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SYNTHESIS OF DERIVATIVES OF COAL HYDROXYLATED

Annotation. The paper presents the study of the reaction of chlorinated coal (CC) with sodium hydroxide and potassium acetate in glacial acetic acid. It is established that as a result of alkaline hydrolysis dihydroxy CCs are obtained and monohydroxychlorinated coals are formed in an acid medium. Reactivity of different aliphatic chlorine is different as chlorine atom separated from one σ -bond of the aromatic ring, enters the active nucleophilic substitution reaction than another part of the alkyl radical. Substitution of a hydroxy group chlorine is a typical example of a nucleophilic substitution reaction. On the mechanism this reaction belongs to the typical processes of nucleophilic substitution SN_2 , flowing through the synchronous rupture of the same bond and formation of the new.

Keywords: organic mass of coal, chlorinated carbon, alkaline and acid hydrolysis.

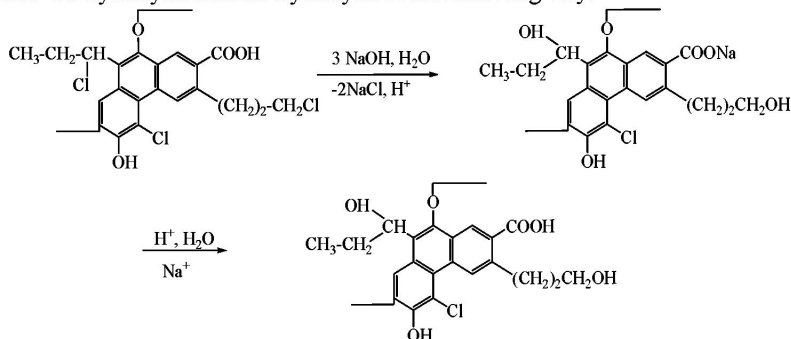
Currently, the general concept of the chemical structure of the organic mass of coal (OMC) is formulated, in which the concept of a carbon skeleton is represented as a set of non-uniform size fused aromatic moieties linked by a variety of side radicals. The presence of coal in the structure of mobile hydrogen atoms determines the possibility of their chemical modification [1-3].

A promising method of modification of coal is to obtain chlorinated coal products [4-5] distinguished by good solubility in organic solvents, highly reactive in nucleophilic substitution reactions.

Reaction of chlorinated carbons hydrolysis was studied to assess the reactivity of coals with different derivatives and aromatic substituted aliphatic and chlorine for the synthesis of new derivatives of the chlorinated carbons CC (1) enriched alcohol groups. We studied the hydrolysis reaction XY under alkaline and acid hydrolysis. In these conditions, it is possible the flow of several parallel-consecutive reactions that determine the functional composition of hydrolysis products.

Alkaline hydrolysis was performed with CC 4% aqueous sodium hydroxide solution, the reaction is carried out in an argon medium to prevent side reactions. As a result of the basic hydrolysis of XY dihydroxylated sodium chlorinated coal was obtained, and then reacting with mineral acids dihydroxylated chlorinated coal HCC was taken (2).

The presence of two aliphatic chlorine atoms in the structure of the CC involves the reaction conditions in the CC hydrolysis alkaline hydrolysis in the following way:



The products of hydrolysis of chlorinated carbons were characterized by functional analysis. In these substances acidic groups (carboxyl, phenolic), chlorine, alcohol groups are identified, formed by the hydrolysis reaction of CC (Table 1).

Functional analysis hydroxyl group shows that the composition of HCC (2) contains alcohol groups 4.5 mgeq/g, which correspond to the contents of the two OH groups of substances.

