

## THE SORPTION OF SET METAL IONS BY MAGNET-ACTIVE HUMIC NANOCOMPOSITES

Jorobekova Sh.J.<sup>1</sup>, Zaripova A.A.<sup>2</sup>, Kerimbaeva A.D.<sup>3</sup>, Mambetjanova N.N.<sup>4</sup>  
Email: Jorobekova1134@scientifictext.ru

<sup>1</sup>Jorobekova Sharipa Jorobekovna – Doctor of Chemistry, professor, the academician,  
NATIONAL ACADEMY OF SCIENCES OF THE KYRGYZ REPUBLIC;

<sup>2</sup>Zaripova Anar Ascarbekovna – Doctor of Chemistry, professor,  
UNESCO (UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION) DEPARTMENT OF  
PHYSICAL AND COLLOIDAL CHEMISTRY,  
KYRGYZ NATIONAL UNIVERSITY OF ZH. BALASAGYN;

<sup>3</sup>Kerimbaeva Alina Djekshenbekovna –graduate student,  
INSTITUTE OF CHEMISTRY AND CHEMICAL TECHNOLOGY,  
NATIONAL ACADEMY OF SCIENCES OF THE KYRGYZ REPUBLIC;

<sup>4</sup>Mambetjanova Nurila Narynbekovna – graduate student.  
UNESCO (UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION) DEPARTMENT OF  
PHYSICAL AND COLLOIDAL CHEMISTRY,  
KYRGYZ NATIONAL UNIVERSITY OF ZH. BALASAGYN,  
BISHKEK, REPUBLIC OF KYRGYZSTAN

**Abstract:** several experimental data of sorption properties of magnetoactive-nanocomposites on the base of humic acids (HA) were established. Humic acids and their derivatives have such specific properties as rigid conformation of the structure, high amount of the ligand groups in the volume unit and non-uniform distribution of these groups into the matrix volume. So, degree of extraction of metal ions from solutions by ion exchange sorption method depends on a number of factors among which the cores are: concentration of metal ions and sorbent in a reaction mixture, process time and pH.

**Keywords:** humic acids, ion exchange, heavy metals ions, magnet-active nanopolymeric sorbents, nanocomposites

## СОРБЦИЯ РЯДА ИОНОВ МЕТАЛЛОВ МАГНИТО-АКТИВНЫМИ ГУМИНОВЫМИ НАНОКОМПОЗИТАМИ

Жоробекова Ш.Ж.<sup>1</sup>, Зарипова А.А.<sup>2</sup>, Керимбаева А.Д.<sup>3</sup>, Мамбетжанова Н.Н.<sup>4</sup>

<sup>1</sup>Жоробекова Шарипа Жоробековна – доктор химических наук, профессор, академик,  
Национальная Академия наук Кыргызской Республики;

<sup>2</sup>Зарипова Анар Аскарбековна – доктор химических наук, профессор,  
кафедра ЮНЕСКО (Организации Объединенных Наций по вопросам образования, науки и культуры) физической и  
коллоидной химии,

Кыргызский национальный университет им. Ж. Баласагына;

<sup>3</sup>Керимбаева Алина Джекшенбековна – аспирант,  
Институт химии и химической технологии

Национальная Академия наук Кыргызской Республики;

<sup>4</sup>Мамбетжанова Нуриля Нарынбековна – аспирант,  
кафедра ЮНЕСКО (Организации Объединенных Наций по вопросам образования, науки и культуры) физической и  
коллоидной химии,

Кыргызский Национальный университет им. Ж. Баласагына,  
г. Бишкек, Кыргызская Республика

**Аннотация:** в работе представлены экспериментальные данные по изучению сорбционных свойств магнитоактивных наноконкомпозитов, полученных на основе гуминовых кислот. Гуминовые кислоты и их производные характеризуются такими специфическими свойствами, как жесткая конформационная структура, большое количество лигандных групп в единице объема, неравномерное распределение этих групп в объеме матрицы. Поэтому степень извлечения ионов металлов из растворов с использованием метода ионообменной сорбции зависит от ряда факторов, среди которых можно выделить: концентрация ионов металлов и сорбента в реакционной смеси, продолжительность процесса и pH.

**Ключевые слова:** гуминовые кислоты, ионный обмен, ионы тяжелых металлов, магнитоактивные нанополлимерные сорбенты, наноконкомпозиты.

