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GETTING HUMATE IN A COAL OXIDATION PROCESS

Abstract. During last decades the problems of increasing the soil fertility, usage of organic additives to increase the crops yield is becoming more and more relevant. One kind of such additives are humates - sodium and potassium salts of humic acids. Humates and humic acids – chemical basis of soil humus, it's concentrate. And humus – is a basis of activity and stability of the most biochemical soil processes. Raw materials for the production of sodium humates are easily obtainable - these are brown coals, peat, oxidized hard coal, a production technology is complex with low production costs. Especially relevant for the production of humates is the use of oxidized coal. Oxidized coals have a wide range of macro- and microelements, a large number of humic acids, which are similar in composition to soil. The coal oxidized in the seams is practically not used in the national economy and goes to dumps together with overburden. The proposed method allows to improve the cost of the finished product. A method of producing humate by oxidation of coal is known. To study the costs of humic acids, as well as to study the qualitative and quantitative composition of humic acids, alkaline solutions of various concentrations were used. Tasks set during the study: a review of the scientific literature on the properties of HA, their composition and method of production; a technique was developed for conducting an experiment on the effect of alkali concentration, temperature and extraction time on the degree of extraction of HA from the coals of Central Kazakhstan; the regression equations were obtained during mathematical processing of the experimental results, which made it possible to establish the influence of each of these factors on the output of HA; Qualitative and quantitative composition of HA obtained by extraction with alkali of various concentrations was carried out.

Key words: humates, coal oxidation, alkali solutions, brown coal, NaOH, qualitative and quantitative composition.

Introduction. The relevance of this work is associated with the growing tendency to use coal not only as a fuel, but also as a valuable chemical raw material. Specifically, one of the products of the chemical processing of coal is humic compounds, which are widely used in various sectors of national economy.

Humic acids are capable of ion exchange reactions, form soluble and insoluble humates. Humic acids are a powerful geochemical agent that contributes to the decomposition of rocks and minerals, the concentration, dispersion and redeposition of elements in the earth's crust. Humic acids is the main part of the organic matter of the soil (humus), which determines its fertility [1].

All humic acids are soluble in alkalis, humates (salts of humic acids) of alkali metals are soluble in water, humates of other metals are insoluble. Humic acids are thermally unstable, in the temperature range of 100-200° C they are decarboxylated and lose their solubility. With an increase in the degree of coalification (the conversion of peat sequentially to brown, hard coal and anthracite) in the composition of humic acids, the proportion of carbon bound in aromatic cycles increases, which form condensed structures including a large number of rings.

Humic acids are completely cleaved by metallic sodium in liquid ammonia to form ether-soluble products, which, according to T. A. Kukharenko, is evidence of the presence of simple ether bonds in the humic acid molecule, which are the main type of bonds.

The chemical composition of humic acids depends mainly on the acidity of the aquatic environment and the degree of decomposition of plant material.

Of the physical properties of humic acids, we should mention their developed surface, which determines a number of their qualities as biologically active substances and collectors of heavy metals. The specific surface area is estimated to be approximately $900 \text{ m}^2 / \text{g}$, which is comparable to the specific surface area, for example, of activated carbon. These properties of humic acids are enhanced by the presence in their molecules of functional groups characteristic of effective complexing agents. The structure of humic acids suggests that their presence in the composition of coals and peats leads to the concentration of heavy metal ions by the latter, which is caused by complexation, sorption and ion exchange.

Humic acids are used in the production of lead-acid accumulators, to stabilize clay slurries during well drilling, as plant growth stimulants and components of organomineral (humic) fertilizers [2].

In recent years, humic acids and humates are increasingly used in various sectors of national economy. They are used as peptizing additives (viscosity reducers) to clay solutions used in well drilling, antiscale to soften water in steam columns, in the ceramic and cement industries, as a means to reduce the permeability of soils.

