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STUDY OF THE YIELD OF HUMIC ACIDS IN A HYDRODYNAMIC ROTARY-PULSATING APPARATUS

Abstract. In order to better understand what happens to the composition and structure of humic acids under the influence of hydrodynamic processing, we processed the same treatment under the most severe conditions: coals with a degree of crushing of 0-3 mm were treated in the HRPA with an alkali solution at S: L = 1: 4 at the ratio of 20% of alkali for total raw material, at temperature 70 °C and duration of one minute. After that, the chemical characteristics and fractional composition of the initial humic acids and processed in HRPA were established. The results showed that the effect of hydrodynamic forces leads to an increase in the content of carbon and hydroxyl groups in humic acids. The amount of total oxygen of the functional groups for humic acids of coals increase significantly and the oxygen content drops noticeably in an unaccounted form, which may occur due to rupture of ester bonds or of heterocycles.

Keywords: hydrodynamic rotary pulsation apparatus, pulp, humic acid, extraction, alkali, coal.

Introduction. The extraction of humic acids of different coals and transfer to the solution proceeds in different ways [1-5]. Quantitative extraction of humic acids are different as well depending on the alkaline reagent. Humic acids are most easily extracted by a caustic soda. The extraction with sodium carbonate and ammonium hydroxide changes in a different way. Humic acids of Karazhira coal (Kazakhstan deposits)and waste of Kyzylkiya Coal have the greatest reactivity to interaction with solutions of alkalis and ease of recovery.

One of the tasks of our work was the selection of raw materials for the production of humic acid salts for the national economy. From these positions, raw materials should contain not only a large amount of humic acids, but the latter must be easily extracted with alkali. As alkali, we used sodium hydroxide, a mixture of sodium hydroxide and sodium carbonate. The process of dissolution of humic acids in various solvents and alkalis is directly dependent on the content of acidic functional groups and in the reverse of the aromatic condensation [6, 7].

Experimental part. To intensify the process of extraction of humic acids by alkaline reagents, we applied a hydrodynamic rotary-pulsation apparatus.The apparatus includes a housing 1 with a suction pipe 2 and an unloading port 3, a conical rotor 5 is fixed to the shaft 4, and a stator 7 is mounted on the housing cover 6, which can move in the longitudinal direction. On the conical surfaces of the rotor and stator there are grooves 8 located along the generatrix.

The device works as follows. The pulp through the suction pipe gets into the zone of the first row of the rotor indentations, from which it is thrown into the stator grooves. Under the pressure of the following portions, the pulp from the stator enters the next row of rotor depressions, etc. Since the conical surface of the stator is pressed against the surface of the rotor by springs 9 and the recesses on them are made with an overlap of more than one, the pulp is subjected to intense pulsating action due to both hydraulic shocks and a high-gradient velocity field and accelerations with high shear stresses.

Results and its discussion. The process of extraction of humic acids from coals depends not only on the structural features of the latter, on the type of the extracting alkaline reagent, but also on the time of contact of the coal with the alkali solution, the process temperature, the concentration of the alkaline solutions used, the ratio of coal to the water-alkaline solution, and the degree of coal crushing. Investigation of the dependence of the rate of extraction of humic acids on the contact time and concentration of alkaline solutions revealed that after 30 minutes of interaction of Karazhira brown coal with a 20 % aqueous solution of sodium hydroxide at a ratio of 1: 1 and a temperature of 20 °C, only 61.3 % of humicacids, while at 95 °C – 80.5 % (table 1).

Table 1 – Dependence of the degree of extraction of humic acids on the temperature and concentration of alkali

Interaction temperature, °C	95						65			
Concentration of alkaline reagent, %	20		10		5		20		10	
Time of interaction, min	15	30	15	30	30	60	30	60	30	60
Has passed into a soluble state of humic acids, %	80,4	80,5	80,4	95,9	97,6	100	61,3	62,8	65,1	69,6

In a 10% solution of alkali, the transition of humic acids into a solution at 30 minutes interaction increases from 65.1 to 95.9%, and in a 5% solution of alkali at 95 °C for 30 minutes, the extraction of humic acids is almost complete and is equal to 97, 6%. From this it follows that the recovery of humic acids strongly depends on the temperature and the ratio S:L.

Treatment of coal with a 40% sodium hydroxide solution in an amount of 20% with respect to dry coal does not lead to a complete transition of humic acids to sodium humates. The reason for this is incomplete wetting of the ratio S:L.

