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THE ANALYSIS OF STRUCTURAL FEATURES OF HUMIC ACIDS FRACTIONS AFTER MECHANOCHEMICAL MODIFICATIONS

[1]M.P. Mirzobekzoda, [2]E.V. Maltseva, [1]N.S. Shekhovtsova

Scientific Supervisor: Ph. D, E.V. Maltseva; associate professor N.S. Shekhovtsova

[1]Tomsk Polytechnic University, Russia, Tomsk, Lenin ave., 30, 634050

[2]Institute of Petroleum chemistry SB RAS, Russia, Tomsk, Academichesky ave., 4, 634021

E-mail: maltseva2@gmail.com

АНАЛИЗ СТРУКТУРНЫХ ОСОБЕННОСТЕЙ ФРАКЦИЙ ГУМИНОВЫХ КИСЛОТ ПОСЛЕ МЕХАНОХИМИЧЕСКОЙ МОДИФИКАЦИИ

М.П. Мирзобекзода[1], Е.В. Мальцева[2], Н.С. Шеховцова[1]

Научный руководитель: к.х.н. Е.В. Мальцева; доцент, к.х.н. Н.С. Шеховцова

[1]Национальный исследовательский Томский политехнический университет,

Россия, г. Томск, пр. Ленина, 30, 634050

[2]Институт химии нефти СО РАН, Россия, г. Томск проспект Академический, 4, 634021

E-mail: maltseva2@gmail.com

Впервые изучено влияние модифицирующего агента тиомочевины в процессе механоактивации на структурный состав и кислотно-основные свойства основных фракций гуминовых кислот – гиматомелановые и протогуминовые кислоты.

Humic substances take an essential role in environmental protection. With growing of world production, the amount of chemical substances, that are able to migrate through the atmosphere and hydrosphere, increase. Thus, protection function of the humic substances that irreversibly absorb a lot of man-induced toxicants with detoxification of soil pollutant, plants of living substances due to the variety of functional groups, becomes very important [1,2]. In the previous works was shown that mechanoactivation (MA) modifies the structure and properties of humic acids, increasing their detoxication ability [3, 4]. However, investigation of mechanoactivation influence on humic acids fractions, possessing unique physiological activity, represent huge interest.

Therefore, the main purpose of this work is an investigation of mechanoactivation influence on the acid-base properties of humic acids after their fractionation.

Humic (HA) and fulvic (FA) acids were extracted from transitional peat of the Tomsk region with decay

degree of 20%. Peat was treated at planetary activator mill AGO-2S with speed of drums 1820 revolution per minute. As modifying agents were used solid NaOH and thiourea. Investigation of modifying agents influence on composition and acid-base properties of separated humic acids (hymatomelanic HMA and proto-humic prHA) were performed by potentiometric titration, IR and ^{1}H MRS spectroscopy. Influence of modification on yield of fulvic acids and partial fractions of humic acids is presented in table 1.

Corresponding to this table, mechanoactivation in case of usual modification lead to the increase in yield of FA twice, and adding of modifying agent increases it for 3 times. The total yield of humic acids from mechanoactivated peat increases up to 4-7 times, and maximum yield was recorded for the sample, that was extracted from treated peat without reagents.

Table 1. Influence of mechanochemical modification on yield of humic acids

Sample	Content, %			
	FA	HMA	prHA	Total contain of humic acid
Initial reagent (1)	0,53	0,86	1,90	2,76
MA (2)	1,08	4,20	13,84	18,04
MA+NaOH (3)	1,41	4,60	10,35	14,95
MA+CS$(NH_2)_2$ (4)	1,46	3,52	7,95	11,47

Correspondingly to the published data, alcoholic fraction of HA and HMA characterized by saturation of carbon bonds and aliphatic fragments prevails over the aromatic components [5]. From Table 1 it is seen that hymatomelanic contains increases up to 4−5 times. Part of hymatomelanic acids is 30% from total HA contain, and it does not depend on the peat modification conditions. The most important affect modification has on yield of proto humic acids, whose structure has aromatic bounds. Especially, yield of proto-humic acids fraction increased up to 7 times in case of modification without reagents. This fraction has the most of interest for investigation of interaction with poly-aromatic substances.