Table 1 - Functional composition in the hydrolysis products

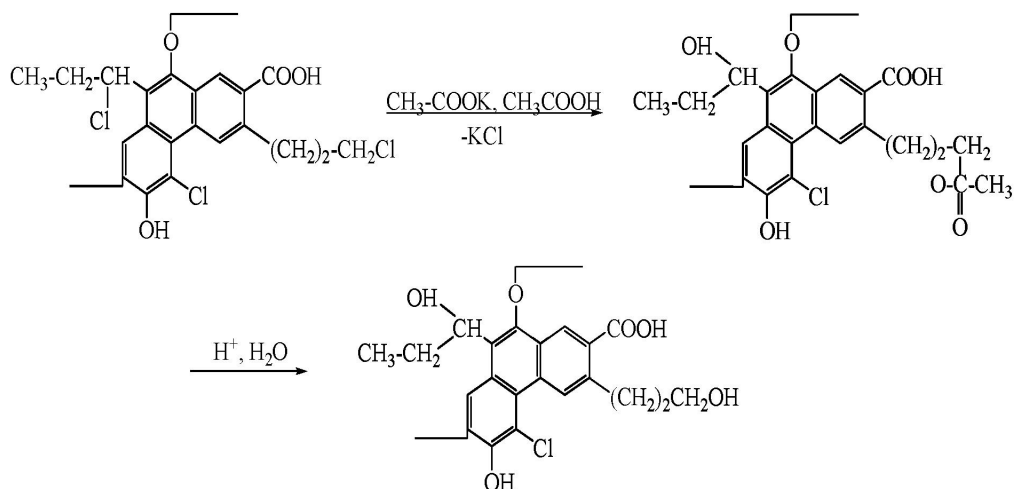
Number and the code compound	hydrolysing agent	output, %	Cl, %	Acid composition, mEq / g		
				Σ COOH+OH	COOH	OH (alcohol.)
CC (1)	-	-	28,1	5,7	1,2	-
(di)HCC (2)	NaOH	88,0	8,9	5,8	2,5	4,5
(mono)HCC (3)	CH ₃ COOH	68,1	12,6	5,0	2,1	2,2

Thus, basic hydrolysis of the chlorinated carbon dihydroxy proceeds with the formation of chlorinated carbons. In the conditions of the alkali hydrolysis reaction flows only with two atoms of aliphatic substituted chlorine, and aromatic chlorine is not involved in this process.

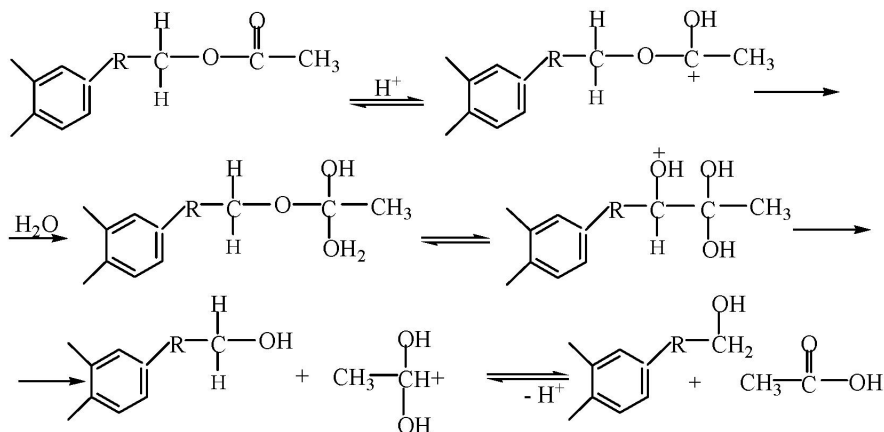
Acid hydrolysis was carried out in glacial acetic acid as the hydrolyzing agent potassium acetate is used.

During hydrolysis CC (1) mono hydroxylate chlorinated coal was received (3). Table 1 shows the results of the functional analysis of the products isolated from the reaction mixture.

From the obtained data it follows that functional structure is similar to the original substance, only mono hydroxylate chlorinated coal (3) has identified alcoholic -OH groups - 2.2 mgeq/g. This corresponds to one alcoholic OH - group of HCC(3). Reaction of acid hydrolysis of chlorine coal (1) is carried out according to the scheme:



Acid hydrolysis of the chlorinated coal CC (1) proceeds as follows; potassium acetate is reacted with chlorine to form alkyl-substituted ester. Further, in an acid medium under the influence of water at (pH <3) acid hydrolysis of the ester group occurs to form the alcohol group:



Thus, the CC hydrolysis reaction feature is that it forms different hydrolysis products depending on reaction, characterized by functional composition, the content of chlorine. Comparison of the results of hydrolysis CC functional studies showed that the content of the alcohol groups is longer in reaction products under alkaline catalysis (2) than in acid (3). Under acidic conditions the formation of the alcohol group in these conditions proceeds through the formation of a compound ester bond.