Due to the presence of active functional groups and a highly developed surface, humic acids are good sorbents (absorbers) and surface active agents. Carbon-alkali extraction of brown coals is used as a pickling material for wood finishing. In known doses, humic acids are antiseptics and can be used, in particular, for the healing of damaged skin of animals. Humic acids also have tanning and coloring properties and are used for the preparation of adhesive and oil paints, as skin tanning agents, for emulsification of bitumen and asphalts, as binders [3-4].

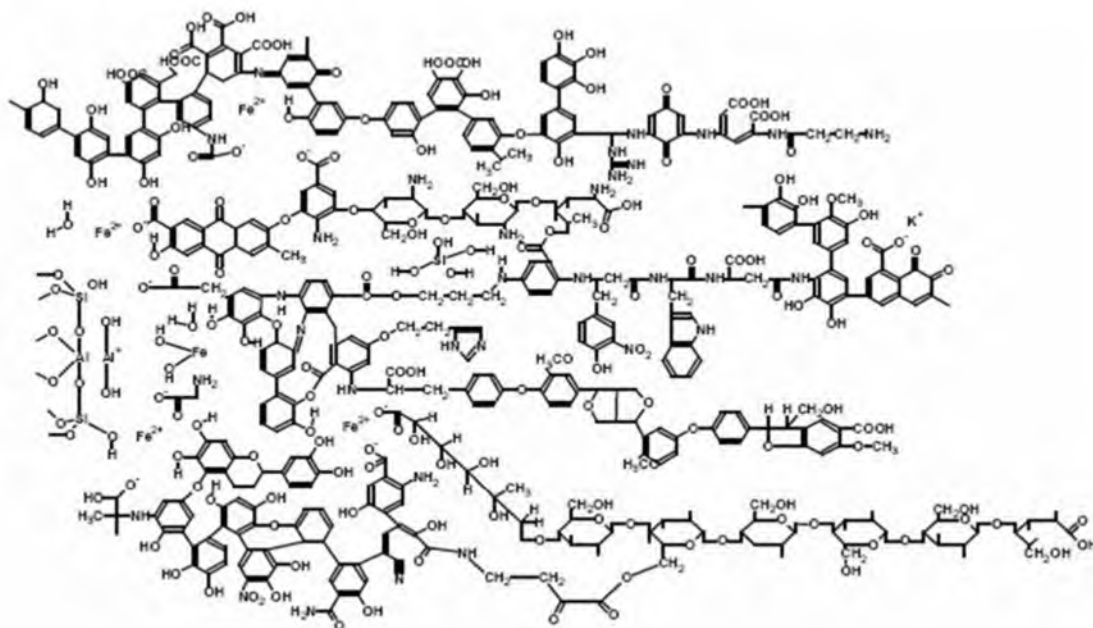


Figure 1 - Hypothetical model of soil humic acid structure

Experimental part. The brown coal from the “Kumyskuduk” open pit mine of the Verkhne-Sokurskoye deposit and the commercial preparation of sodium humate from “Asia COMPOGUM” LLP were used as HA sources according to the following procedure.

When conducting studies on the release of HA, brown coal was chosen as the object of research. For the experiment, a fraction no larger than 50 mm was used. Then, the initial brown coal was crushed on a jaw crusher to a size of 0.5 mm. After that, the crushed brown coal was abraded on VKMD 6 with a size of not more than 0.2 mm. Next, brown coal is placed in a plastic bucket and closed with a lid so that it does not oxidize. Then, for each experiment, the required mass of ground brown coal was taken and experiments were carried out [5].

A portion of crushed brown coal weighing 10 g was embathed with 100 ml of a NaOH solution of a given concentration (2%, 4%, 6%) and thoroughly mixed for a certain time (10 minutes, 25 minutes, 30 minutes). In this case, humic compounds pass into a soluble form in the form of sodium humate. After this, the undissolved brown coal precipitate was filtered off. The filtrate was neutralized with a hydrochloric acid solution until acidic (pH = 2 ... 3), while humic acids insoluble in water and acidic solutions precipitated. The precipitate HA is separated by centrifugation, then washed with distilled water and dried at a temperature of 105° C to constant weight.