**Introduction.** Study of detoxifying properties of the produced magnet-active nano-hybrid sorbents has been performed regarding to model ecotoxicants – heavy metals ions. Evaluation of sorptive ability of nanosorbents obtained using different technological regimes in model solutions containing set of metals (Cd, Co, Ni).

Process of isolation of heavy metals ions from solutions is based on sorption them onto magnetoactive sorbent consisting of humic acids and magnetoactive nanoparticles of magnetite  $\text{Fe}_3\text{O}_4$ . In the real environmental conditions the isolation of them is appeared from complicated suspension consisting of clay soil components possessed by high complexing properties towards toxic metal ions including Cd, Co and Ni. In the sorption process these ions will be compete with another ions. In the previous works basic possibility of sorption of Cd, Co and Ni on magnetic humic based sorbent, and also possibility of separation of insoluble components of soil has been shown.

It is known, that humic acids and their derivatives have such specific properties as rigid conformation of the structure, high amount of the ligand groups in the volume unit and non-uniform distribution of these groups into the matrix volume. These properties caused the specific peculiarities of the complex formation of HA and their nanocomposites with metal ions. That is why, the correct choice of the model to describe the complex formation process and the methods for evaluation of stability constants of the formed complexes are very important. One of the methods of the study of complex formation between HA and metal ions is ion-exchange sorption method [1-4].

**Materials and methods.** Native humic acids were isolated from brown coal (Kyzyl-Kiya deposit of Kyrgyzstan) by extraction with 1% water solution of NaOH at heating on the boiling water bath-vessel during two hours. The supernatant was acidified to pH 2 with 5% HCl and centrifuged. The precipitations of humic acids (HA) were collected and dried on the air to the constant weight.

In order to obtain nanosorbent solution, we have prepared 10-% salt solutions:  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2$ . In 2-L volume flask 250 mL of 10%-solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 85 mL of 10%-solution of  $\text{FeCl}_2$  were mixed. The mixture was mixed on magnetic stirrer for 15 min with the pH of the solution – 2.6. Then at constant mixing 120 mL of 25%-solution of  $\text{NH}_4\text{OH}$  was added. In the flask, small-dispersive precipitate of  $\text{Fe}_3\text{O}_4$  of dark-brown color was produced. At the first stage of the process the temperature of the reaction mixture increased up to  $28^\circ\text{C}$  at the expense of the exothermal reaction, pH value of the mixture was 11.2. The process was performed at constant mixing for an hour, and the temperature of the mixture reduced to  $23^\circ\text{C}$ . After this time, 25 g of sodium humate was introduced into the flask as small-dispersive powder. The mixture was mixed for 1 hour more. Temperature of the mixture and pH did not change. Concentration of dry substances in the finished solution of nanosorbent was 21.86%.

Produced nanosorbent was tested to the ability for the sorption of the Cd, Co and Ni from the solutions of salts. The experiments with the sorption of the Cd, Co and Ni from the solutions with metals concentration from 0.55 to 1.53 mg/mL showed that the volume of this metals extraction was 75–95% from the initial content.

For sorption of heavy metal ions by nanosorbent on the basis of humic acids, isolated from coals of Kyzyl-Kiya deposits, two kinds of regimes of sorption were obtained.

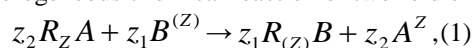
*Regime 1.* Initial 3 mg/mL - solution of metals was prepared by dilution 1.35 g salt  $\text{Me}(\text{NO}_3)_2$  ( $\text{Me} = \text{Cd}, \text{Co}, \text{Ni}$ ) in 150-mL of water in graduated flask. Into three numbered flasks containing per 10 mL of sorbent solution the prepared metal solution was added in various amounts: into 1<sup>st</sup> – 10; into 2<sup>nd</sup> - 20 mL, into 3<sup>rd</sup> -30 mL, accordingly. Then acidity of solution was brought to pH3 by 0.1N of HCl at constant mixing.

