbid for AII.

Then, to determine the dissolved cations in the water samples, titration was carried out using Trilon B. Due to its chemical properties, this reagent has a very wide application, since it forms very stable complex compounds with most cations. By reacting with strong oxidizing agents, it allows one to obtain soluble metal salts: Ca, Mg, Cu, Co, Ni, Zn, Fe, Mo, Al, etc. Titration showed that Eriochrome black can be used as an indicator. This indicator, entering into reversible color reactions with Mn^{2+}, Zn^{2+}, Mg^{2+} cations, makes it possible to determine their trace amounts in water (Table 2).

Table 2. Data from the analysis of water samples from the Alamedin River (Results obtained by the authors as part of the experiment)

№	Color	Smell	Smell at t°	Titration, mg/l	pH
AI -1	Faint yellow, contains impurities, cloudy	Soil (ground)	Clear (strong) smell of earth	84,98	6,80
AI - 2	Impurities in large quantities	Soil (ditch)	Faint smell of vegetation	72,84	6,76
AII -1	Transparent, there are impurities	Faint smell of earth	Weak rotten	59,48	7,05
AII - 2	Cloudy, yellowish, contains impurities	Rotten, putrid	Strong rotten	61,9	7.10

After determining this series of cations, a series of sorbents - humic composites - were prepared to carry out the process and select sorption models:

1. analysis of water samples from the Alamedin River by the method of ion exchange sorption (static mode) using composite sorbents containing hybrid nanoparticles.
2. analysis of water samples from the Alamedin River by the method of ion exchange sorption (dynamic mode) using composite sorbents containing hybrid nanoparticles.

Samples of sorbents used in two models. Model 1. Using this model allows you to increase the duration of the sorption process (Table 3).

Table 3. Dependence of sorption parameters on the amount of sorbent in the reaction system (Results obtained by the authors as part of the experiment)

№	V, ml	m, g	C_{init}, mg/l	C_p, mg/l	A, mg
1	10	0.3	50.0	0.5	24.5
2	10	0.8	50.0	1.3	23.9
3	10	1.5	50.0	3.5	25.6

Carrying out sorption under static conditions made it possible to obtain the dependence of the exchange constants on the pH value of the solution (Table 4).

Table 4. Exchange constant M^{z+}- H^+ on ion - exchangers at different pH (Results obtained by the authors as part of the experiment)

Samples	*pH*	K_{exch}	pK_{exch}	*pH*	K_{exch}	pK_{exch}	*pH*	K_{exch}	pK_{exch}
Me^{z+}-H^+	Cu^{2+}-H^+			Fe^{2+}-H^+			Co^{2+}-H^+		
PM ($HA\text{-}Me_nO_m$)	2.9 3.6 4.5 6.0	$4.40 \cdot 10^{-3}$ $3.75 \cdot 10^{-3}$ $3.79 \cdot 10^{-3}$ $3.35 \cdot 10^{-3}$	2.554 2.779 2.758 3,475	2.9 3.6 4.5 6.1	$1.25 \cdot 10^{-3}$ $1.00 \cdot 10^{-3}$ $0.75 \cdot 10^{-3}$ $0.67 \cdot 10^{-3}$	2.903 3.000 3.125 4,174	3.3 3.6 4.5 6.2	$1.30 \cdot 10^{-3}$ $1.00 \cdot 10^{-3}$ $0.60 \cdot 10^{-3}$ $0.43 \cdot 10^{-3}$	2.886 3.000 3.222 4,367

Model 2. The use of the dynamic mode showed that by varying the flow rate, filter thickness, as well as the sorbent content in the filter, it is possible to obtain certain dependencies of the sorption process.

The work revealed that the sorption values of metal cations depend not only on the nature of the functional groups and the concentration of cations in the samples under study. The study of the sorption process in a dynamic mode showed that the difference in the values of sorption and leaching of cations is determined by the strength of the bond of metals with the functional groups of humic sorbents, as well as their selectivity, which is due to the structural features of the surface of the polymer matrix (Table 5).

Table 5. Results of calculations obtained under dynamic sorption model (Results obtained by the authors as part of the experiment)

№	V, ml	m, g	C_{int}., g/l	C_P, mg/l	A, mg	DEC, mg/g
1	10	0.3	50.0	0.5	20.5	21.0
2	10	0.8	50.0	0.3	21.9	
3	10	1.5	50.0	0.8	20.6	

4. Conclusion

In this regard, it was revealed that the values of SEC and DEC always depend on the experimental conditions and are determined mainly by the nature of the cation and the number of functional groups capable of substitution at a given pH value.

It has been shown that modified humic acids, in particular composites based on them containing hybrid nanoparticles, can be used as sorbents for water purification.

It has been revealed that the use of such sorbents in two sorption modes, both static and dynamic, makes it possible to accelerate the sorption process due to the magnetic properties of the latter.

It was revealed that the values of SEC and DEC depend on the experimental conditions and are determined mainly by the nature of the cation and the number of functional groups of the polymer matrix capable of substitution at a given pH value.

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