The yield of humic acids is determined by next formula:

$$\eta = (m_2/m_1) \times 100\%, \tag{1}$$

where m_1 – mass of brown coal; m_2 - mass of humic acids.

Table 1- Calculated data for building a dependency $Y = f(C)$

C,%	$X_2=-1$	$X_2=0$	$X_2=+1$
2,0	4,680	7,034	4,712
2,5	4,044	6,461	4,201
3,0	3,546	6,025	3,828
3,5	3,188	5,729	3,595
4,0	2,968	5,572	3,500
4,5	2,887	5,554	3,544
5,0	2,946	5,675	3,728
5,5	3,143	5,934	4,050
6,0	3,480	6,334	4,512

Graphical dependences $Y = f(C)$ of the HA output at fixed concentration values (X_2) are presented in figure 1.

From Figure 1 it follows that the dependence of the HA yield on alkali concentration has a nonlinear dependence. So for an average extraction time of 20 min with an increase in alkali concentration from 2% to 4%, the yield of HA decreases from 7% to 5.6%, and with a further increase in alkali concentration to 6%, the yield of HA increases to 6.5%. With an increase in extraction time of 30 min with an increase in alkali concentration from 2% to 4%, the yield of HA decreases from 4.7% to 3.5%, and with a further increase in alkali concentration to 6%, the yield of HA increases to 4.5%. With a decrease in extraction time of 10 min with an increase in alkali concentration from 2% to 4%, the yield of HA decreases from 4% to 2.9%, and with a further increase in alkali concentration to 6%, the yield of HA increases to 3.5% [6].

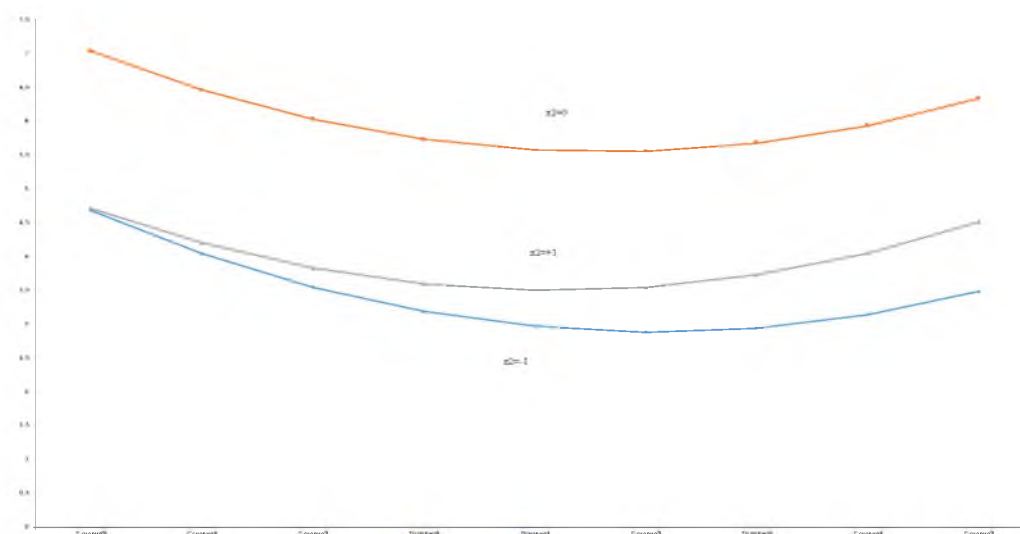


Figure 2 – Dependency diagram of the yield of humic acids on alkali concentration (-1 = 10 min, 0 = 20 min, + 1 = 30 min).