*Regime 2.* Into three numbered flasks containing 100 mL of metal nitrate  $\text{Me}(\text{NO}_3)_2$  ( $\text{Me} = \text{Cd}, \text{Co}, \text{Ni}$ ) with 0.3 mg/mL concentration the various volumes of sorbent were added at constant mixing: into 1<sup>st</sup> flask –1 mL, into 2<sup>nd</sup>. 0.5 mL, into 3<sup>rd</sup>. 0.25 mL. The solutions were mixed for 5 h, after then were kept during night. Then acidity of solution was brought from pH 5.8 to pH 3 by 0.1N of HCl at constant mixing. It was observed the precipitation of sorbent. The precipitate was centrifuged at 8000 rev/min. After 1 h of mixing the solution was filtered.

### Experimental part

**Results and discussion.** There is “cooperative” influence of the functional groups of the polymeric ligands (HA and their derivatives) on the complex formation processes. Therefore the questions on interaction of metal ions with the functional groups of polymeric ligands are very important.

Complex formation of metal ions with HA and synthesized nanosorbents on their basis was researched by the method of ion-exchange sorption. The equilibrium of the ion exchange process was considered as the heterogeneous chemical reaction of two fold exchange:



where  $R_z$  – functional polymeric materials;  $A$  and  $B$  – exchange ions;  $z, (z)$  – their charges. The equation for the calculation of the exchange constant is express as:

$$\frac{a_1^{-z/(z)}}{a_2^{-(z)/z}} = K_e \cdot \frac{C_1^{z/(z)}}{C_2^{(z)/z}}, (2)$$

Where  $\bar{a}_1$  and  $\bar{a}_2$  - the amounts of the ions in the phase of polymeric materials;  $C_1$  and  $C_2$  - the concentrations of these ions in the solution. It may be used the following form of the isotherm equation:

$$\frac{\bar{a}_1^{-1/Z}}{\bar{a}_2^{-1/(Z)}} = K_e \frac{C_1^{1/Z}}{C_2^{1/(Z)}} \quad (3), \text{ where } K_e' = K_e^{1/(Z)}$$

Following experiment was carried out for the use of this calculation method. After achievement of the equilibrium in the reaction system (HA or Fe<sub>3</sub>O<sub>4</sub>-HA + solution of metal ions) the amount of the metal ions in the solid phase and the concentration of these in the solution were determined. Probably, in order to determine the change of the sorbed ions concentrations and other values for exchange constant it is necessary to calculate on the base of the equilibrium regulations.

The values of the constants characterized the stability of the certain coordination centers formed by chemisorption of the metal ions on the polymeric sorbents (native humic acids and nanocomposites synthesized on the base of HA) are presented in the Table 1. These data characterize "microcoordination" process.

Table 1. Stability constants of the coordination centers of metal complexes of HA and nanocomposites

Sorbent	Ni <sup>2+</sup>		Co <sup>2+</sup>		Cd <sup>2+</sup>	
	lg K <sub>1</sub>	lg β <sub>2</sub>	lg K <sub>1</sub>	lg β <sub>2</sub>	lg K <sub>1</sub>	lg β <sub>2</sub>
HA	3.91	5.75	3.75	5.50	3.69	5.35
Fe <sub>3</sub> O <sub>4</sub> - HA	4.17	5.83	3.86	5.65	3.72	5.49

These data show that the stability of the coordination centers depends on the nature of metals and corresponds to row of Irving-Williams. The increase in the metal coordination centers stability for the investigated polymeric sorbents was observed at the following order: Fe<sub>3</sub>O<sub>4</sub>- HA > HA.

Ion exchange on the HA and nanocomposites, synthesized on their basis, flows as mentioned above, with participation of protogene groups, differing by its chemical nature and capability to the ionization. In connection with this, it should be expected that adsorption centers of the investigated humic derivatives should be differed by activity. To explain this, we have conducted a conventional gradation of the sorption centers by degree of affinity with metal ions and thus there have been carried out their division into the groups, characterized by different levels of binding energy.

On the Langmuir isotherms for the ion adsorption in the wider interval of concentration there is observed several line parts (Figures 1, 2) that is the evidence of existence of corresponding number of the same type of active centers.

One can assumed that in narrow interval of concentrations of external solution, answering to infill of sorption centers with high affinity with metal-ions from the beginning to saturation, the binding energy of metal-ions by HA and nanocomposites on their basis is the same, and at the same time the sorption of isotherm is described by line form of Langmuir equation. Thus, this group of adsorption centers will be characterized the corresponding value  $a_\infty$  and value of constant of adsorption equilibrium  $K_a$ .