When considering the degree of extraction of humic acids as a function of the S: L ratio (table 2), it can be seen that an increase in the latter results in a decrease in the yield of acids in the solution. So by treatment with a solution of alkali and a single wash with water from Karazhira coal at a ratio of S: L = 1:7, humic acids are recovered by 100%, at S:L = 1:4 only by 96 %. In the same sequence, the extraction of humic acids from other coals also takes place.

Table 2 – The degree of extraction of humic acids
as a function of the concentration of the alkali solution and the ratio of S:L at 80 °C

Humic acids from coals of Kazakhstan deposits	Humic acids extracted % at:							
	The treatment with 3% solution of NaOH (S:L = 1:7)	Rinsing the sediment with water			Treatment with 5% NaOH (S: L = 1:4)	Rinsing the sediment with water		
		1st	2nd	3rd		1st	2nd	3rd
Karazhyra	38,3	35,8	19,5	6,4	35,1	34,6	20,3	10,0
Kumertau	85,0	15,0	–*	–	78,0	18,0	4,0	–
Kyzylkiya	70,5	26,9	2,6	–	64,9	25,1	10,0	–
* «–» means absence.								

The processing of coals in the hydrodynamic rotary-pulsating apparatus (HRPA) greatly accelerates the process of extraction of humic acids from them. Coals and waste products of briquette production with a degree of crushing of 0-3 mm were processed in the HRPA alkaline solution at S:L = 1: 4 at the rate of 20% of alkali for the total amount of raw materials. The suspension was separated into an insoluble residue and a solution of humates by centrifugation. Table 3 shows the results of treating an alkaline suspension of various coals in HRPA at 25 °C.

As we see, when processing coal with a solution of sodium hydroxide in HRPA, the process of recovery of humic acids takes place in a few seconds. The most easily interact with alkali with complete recovery of humic acids Kumertau coals and waste from Kumertau briquette factory.

Karazhyra coals under mechanical destruction behave somewhat differently. After treatment in a hydrodynamic apparatus 3-5 sec. at 25 °C, humic acids pass into a soluble state only by 50% of the total

Table 3 – Yield of humic acids after treatment of the suspension in HRPA

Type of coal	The content of humic acids in the feedstock,%	Processing time in HRPA, sec	Humic acids are extracted, % of their content in raw materials
Karazhyra deposit	52,2	10	92,4
Kyzylkiya deposit	40,1	5	100,0
Kumertau deposit	63,1	3	100,0
Wastes from the Kumertau briquette factory	58,9	3	100,0

content in coal, and at 70 °C the process accelerates and the solution passes at the same time 92.4%, and in 10 seconds. - almost completely (98.7%).

Further, the influence of the temperature and the type of alkaline reagent on the degree of extraction of humic acids at a 10-second exposure was established during the processing of Kyzylkiya coal in the HRPA (table 4).

Table 4 – Yield of humic acids from Kyzylkiya coal when treated with alkali in GRPA

Alkalis	Processing temperature, °C	The yield of humic acids, %	
		From coal	From their general content
NaOH	25	51,2	89
NaOH	70	59,0	97
Na_2CO_3	25	32,0	74
Na_2CO_3	70	39,9	79
NaOH : Na_2CO_3 = 1:1	25	46,0	91
NaOH : Na_2CO_3 = 1:1	70	50,0	96

From the data given, it can be seen that the yield of humic acids depends strongly on the type of alkaline reagent and, to a lesser extent, on the temperature. When processing coal in GRP due to degradation of molecules of coal matter, the yield of humic acids increases by 19-37% in the case of sodium hydroxide and by 7-16% in the case of a mixture of carbonate, in comparison with extraction according to standard GOST 9517-76.

Carbonate does not allow complete recovery of humic acids from Kyzylkiya coal even when heated.

We established the dependence of the extraction of humic acids on the treatment time in the HRPA and the degree of approach of the rotor to the stator (table 5).