Similarly, to construct the graphical dependencies $Y = f(T)$, equations (2.39-2.41) were used, with the help of which the HA output was calculated for fixed time values. The calculated data are presented in table 2.

Table 2 - The calculated data for constructing the dependence $Y = f(\tau)$

T	$X_1=-1$	$X_1=0$	$X_1=+1$
10	4.72	3.008	3.52
12.5	5.769	4.119	4.694
15	6.53	4.943	5.58
17.5	7.004	5.479	6.179
20	7.19	5.728	6.49
22.5	7.089	5.689	6.514
25	6.7	5.363	6.25
27.5	6.024	4.749	5.699
30	5.06	3.848	4.86

The graphical dependences $Y = f(\tau)$ of the HA output at fixed concentration values (X_2) are presented in figure 3.

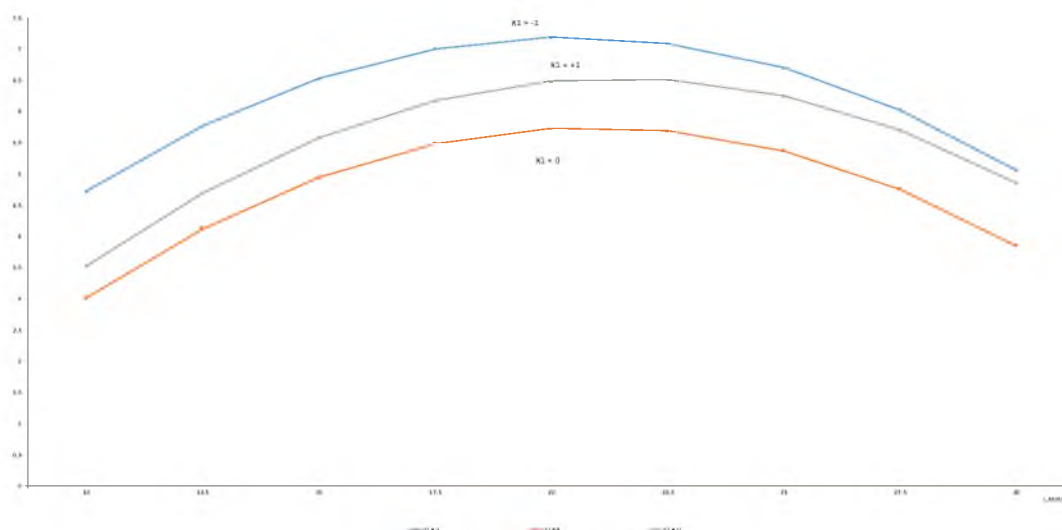


Figure 3 - Dependency diagram of the yield of humic acids on the processing time (-1= 2%, 0= 4%, +1= 6%)

The graphical dependences of the HA yield on the time of processing the coal with NaOH solutions show the presence of a maximum. The maximum value, that is, the time at which the maximum yield of HA can be determined by analyzing equations. The maximum point corresponds to the derivative $dy/d\tau = 0$.

Qualitative and quantitative composition of humic compounds extracted from coal.

The qualitative and quantitative composition of the organic matter extracted from coal by extraction with alkali solutions was determined using an Agilent 7890A gas chromatograph with an Agilent 5975C mass selective detector. Results are processed automatically using the GS-MSDDataAnalysis program.

From the presented data it follows that the qualitative and quantitative composition of the obtained humic acids depends on the concentration of the alkali extractant. This is evidenced by different peak heights corresponding to individual organic compounds. Differences in the number of peaks corresponding to individual chemical compounds can also be noted. Identification of individual organic compounds showed that the composition of the obtained humic compounds is complex and multicomponent. Thus, the qualitative and quantitative composition of HA obtained by extraction of coal with alkali solutions depends on many factors, primarily on the concentration of alkalis. It is likely that in this case various chemical compounds with different degrees of solubility in water and alkalis are formed. This explains the dependence of the HA yield on alkali concentration [7].