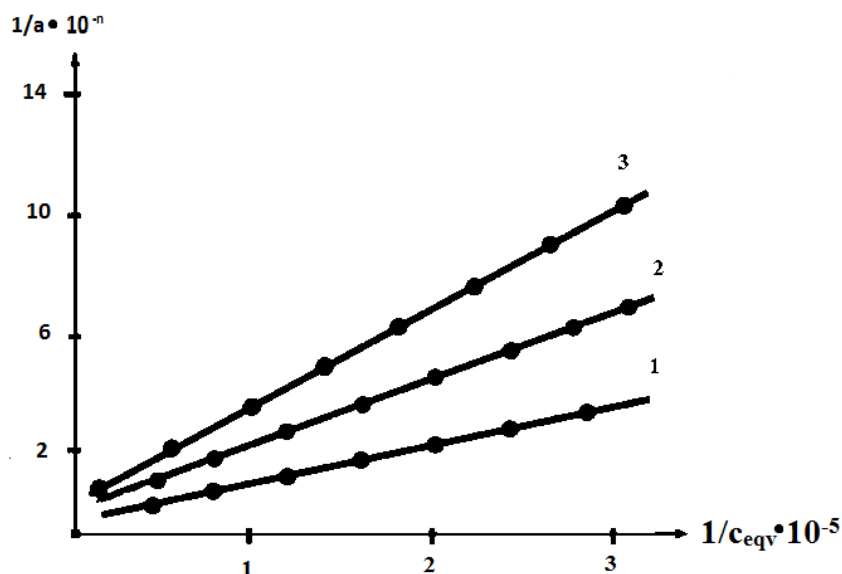


Fig. 1. Isotherms of Langmuir for sorption on the HA of Cd<sup>2+</sup> ions from the water solutions of nitrate salt 1- n=5; 2 - n=4; 3 - n=3

Figure 1. Isotherms of Langmuir for sorption on the HA of Cd<sup>2+</sup> ions from the water solutions of nitrate salt 1- n=5; 2 - n=4; 3 - n=3

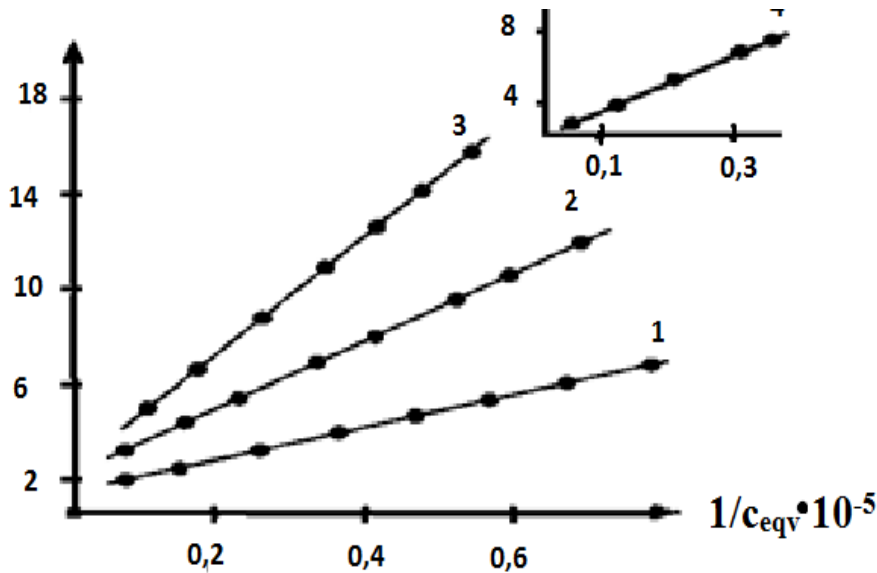


Fig. 2. Isotherms of Langmuir for sorption on the Fe<sub>3</sub>O<sub>4</sub>- HA of Ni<sup>2+</sup> ions from the water solutions of nitrate salt of proper concentrations: 1 - n=5; 2 - n=4; 3, 4 - n=3

Figure 2. Isotherms of Langmuir for sorption on the Fe<sub>3</sub>O<sub>4</sub>- HA of Ni<sup>2+</sup> ions from the water solutions of nitrate salt of proper concentrations: 1 - n=5; 2 - n=4; 3, 4 - n=3

Table 2. Parameters of Langmuir equation for sorption of metal ions by humic derivatives

