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MODIFICATION OF COAL-BASED SORBENTS FOR THE PURPOSE OF REMOVING HEAVY METALS

Abstract. Sources of environmental and wastewater pollution with heavy metals include chemical detergents used in everyday life, as well as various pollutants discharged from large industrial factories. Even small amounts of heavy metals, including copper and lead ions, can cause significant harm to the human body. In order to reduce the harmful effects of heavy metals, various methods and approaches for their removal have been investigated. Based on a comparison of many scientific studies, the beneficial properties of natural sorbents have been identified. According to our research, it was found that coal exhibits the highest sorption capacity among natural sorbents. In addition, elemental analysis of both raw and modified coal was performed, showing changes in carbon and oxygen content, as well as a reduction in mineral impurities. These changes are explained by the formation of oxygen-containing functional groups on the coal surface and an increase in active sites. Thus, modification of hard coal with hydrogen peroxide demonstrated that its ability to remove heavy metals and its static exchange capacity depend on temperature (60–120°C), contact time (60–120 minutes), and concentration (2.5 mol). Under these optimal conditions, the sorption capacity increases by approximately 40%.

Key words: hard coal, adsorption, sorption, modification, wastewater, heavy metals, coal.



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Introduction. Introduction Pollution of the environment with heavy metals leads to a huge environmental problem, as damage due to the toxicity and bioaccumulation capacity of heavy metals [1-2]. The aim of the study is to modify coal-based sorbents in order to enhance their efficiency in removing heavy metals from aqueous solutions and to investigate their sorption properties. Heavy metals are used in various industries, i.e. metallurgy and battery production, which leads to losses due to their accumulation in aquatic ecosystems and soils [3]. Even a

small concentration of copper and lead metals negatively affects living organisms and ecosystems.

Among the various methods of removing heavy metals from aqueous solutions, the method of sorption using natural minerals has the highest efficiency [4-5]. At the same time, it is environmentally friendly and has economic accessibility. Among such minerals, zeolite, bentonite clays, stone coal, activated charcoal are widely used [6].

Materials and methods. The studied coal is first thoroughly rinsed with distilled water and then dried in a drying oven in the amount of two hours at the rate of one hundred and ten gardus until all unnecessary substances are removed. In the process of improving the sorption capacity of pure processed stone coal, we modify it with hydrogen peroxide, the ratio of solid and liquid phases undergoes various changes (Table 1).

Table 1

Conditions for coal modification

| № | Mass Ratio (Coal : H ₂ O ₂) | T (°C) | t (min) |
|---|--|--------|---------|
| 1 | 1 : 3 | 60-110 | 30-120 |
| 2 | 1 : 2,5 | | |
| 3 | 1 : 2 | | |
| 4 | 1 : 1,5 | | |
| 5 | 1 : 1 | | |
| 6 | 1 : 0,5 | | |

Post-Modification Treatment and Analysis after modification, the residual coal was washed with a 5% alkaline solution to remove unwanted dust and fine particles. As a result, a loose black product was obtained. The effectiveness of the modification was evaluated by determining the static exchange capacity (SEC) method.

Research results. The static exchange capacity (SEC) increases depending on the concentration of H₂O₂ used in coal modification figure 1. However, increasing the hydrogen peroxide concentration above 2.5 mol does not lead to a further rise in SEC.

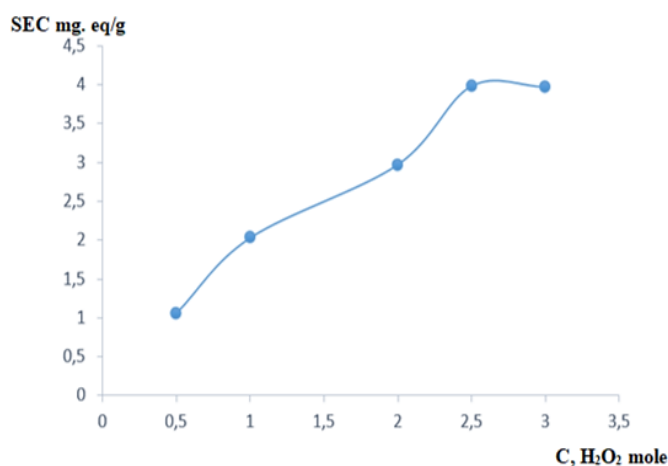


Fig. 1. Dependence of the static exchange capacity (SEC) of coal on the concentration of the modifying agent

The highest SEC value is observed when the temperature is increased up to 110°C figure 2. With further temperature increase, the high values gradually decrease. During the synthesis process, a heating time of 120 minutes demonstrated the best performance figure 3.