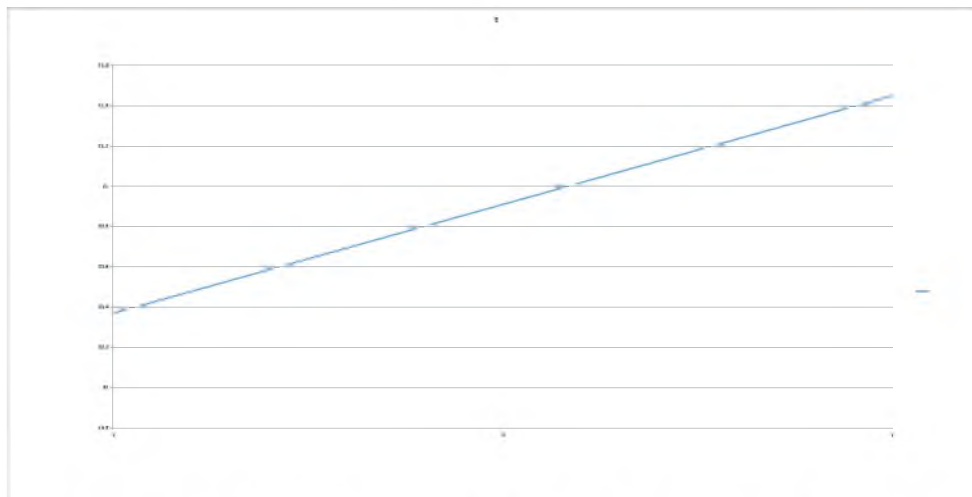


Figure 4 – Dependency diagram of the yield of humic acids in the presence of a maximum

The goal is a financial justification for the extraction of humic acid from brown coal.

The implementation of the process of obtaining the product involves extraction of humic acid by acidifying an aqueous solution of the preparation of sodium humate with hydrochloric acid to pH = 2 and preliminary preparation of humic acid for reactions (centrifugation, washing, drying). During the experiment, Kumyskuduksky coal was selected. The work was carried out in classical conditions.

The methodology of the experiment: 10 grams of brown coal are placed in a beaker (flask), the required volume of extractant is added and the resulting system is mixed for a given time (the volume of extractant and mixing time are selected in accordance with the experimental design matrix for a specific experiment). After mixing, the mixture is settled; filtered; dried. The calculations performed on the experiment planning matrix made it possible to reduce the total number of experiments to 9. Based on the dependence of the yield of the substance on time and the ratio of solvents, optimal synthesis conditions were calculated [8].

The experimental part consisted of 9 experiments. Each experiment was conducted separately. Thus, the total number of experiments was 18.

Qualitative and quantitative composition of the civil code. The alkalis obtained by extraction of coals with solutions of alkalis depend on many factors, primarily on the concentration of alkalis. It is likely that various chemical compounds are formed that have different degrees of solubility in water and alkalis. This explains the dependence of the GC yield on the alkali concentration.