The structure of obtained hydroxide chlorine derivatives coal (2-3) proved by the IR spectroscopy, structure is confirmed by functional analysis (Table 1).

In the IR - spectra hydroxylated chlorinated carbons RXY (2-3) absorption bands in the region of 797 cm^{-1} (stretching vibrations of C - Cl), 3030 cm^{-1} (stretching vibrations of C - N), 1610 cm^{-1} (stretching vibrations of benzenoid C = C). Expansion of plane vibrations of C - H at 693 cm^{-1} are characteristic to polysubstituted arenes, for carboxyl groups the absorption bands of stretching vibrations of C = O are in the range of 1700 cm^{-1} . Stretching vibrations of O - H [6] are located in the $3500\text{--}3600\text{ cm}^{-1}$.

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al-Farabi Kazakh National University, Almaty, Kazakhstan
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LIGNIN ION-EXCHANGERS**

Annotation. Sorption of molybdenum ions by lignin based ion-exchangers has been studied. Influence of metal ions concentration, pH and duration of extraction on sorption effectiveness has been established. It is shown that sorption ability of lignin ion-exchangers in diluted and strong solutions is much higher than sorption ability of initial lignin biopolymer. It is established that sorption maximum for Mo^{VI} occurs in the pH range of 2 to 4. That is caused by increasing of protonation of the amino groups and polymerization of molybdenum ions with formation of octa- and paramolybdate anions. Further increasing the pH significantly decreased sorption degree of metal ions. It is due to deprotonation of the amino groups and depolymerization of polymolybdate anions $\text{Mo}_7\text{O}_{24}^{6-}$ (pH 4-6) to monomolybdate ions MoO_4^{2-} (pH>6). In strong acidic solution ($\text{CH}_2\text{SO}_4=0,5-2\text{N}$) the sorption proceeds with participation of the protonated amino groups and the anionic complexes $\text{MoO}_2(\text{SO}_4)_2^{2-}$ which are in equilibrium with molybdenyl cations MoO_2^{2+} . Increasing the acid concentration decreased anionic complexes concentration that leads to decreasing of sorption capacity. It is clearly demonstrated that novel lignin ion exchangers have high kinetic characteristics in comparison with well-known synthetic gel and macroporous anion-exchangers. These advantages open up the broad prospects for their application in environment protection and hydrometallurgy for removal of molybdenum ions from industrial solutions and waster waters.

Key words: anion-exchangers, lignin, sorption, molybdenum ions, extraction efficiency.

It is known [1-9] that the most effective methods for isolating molybdenum from solutions are sorption methods using ion exchangers of porous and network structure. They have found wide application in the industry for the production of highly pure metal salts. However, the insufficient efficiency and high cost of synthetic ion exchangers, used in molybdenum technology (AN, AB, EDE-10P, XAD-4, D-309, etc.) [1,2,4-9], require the development and creation of fundamentally new sorption - active materials on the basis of affordable and cheap raw materials. This is especially relevant now, since the republic does not have its own production of ion exchangers.

In this connection, the sorption properties of ion exchangers based on hydrolytic lignin (HL) - a large-tonnage waste of the hydrolysis industry with respect to molybdenum ions - have been investigated in this work. The use of cheap local raw materials for the synthesis of sorbents is dictated by the possibility of recycling waste production and the creation of progressive sorption technologies for the extraction of molybdenum from the ore raw materials of Kazakhstan.

Ionites are obtained by chemical modification of HL by epoxy-diane resin ED-20 and amines [10, 11]. Their composition and physicochemical properties are presented in the works [10, 11]. Sorption of molybdenum ions was carried out from Na_2MoO_4 solutions under static conditions at a ratio of ionite:solution = 1: 600. The concentration of metal ions was determined by the polarographic method. Polarograms were recorded on the PU-1 polygraph in a thermostated cell at $25\pm 0,5^\circ\text{C}$ against a background of $0,1\text{n H}_2\text{SO}_4$ ($E_{1/2}=-0,08\text{B}$). A saturated calomel electrode was used as the reference electrode. The oxygen was removed from the solutions by purging with argon for 5 minutes.