With an increase in the duration of treatment of the carbon-alkaline suspension in GRPA, the yield of humic acids slightly increases. It also depends on the degree of rendezvous of the disks. With carbonate

Table 5 – Yield of humic acids with a different gap between the rotor and the stator GRPA

The dispersion time and the degree of approach of the disks	Type of alkali	Temperature, °C	Yield of humic acids, %
Source coal	NaOH		38,3
3 seconds, average	NaOH	25	51,2
3 seconds, maximum	NaOH	70	58,1
15 seconds, maximum	NaOH	70	60,0
3 seconds, average	NaOH : Na_2CO_3 = 1 : 1	70	50,0
	NaOH : Na_2CO_3 = 2 : 1	70	49,2
	NaOH : Na_2CO_3 = 3 : 1	70	46,2
3 seconds, maximum	Na_2CO_3	70	33,9
15 seconds, maximum	Na_2CO_3	25	32,0

extraction of cycles is not reflected in the output of humic acids. The increase in the content of caustic soda in a mixture with carbonate more than 1: 1 does not increase the yield of humic acids.

Conclusions. Processing of coals in the hydrodynamic rotary-pulsating apparatus greatly accelerates the process of extraction of humic acids. When processing coal with a solution of sodium hydroxide in HRPA, the process of recovery of humic acids takes place in a few seconds.

The yield of humic acids depends strongly on the type of alkaline reagent and, to a lesser extent, on the temperature.

When processing coal in HRPA due to degradation of molecules of coal matter, the yield of humic acids increases by 19-37% in the case of sodium hydroxide and by 7-16% in the case of a mixture of carbonate, in comparison with extraction according to GOST 9517-76 standard.

The effect of hydrodynamic forces leads to an increase in the content of carbon and hydroxyl groups in humic acids. The amount of total oxygen of the functional groups for humic acids of coals will increase significantly and the oxygen content will drop noticeably in an unaccounted form, which may occur due to rupture of ester bonds or heterocycles.

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ГИДРОДИНАМИКАЛЫҚ РОТАЦИЯЛЫҚ-ПУЛЬСАЦИОНДЫҚ ҚОНДЫРҒЫЛАРДА ГУМИН ҚЫШҚЫЛЫНЫҢ ШЫҒЫМЫН ЗЕРТТЕУ

Аннотация. Гидродинамикалық өңдеудің әсерінен гумин қышқылдарының құрамы мен құрылымы қандай болатындығын дұрыс анықтау үшін, біз сол өңдеуді аса қатаң жағдайда жүргіздік: ұнтақталуы дәрежесі 0-3 мм көмірлер ұзақтығы бір минут аралығында 70°С температурада шикізаттың жалпы мөлшеріне 20% сілті есебінде Қ:С = 1:4 кезінде сілті ертінідісімен ГРПА да өңделді. Содан кейін бастапқы және ГРПА-да өңделген гумин қышқылдарының химиялық сипаттамасы және фракциялық құрамы анықталды.

Алынған нәтижелер, гидродинамикалық әсер гумин қышқылдарында көміртегі және гидроксил топтарының құрамының артуына алып келетіндігін көрсетті. Көмірлердің гумин қышқылдары үшін функционалды топтарда жиынтық оттегі мөлшері айтарлықтай артады және есептелмеген формадағы оттегі құрамы төмендейді, бұл эфирлі байланыстардың үзілуі немесе гетероциклдердің есебінен болуы мүмкін.

Түйін сөздер: гидродинамикалық айналмалы пульсация аппараты, пульпа, гумин қышқылы, экстракция, сілтілі, көмір.

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ИССЛЕДОВАНИЕ ВЫХОДА ГУМИНОВЫХ КИСЛОТ В ГИДРОДИНАМИЧЕСКОМ РОТОРНО-ПУЛЬСАЦИОННОМ АППАРАТЕ

Аннотация. Для того, чтобы лучше разобраться что же все таки происходит с составом и структурой гуминовых кислот под влиянием гидродинамической обработки, мы ту самую обработку провели в наиболее жестких условиях: угли со степенью дробления 0-3 мм обрабатывались в ГРПА раствором щелочи при Т:Ж = 1:4 из расчета 20% щелочи на общее количество сырья, температуре 70°С и продолжительности одна минута. После этого устанавливалась химическая характеристика и фракционный состав исходных и обработанных в ГРПА гуминовых кислот.

Результаты показали, что воздействие гидродинамических усилий приводит к повышению содержания углерода и гидроксильных групп в гуминовых кислот. Значительно увеличатся количество суммарного кислорода функциональных групп для гуминовых кислот углей и заметно снижается содержание кислорода в неучтённой форме, которое возможно происходит за счет разрыва эфирных связей или гетероциклов.

Ключевые слова: гидродинамический роторный пульсационный аппарат, пульпа, гуминовая кислота, экстракция, щелочь, уголь.