Abundance

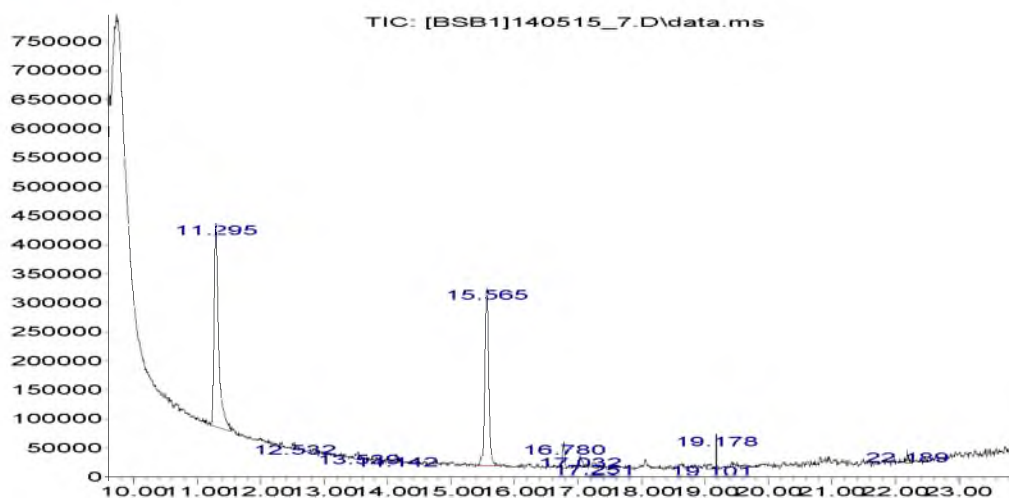


Figure 5 – Chromatogram of humic compounds after coal extraction with 2% alkali solution

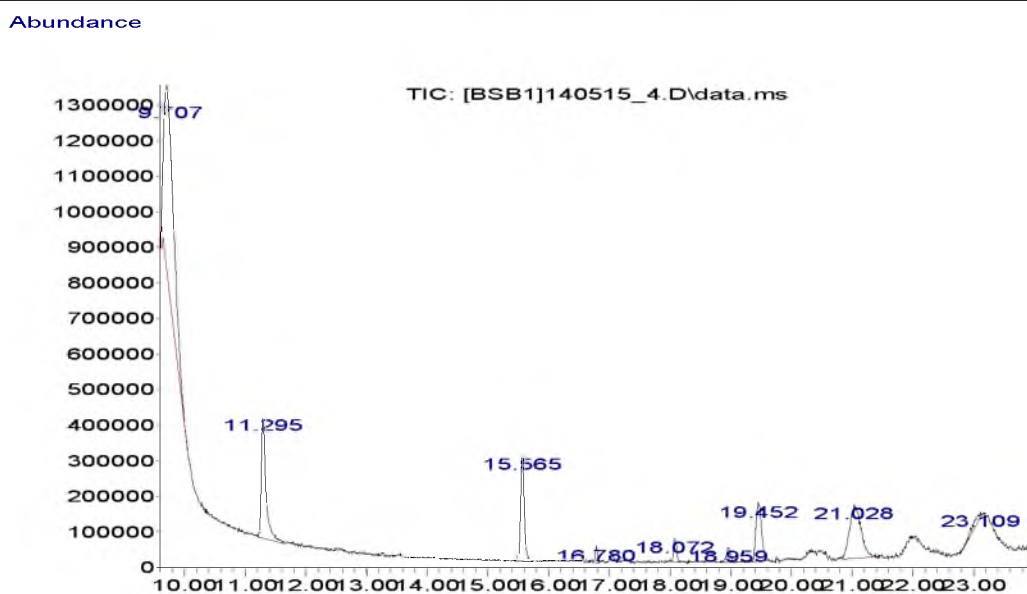


Figure 6 - Chromatogram of humic compounds after coal extraction with 4% alkali solution
Composition of humic compounds obtained during coal extraction with 4% alkali solutions

№	Chemical compounds	Chemical compound content in the sample, %
1	Trichloromethane	45.24
2	O-xylene	14.26
3	Naphthalene	10.27
4	Tetracosane	0.93
5	Dodecane, 2-methyl-6-propyl-eicosan	1.72
6	Sulphurous acid	1.65
7	Pentadecan	8.45
8	Tridecane	15.34
9	Dodecane, 2,6,11-trimethyl-Heptadecane	2.13

Conclusion. The essence of the method involves a single extraction of humic acids from an analytical coal sample with a dilute sodium hydroxide solution when heated, followed by their precipitation with an excess of hydrochloric acid. After processing the initial coal with water vapor in the reactor, the yield of humic acids from them increased. The obtained data shows the possibility of efficient production of humates from oxidized coal. The yield of humic acids depends on alkali concentration, extraction time and process temperature.