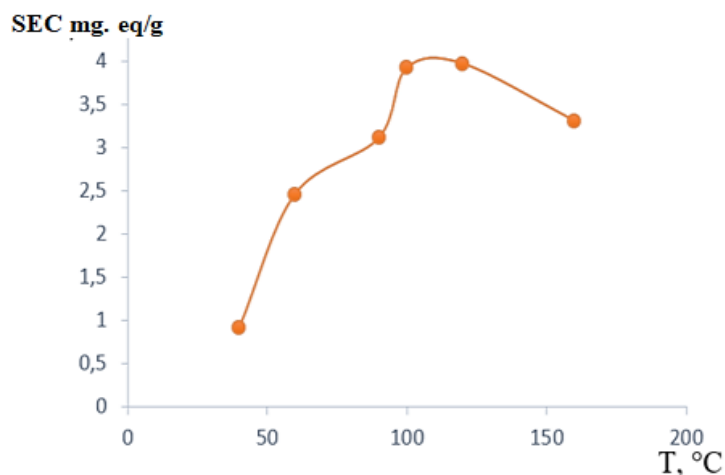


Fig. 2. Dependence of the static exchange capacity (SEC) of modified coal on heating temperature

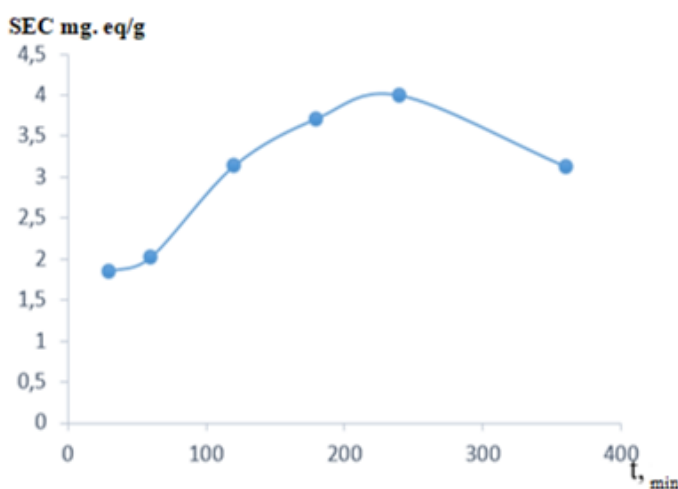


Fig. 3. Dependence of the static exchange capacity (SEC) of modified coal on contact time

Hydrogen peroxide modification increases oxygen-containing functional groups ($-OH$, $-COOH$) on the coal surface, leading to an increase in oxygen content and a relative decrease in carbon content. A reduction in some mineral impurities, especially iron, may also be observed. (Table 2).

Table 2

Elemental composition analysis

| Element | Raw coal (Wt%) | H ₂ O ₂ -modified coal (Wt%) |
|---------|----------------|--|
| C | 90.3 | 86 |
| O | 7.5 | 15 |
| Si | 0.6 | 1.3 |
| S | 0.9 | 1.2 |
| Al | 0.4 | 0.5 |
| Fe | 0.2 | 0.0 |
| N | 0.0 | 0.0 |

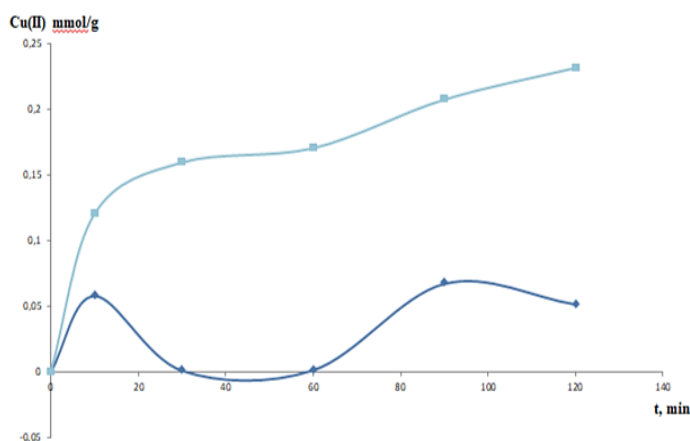


Fig. 4. Time dependence of Cu(II) ion adsorption on raw and modified coal

The given graph shows the time-dependent (t , min) adsorption of Cu(II) ions (mmol/g) and demonstrates that the modified coal has a significantly higher sorption capacity compared to the raw coal figure 4.

Overall, the modified coal exhibits a gradual and steady increase in Cu(II) adsorption over time. At the initial stage, adsorption occurs rapidly, and then the process slows down as it approaches equilibrium. This behavior is attributed to the presence of a higher number of active functional groups ($-OH$, $-COOH$) and an increased number of active surface sites.

In contrast, the raw coal shows lower and unstable adsorption values. A decrease and subsequent increase are observed at certain time intervals, indicating an uneven distribution and a lower number of active adsorption sites on its surface.

The graph results confirm that hydrogen peroxide modification enhances the ability of coal to effectively bind Cu(II) ions and significantly improves its sorption properties.