It is known [1, 2] that the sorption equilibrium of molybdate ions on ion exchangers depends on three main factors: the ionic state of the metal in the solution and the pH of the medium; physical structure (nonporous, macroreticular, porous, macroporous) and chemical structure (the nature of the matrix and functional groups) of ionites; statics and kinetics of ion-exchange equilibrium, determined by the structure of ion exchangers and the pH of the salt system.

The equilibrium absorption isotherms of molybdenum ions graphically depicting the static structure of the sorption process are shown in Fig. 1. It can be seen that as the concentration of molybdenum ions in solution increases, the sorption capacity (SC) of the original lignin and ion exchangers based on it, modified with polyethyleneimine (PEI), polyethylene polyamine (PEPA) and 2-vinylpyridine (2-VP), increase and reach 100, 259, 230 and 192 mg/g at the equilibrium content of ions in solution of 2.80; 2.40; 2.50 and 2.60 g/l, respectively. The ions are extracted at 8, 21, 19 and 16%. Such low values of the recovery degree (R) are evidently due to saturation of ion exchangers with an increase in the concentration of metal ions in the solution.

From dilute solutions, molybdate ions are absorbed more efficiently by chemically modified samples than by a natural sorbent. The degrees of extraction of metal ions by ion exchangers reach 82.5 % (PEI), 62.5% (PEPA, 2-VP), and the original lignin - no more than 20%. In the entire investigated region of equilibrium concentrations of metal ions, the initial polymer-lignin by sorption capacity is significantly inferior to the aminated samples. The latter, in comparable conditions, are extracted better by AB-17, which capacity, depending on the type and amount of pore former, varies from 70 to 150 mg/g [1].

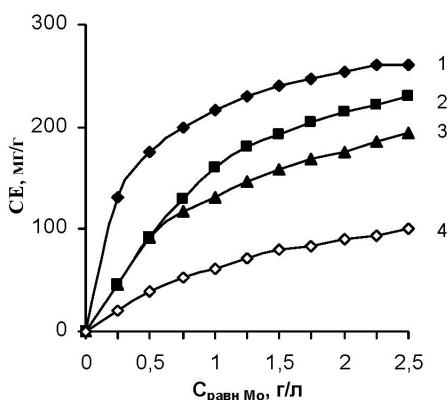
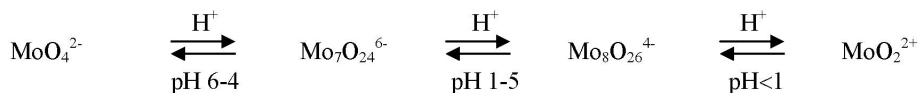


Figure 1 - Sorption isotherms of molybdate ions by HL (4) and anion exchangers on its basis with the groups PEI (1), PEPA (2) and 2-VP (3)

The sorption capacity of anion exchangers is significantly influenced by the pH of the medium, since, in this case, the ionic state of the functional groups of ionites and molybdate ions in solution changes, which can be schematically represented as follows [1]:



In alkaline solutions (pH>6) molybdenum ions are in the form of monomeric anions MoO_4^{2-} , in slightly acidic (pH 2-6) - polyanions of various composition, in strongly acidic - cations molybdenyl MoO_2^{2+} and complex anions depending on the type of mineral acid [1].

Ionites show the greatest sorption ability at pH 2.3 (PEI), 2-4 (PEPA, 2-VP), which is associated with an increase in the degree of protonation of amino groups and the presence of molybdenum in the form of highly polymerized octa-, paramolybdate-anions, which, due to a lower specific charge and a larger content of metal atoms in the associate, increase the SC of ion exchangers, which reach 480 (PEI), 402 (PEPA), 490 (2VP) with a recovery rate of 97, 82 and 99%, respectively (Figure 2a). The decrease in the extractive ability of ion exchangers with a further decrease in the acidity of the medium is due to the gradual deprotonation of nitrogen atoms and the depolymerization of molybdenum polyanions to $\text{Mo}_7\text{O}_{24}^{6-}$ (pH 4-6) and MoO_4^{2-} (pH>6). At pH 6.86 SC of all ion exchangers are reduced in 1.5-2.5 times and reach 192 (PEI), 154 (PEPA), 130 mg/g (2-VP) with a recovery of 37, 30, 25%, respectively.