Table 2. Differential coefficients of humic acids fractions by results of IR spectroscopy

Sample	D_{3400}/D_{1610}	D_{2920}/D_{1610}	D_{2860}/D_{1610}	D_{1720}/D_{1610}	D_{1270}/D_{1610}	D_{1040}/D_{1610}
HMA1	0,93	**0,79**	0,65	-	1,10	0,86
HMA2	1,10	0,79	-	-	1,02	0,79
HMA3	1,06	0,83	0,83	-	1,09	0,95
HMA4	0,93	0,76	0,61	-	0,96	0,80
prHA1	1,2	0,97	-	0,87	0,63	0,76
prHA2	1,18	0,94	-	0,87	0,7	0,72
prHA3	1,21	1	-	0,9	0,72	0,76
prHA4	1,19	1	-	0,9	0,67	0,63

Differential coefficients were calculated according to the IR spectroscopy results. This coefficient let us estimate structural changes in fractions of humic acids (Table 2).

Obtained data let us conclude that in structure of HMA part of functional groups (COOH, OH) is more than quantity of multiple bonds. However, relation of methyl groups and multiple bounds is lower than for proto-humic acids. Influence of modification is more appreciable for samples HMA3, prHA3 and for prHA4 only decreasing part of carbohydrate contain.

Table 3. Contain of functional groups in fractions of humic acids after modification

Sample	HA	HMA	prHA
Initial (1)	26,6	16,2	25,0
MA (2)	10,0	9,0	8,0
MA+NaOH (3)	10,2	11,8	11,4
MA+CS$(NH_2)_2$ (4)	13,4	14,2	15,0

Samples of humic acids and their fractions were titrated in order to estimate the amount of oxygen-containing poly-functional groups (Table 3).

For initial substance, oxygen-containing groups are concentrates at proto-humic acids. However, after modification we can see decrease of functional groups contain for all fractions and total sample of HA up to 2−3 times. This increase has an extremum (MA2), then contains of functional groups increase up to 30% from the initial one for all substances, that were obtained within the modifications with thiourea.

Thus, it was shown that modification let us to increase the yield of humic acid up to 4−7 times and their fraction – up to 4−5 times. Contain of HMA is 30% from total HA contain, and in result of modification part of HMA is almost constant. IR spectroscopy was performed to characterization of humic acids fractions bonds saturation.

Also, it was shown that modification decrease the amount of acid groups in HA, thus the tendency remains separately for fractions of HMA and prHA.

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НАНОРАЗМЕРНЫЕ ПОРОШКИ МЕТАЛЛОВ КАК ДЕЭМУЛЬГАТОРЫ ВОДОНЕФТЯНЫХ ЭМУЛЬСИЙ

М.А. Морозов[1], А.С. Акимов[2]

Научный руководитель: ст.науч.сотр., канд.хим.наук Т.А. Федущак[2]

[1]Национальный исследовательский Томский государственный университет,
Россия, г.Томск, пр. Ленина, 30, 634050

[2]Институт химии нефти СО РАН, Россия, г.Томск, пр. Академический, 4, 634021

E-mail: fr0stm4n@mail.ru

NANOSIZED METAL POWDERS AS DEMULSIFIERS OF OIL-WATER EMULSIONS

M.A .Morozov[1], A.S. Akimov[2],

Supervisor: Senior Researcher, Ph.D. T.A. Feduschak

[1]National research Tomsk state university, Russia, Tomsk, Lenin str. 36, 634050

[2]Institute of Petroleum Chemistry SB RAS, Russia, Tomsk, Academic av. 4, 634021

E-mail: fr0stm4n@mail.ru

The ability of electroexplosive metal nanopowders and their derivatives to affect at the stability of hydrophobic emulsions was discovered for first time . Nanoreagent was revealed and its efficiency is not only exceeds foreign nonionic demulsifiers, but also have the unique ability to be easily separated and maintains its effectiveness with repeating use. The mechanisms of the process were discussed.

Традиционные подходы, связанные с регулированием агрегативной устойчивости лиофобных дисперсных систем, предполагают преимущественным образом использование ионогенных и