Discussion. According to the elemental analysis results, noticeable changes were observed in the composition of coal after modification with hydrogen peroxide (H_2O_2). The carbon content decreased from 90.3 wt% to 86 wt%, while the oxygen content increased significantly from 7.5 wt% to 15 wt%. This indicates the formation of oxygen-containing functional groups such as hydroxyl and carboxyl groups on the coal surface during the oxidation process. In addition, slight increases were observed in the contents of silicon, sulfur, and aluminum, which may be related to changes in the mineral composition of the coal after treatment. The iron content decreased from 0.2 wt% to 0.0 wt%, indicating partial removal of

mineral impurities during modification. No significant change was observed in the nitrogen content.

Each ion exchanger is capable of adsorbing a certain amount of ions, meaning it possesses a specific exchange capacity. The static exchange capacity (SEC) represents the number of milliequivalents of ions absorbed per gram of dry ion exchanger within a given period of time. As shown in Figure 3, the modified coal adsorbs 4.00 mg-eq/g within 120 minutes.

Overall, the obtained results demonstrate that hydrogen peroxide modification changes the surface chemistry and elemental composition of coal, increases the number of active sites, and improves its sorption properties for heavy metal removal.

Conclusion. The research results showed that modification of coal with hydrogen peroxide (H₂O₂) significantly changes its structural and chemical properties. During the modification process, the number of oxygen-containing functional groups on the coal surface increases, leading to the formation of more active sites. This positively affects the sorption and ion-exchange properties of coal. Elemental analysis revealed a decrease in carbon content and an increase in oxygen content, indicating that the coal surface underwent an oxidation process. In addition, the reduction of mineral impurities demonstrated an improvement in the purification degree of the coal. Overall, H₂O₂-modified coal is a promising sorbent capable of effectively adsorbing heavy metal ions, especially Cu(II) ions. The obtained results indicate the potential application of modified coal in wastewater treatment processes.

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АУЫР МЕТАЛДАРДЫ ЖОЮ МАҚСАТЫНДА КӨМІР НЕГІЗІНДЕГІ СОРБЕНТТЕРДІ МОДИФИКАЦИЯЛАУ

Андатпа. Қоршаған орта және ағынды сулардың ауыр металдармен ластану көздері өзіміздің күнделікті тұрмыстық жағдайда қолданылып отырған химиялық жұғыш заттар сонымен қатар ірі өндіріс фабрикаларынан төгілген түрлі ластағыш заттардың салдарынан болып отыр. Ауыр металдардың соның ішінде мыс, қорғасын иондарының шамалы мөлшерінің өзі адам ағзасына үлкен зиянын тигізіп отыр. Ауыр металдардың ағзамызға зиянын болдырмау мақсатында олардың жоюдың түрлі жолдары мен әдістері қарастырылды. Көптеген ғалымдардың зерттеулерін салыстыра келе табиғи сорбенттердің тиімді жақтары анықталды. Біздің зерттеуіміз бойынша табиғи сорбенттердің ішінде таскөмірдің сорбциялық қабілеті жоғары екендігі айқындалды. Яғни, тас көмірді сүтегі асқын тотығымен модификациялау барысында ауыр металдарды жою қабілеті, статикалық алмасу сыйымдылығы температураға (60-120⁰), уақытқа (60-120 минут), концентрацияға (2,5 моль) тәуелді көрсеткіштерімен сипатталынып сорбция қабілеті 40% артатындығы дәлелденді.

Тірек сөздер: тас көмір, адсорбция, сорбция, модификация, ағынды сулар, ауыр металдар, көмір.

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МОДИФИКАЦИЯ СОРБЕНТОВ НА ОСНОВЕ УГЛЯ С ЦЕЛЬЮ УДАЛЕНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ

Аннотация. Источники загрязнения окружающей среды и сточных вод тяжелыми металлами химические моющие средства, применяемые в наших повседневных бытовых условиях, также являются следствием различных загрязняющих веществ, сбрасываемых с крупных производственных фабрик. Даже незначительное количество ионов тяжелых металлов, в том числе меди, свинца, наносит большой вред организму человека. Были рассмотрены различные способы и методы удаления тяжелых металлов с целью предотвращения их повреждения нашего организма. Сравнивая исследования многих ученых, были выявлены преимущества природных сорбентов. Наше исследование показало, что среди природных сорбентов каменный уголь обладает высокой сорбционной способностью. То есть, в процессе модификации каменного угля перекисью водорода было доказано, что способность к сорбции увеличивается на 40%, характеризующаяся показателями, зависящими от температуры (60-120), времени (60-120 минут), концентрации (2,5 моль), емкости статического обмена.

Ключевые слова: каменный уголь, адсорбция, сорбция, модификация, сточные воды, тяжелые металлы, уголь.