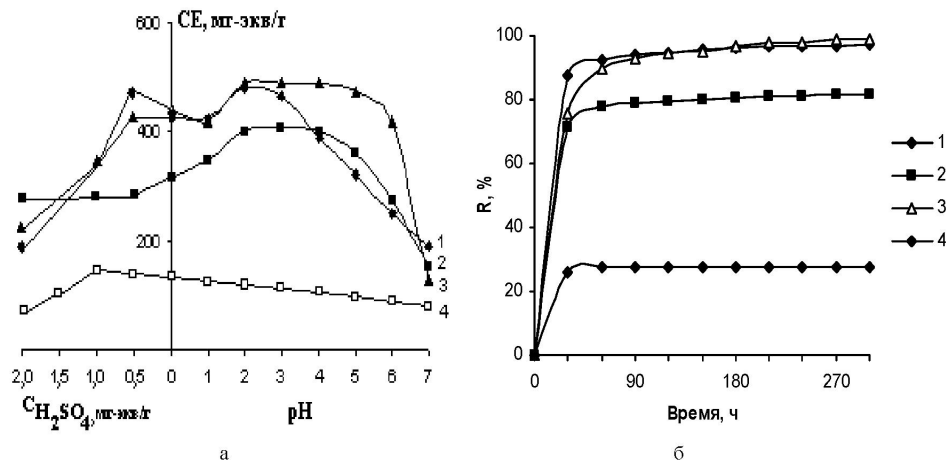


Figure 2 - Influence of pH of the medium (a) and duration of extraction (b) of molybdenum ions on the capacity of HL (4) and ion exchangers based on it, modified PEI (1), PEPA (2), 2-VP (3)

The decrease in the SC of anion exchangers in acidic ($pH \leq 1$) and the strongly acidic areas ($CH_2SO_4 = 0,5-2n$) is associated with competitive acid sorption and the Mo transition into a cationic form that is not capable of sorbing on the protonated amino groups of the ion exchangers. Sorption in sulfuric acid solutions is apparently due to the absorption of anionic complexes of $MoO_2(SO_4)_2^{2-}$, which are in equilibrium with cations of molybdenyl, which concentration decreases with increasing acid content in the solution. The more sharp fall of the SC of ion exchanger with the PEPA groups compared with the PEI in the acidic area is evidently due to its greater basicity. It is known [12] that with increasing basicity of ion exchangers, their affinity to anions of acidic residues at their high content in solution increases, which leads to suppression of sorption of metal ions. Significant absorption of molybdenum ions by pyridinium ion exchanger under these conditions is obviously associated with the participation of aromatic groups in the sorption. The initial HL in the entire investigated area of the acidity of the medium shows less sorption activity than the modified samples.

The kinetic properties of ion exchangers with respect to molybdenum ions were investigated at the pH of their maximum absorption. The integral curves of the dependence of the total amount of sorbed metal ions on the time of contact of the polymer-solution system, shown in Fig. 2b, indicate that on all samples the main amount of ions is extracted within 15-30 min, and for 1 h - 92 (PEI) 77 (PEPA), 90% (2-VP), which is 90-95% of their equilibrium capacity. The half-absorption periods ($\tau_{1/2}$), which are 7, 9, and 15 minutes, respectively, indicate that at the highest rate, highly polymerized octamolybdate ions are absorbed on the ion exchanger with PEI groups. Such an accelerated sorption kinetics is explained by the high permeability of ion exchangers and the availability of amino groups for Mo polyanions, the penetration of which into the ion exchanger phase proceeds without significant diffusion difficulties. In contrast to lignin ionites, the absorption of highly polymerized Mo anions by the gel anion exchanger EDE-10P, AN-1, AM at pH 2, due to their low ion permeability, proceeds extremely slowly. The equilibrium is established for 4-5 days. At the same time, their capacities are much lower than the capacity of lignin-based ion exchangers and are 233, 320 and 394 mg/g, respectively. On macroporous ion exchangers, τ_p is reduced to 10-15 hours. At that, the main amount of ions is extracted within 2 hours [2].

Thus, the results of the studies show that fibrous ion exchangers based on hydrolytic lignin on the efficiency of sorption of molybdenum from model solutions exceed the initial biopolymer, as well as some synthetic ionites of the gel and macroporous structure. The increased sorption and kinetic properties of ion exchangers open wide prospects for their practical use in the technology of sorption extraction of molybdenum from industrial and sewage.

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