Sample	Metal ion	a <sub>L</sub> , M·g <sup>-1</sup>	K <sub>a</sub>
HA	Ni <sup>2+</sup>	0.51 x 10 <sup>-3</sup>	1.40 x 10 <sup>3</sup>
	Co <sup>2+</sup>	0.45 x 10 <sup>-3</sup>	1.26 x 10 <sup>3</sup>
	Cd <sup>2+</sup>	0.35 x 10 <sup>-3</sup>	1.15 x 10 <sup>3</sup>
Fe <sub>3</sub> O <sub>4</sub> - HA	Ni <sup>2+</sup>	0.39 x 10 <sup>-3</sup>	1.20 x 10 <sup>3</sup>
	Co <sup>2+</sup>	0.35 x 10 <sup>-3</sup>	1.05 x 10 <sup>3</sup>
	Cd <sup>2+</sup>	0.29 x 10 <sup>-3</sup>	0.95 x 10 <sup>3</sup>

As followed from these data the number of the coordination centers and the values of Hill coefficient (X) increase simultaneously. This fact shows that the cooperativity of the complex formation by interaction of metal ions with polymeric sorbents increases (Table 3).

Table 3. Characteristics of the complex formation between metal ions and polymeric sorbents

Me <sup>2+</sup>	Sorbent	K <sub>A</sub> , M <sup>-1</sup>	N <sub>A</sub>	X <sub>A</sub>	K <sub>B</sub> , M <sup>-1</sup>	N <sub>B</sub>	X <sub>B</sub>
Ni <sup>2+</sup>	HA	4.3·10 <sup>7</sup>	58.5	1.70	4.5·10 <sup>6</sup>	70.5	2.25
	Fe <sub>3</sub> O <sub>4</sub> - HA	3.8·10 <sup>7</sup>	50.0	1.53	5.3·10 <sup>6</sup>	67.3	2.15
Co <sup>2+</sup>	HA	5.0·10 <sup>7</sup>	43.4	2.00	2.4·10 <sup>6</sup>	65.6	2.30
	Fe <sub>3</sub> O <sub>4</sub> - HA	3.5·10 <sup>7</sup>	37.8	1.85	3.4·10 <sup>6</sup>	54.9	1.85

Cd 2+	HA Fe <sub>3</sub> O <sub>4</sub> - HA	3.7·10 <sup>7</sup> 3.0·10 <sup>7</sup>	25.6 23.7	1.15 1.05	5.3·10 <sup>6</sup> 1.1·10 <sup>6</sup>	43.4 37.6	2.75 2.43
----------	---	--	--------------	--------------	--	--------------	--------------

Shows, that degree of extraction of metal ions from solutions by a sorption method depends on a number of factors among which the cores are: concentration of metal ions and sorbent in a reaction mixture and process time.

### *References*

1. *Vermeerm A.W.P.* Adsorption of Humic Acids to Mineral Particles. 2. Polydispersity Effects with Polyelectrolyte Adsorption / A.W.P. Vermeer, L.K. Koopal // *Langmuir*, 1998. № 14. P. 4210-4216.
2. *Zaripova A.A.* Nanostructured magnetoactive humic based sorbents for radionuclides / Zaripova A.A., Kydralieva K.A., Bondarenko T.F., Gorbunova N.V., Muratov V.S., Dzhardimalieva G.I., Golubeva N.D., Pomogailo S.I., Pomogailo A.D., Jorobekova Sh. // *Books of abstracts: 15<sup>th</sup> International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region with focus on Environmental Threats in the Mediterranean Region: Problems and Solutions (MESAEP)*. October 7-11, Bari, Italy, 2009. P. 492 .
3. *Chekanova A.E.* Humic substances as stabilizing agents for superparamagnetic nanoparticles/ A. Chekanova, T. Sorkina, A. Dubov, E. Goodilin, N. Kulikova, I. Perminova // *Proceedings of the 14-th Meeting of International Humic Substances Society, Moscow-Saint Peterburg, Russia, September 14-19, 2008*. P. 585.
4. *Pomogailo A.D.* Magnetoactive humic based nanocomposites / A.D. Pomogailo, K.A. Kydralieva, A.A. Zaripova, V.S. Muratov, G.I. Dzhardimalieva, S.I. Pomogailo, N.D. Golubeva, Sh.J. Jorobekova // *Macromolecule Symposia*, 2011. № 304. P. 18-23.