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КӨМІРДІ ТОТЫҚТЫРУ ПРОЦЕССІНДЕ ГУМАТ АЛУ

Аннотация. Соңғы онжылдықта топырақтың құнарлылығын арттыру, ауыл шаруашылығы дақылдарының өнімділігін арттыру үшін органикалық қоспаларды қолдану проблемасы өзекті болып отыр. Мұндай қоспалардың бірі-гуматтар-натрий және гумин қышқылдарының калий тұздары. Гуматтар мен гумин қышқылдары-топырақ гумусының химиялық негізі, оның концентраты. Гумус-көптеген биохимиялық топырақ процестерінің белсенділігі мен тұрақтылығының негізі. Натрий гуматтарын алуға арналған шикізат оңай қол жетімді-бұл қоңыр көмір, шымтезек, тотыққан тас көмір, өндіріске төмен шығынмен кешенді алу технологиясы. Тотыққан тас көмір гуматтарын өндіру үшін пайдалану ерекше өзекті. Тотыққан

бұрыштардың макро - және микроэлементтердің кең жиынтығы, құрамы бойынша топыраққа жақын гумин қышқылдарының көп мөлшері бар. Қабаттардағы тотыққан көмір халық шаруашылығында іс жүзінде пайдаланылмайды және аршу жыныстарымен бірге үйінділерге түседі. Ұсынылған әдіс дайын өнімнің өзіндік құнын жақсартуға мүмкіндік береді. Көмірді тотықтыру арқылы гуматты алу әдісі белгілі. Гумин қышқылдарының шығындарын зерттеу үшін, сондай-ақ гумин қышқылдарының сапалық және сандық құрамын зерттеу үшін әртүрлі концентрациядағы сілтілі ерітінділер қолданылды. Гумин қышқылын өндіру бойынша тәжірибе жүргізу кезінде зерттеу нысаны ретінде қоңыр көмір алынды. Тәжірибе үшін 50 мм-ден аспайтын фракция қолданылды. Ары қарай қоңыр көмір 0,5 мм болатын жақтаулы уатқышта ұсақталды. Одан кейін ұсақталған қоңыр көмірді көлемі 0,2 мм УКПТД 6-да ысқылады. Содан соң қоңыр көмір тотығып кетпес үшін оны пластикалық шелекке салып, бетін жауып қоямыз. Әрбір эксперимент үшін қоңыр көмірді тек керекті мөлшерде ғана қолданып, тәжірибелер жүргіздік. Ал егер пайдалану уақытын 30 минутқа артырсақ, гумин қышқылының бөлінуі 4,6%-ды құрайды. Экстракция температурасын 65С°-қа жоғарылатып, экстракция уақытын 10 минуттан 20 минутқа арттырсақ, гумин қышқылының бөлінуі 3,9%-дан 4,7%-ға өседі. Экстракция уақытын 30 минутқа дейін арттырсақ, гумин қышқылының бөлінуі 4,7%-ды құрайды. Экстракция температурасын 20С°-қа төмендеткенде гумин қышқылының бөлінуі 4,1%-дан 5%-ға артады. Экстракция уақытын 30 минутқа дейін арттырсақ, гумин қышқылының бөлінуі 5,3%-ға дейін артады. Эксперимент нәтижелерін математикалық өңдеу кезінде регрессия теңдеулері алынды, бұл көрсетілген факторлардың әрқайсысының ГК шығуына әсерін анықтауға мүмкіндік берді; әртүрлі концентрациядағы сілтілермен экстракциялау алынған ГК сапалық және сандық құрамы жүргізілді. Көмірден алынған органикалық массаның сапалық және сандық құрамын Agilent 5975С масс-селективті детекторы бар Agilent 7890А газ хроматографының көмегімен анықталды. Гумин қышқылдарының сапалық және сандық құрамы сілтінің концентрациясына байланысты, ол туралы алынған хроматограммды дәлденділеді. Математикалық өңдеу зерттелетін факторлардың гумин қышқылдарын алудың тиімділігіне әсерін анықтауға мүмкіндік берді.

Түйін сөздер: гуматтар, көмірдің тотығуы, сілтілі ерітінділер, қоңыр көмір, NaOH, сапалық және сандық құрамы.

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ПОЛУЧЕНИЕ ГУМАТА В ПРОЦЕССЕ ОКИСЛЕНИЯ УГЛЯ

Аннотация. В последние десятилетия все большую актуальность приобретает проблема повышения плодородия почв, применения органических добавок для повышения урожайности сельхозкультур. Одними из таких добавок являются гуматы – натриевые и калийные соли гуминовых кислот. Гуматы и гуминовые кислоты – химическая основа гумуса почв, его концентрат. А гумус – основа активности и стабильности большинства биохимических почвенных процессов. Сырье для получения гуматов натрия легкодоступно – это бурые угли, торфы, окисленные каменные угли, технология получения – комплексная с низкими затратами на производство. Окисленные угли имеют широкий набор макро- и микроэлементов, большое количество гуминовых кислот, которые по своему составу близки к почвенным. Окисленные в пластах угли практически не используются в народном хозяйстве и поступают в отвалы вместе со вскрышными породами. Предлагаемый способ позволяет улучшить себестоимость готового продукта. Известен способ получения гумата путем окисления угля. Для исследования затрат гуминовых кислот, а также для исследования качественного и количественного состава гуминовых кислот были использованы щелочные растворы различной концентрации. При проведении исследований по выходу ГК объектом исследований был выбран бурый уголь. Для эксперимента использовалась фракция не крупнее 50 мм. Далее исходный бурый уголь подвергался дроблению на щековой дробилке до размера 0,5 мм. После чего измельченный бурый уголь истерали на ВКМД 6 размером не более 0,2 мм. Далее бурый уголь помещаем в пластиковое ведро и закрываем крышкой, для того чтобы он не окислился. После чего для каждого эксперимента брали нужную массу измельченного бурого угля и проводили опыты. А если время использования превышает 30 минут, то выделение гуминовой кислоты составляет 4,6%. Если повысить температуру экстракции на 65С, увеличив время экстракции с 10 минут на 20 минут, выделение гуминовой кислоты возрастет с 3,9% до 4,7%. Если увеличить время экстракции до 30 минут, то выделение гуминовой кислоты составляет 4,7%. При снижении температуры экстракции на величину 20С выделение гуминовой кислоты увеличивается с 4,1% до 5%. Если увеличить время экстракции до 30 минут, то выделение гуминовой кислоты увеличится до 5,3%. Задачи, поставленные в ходе исследования: проведен обзор научной литературы по вопросу свойств ГК, их состава и способа получения; разработана методика проведения эксперимента по влиянию концентрации щелочи,

температуры и времени экстракции на степень извлечения ГК из углей Центрального Казахстана; получены уравнения регрессии при математической обработке результатов эксперимента, что позволило установить влияние каждого из указанных факторов на выход ГК; проведен качественный и количественный состав ГК, полученных экстракции щелочами различной концентрации. Качественный и количественный состав органической массы, извлеченной из углей путем экстракции растворами щелочей определялся с помощью газового хроматографа Agilent 7890A с масс-селективным детектором Agilent 5975C. Качественный и количественный состав гуминовых кислот зависит от концентрации щелочи, о чем свидетельствуют полученные хроматограммы. Математическая обработка результатов эксперимента позволила определить влияние исследуемых факторов на эффективность извлечения гуминовых кислот.

Ключевые слова: гуматы, окисление угля, щелочные растворы, бурый уголь, NaOH, качественный и количественный состав.

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