



Modification of activated carbon prepared from black liquor with the copper ion and its application to adsorption phenol

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ARTICLE INFO	ABSTRACT
<p>Article History: Received: 20 June 2024 Revised: 17 July 2024 Accepted: 18 July 2024</p> <p>Article type: Research</p> <p>Keywords: Break Curve, Copper Sulfate, Desorption Process, Kraft Process, Lignin</p>	<p>The growing demand for effective and environmentally friendly phenol removal methods has led to a growing interest in investigating the potential of using biomass-derived activated carbon. This research investigated the absorption process of phenol from wastewater using activated carbon adsorbents and activated carbon modified with copper in a batch system. Activated carbon was obtained from paper mill black liquor. The pore structure and morphology of unmodified and modified samples were investigated by BET and SEM. Modifying activated carbon with copper increased the specific surface area from 283.2 to 517.5 m²/g. The inhomogeneity in the modified AC adsorbent surface is less compared to AC, and it also has a more regular surface in terms of particle size uniformity. The ability of prepared adsorbents to remove phenol in aqueous medium was evaluated by examining the effects of parameters such as adsorbent amount, pH, solution concentration, contact time, temperature effect. Based on the results, it was found that AC/Cu shows the highest adsorption rate after coming in contact with phenol solution with a concentration of 100 ppm for one hour at an optimal pH of 8. The adsorption of phenol by AC/Cu is consistent with the pseudo-second-order kinetic model. The absorption of phenol by the modified AC depends on the temperature and is an endothermic process. The increase in the amount of phenol removal with increasing temperature is more in AC/Cu. The study of the adsorbent saturation in the column system showed that AC/Cu is able to absorb more than 95% of the phenol solution with a concentration of 100 ppm up to a volume of 2700 mL. The findings of this study provide valuable insights into the field and pave the way for further research in the future.</p>

Introduction

Today, the development of various industries has led to more production and use of chemical compounds. This causes the increase of various pollutants in the effluents of various industries.

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Aromatic organic pollutants are among these pollutants, including phenolic compounds [1]. Phenol in a large amount in chemical and petrochemical pulp and paper, pharmaceutical and chemical industries (paints, chemical fertilizers, etc.). Phenolic resins are produced and used in the rubber industry and cooking process [2]. Therefore, phenol is one of the most common and toxic pollutants among other pollutants because the Indian Ministry of Forests and Environment and the American Environmental Protection Agency, have been listed as a pollutant [3].

The very small amounts of phenol present in wastewater and surface water have short and long-term effects on human health as well as on the life of plants and animals [4]. In fact, due to the permeability of phenol compounds through the cell membrane and their ability to destroy nerve cells, it is one of the serious problems for the health of the body and the environment [5].

Phenol is easily soluble in organic solvents, it is present in most wastewaters, even in urban wastewaters. A significant point in environmental pollution with phenolic compounds is the relatively good solubility of phenol in water (8.3 g/100 mL) and its relatively low vapor pressure at room temperature. Hence, its transfer to soil and water is easy. A large amount will remain in the aqueous phase. Systematic disorders diagnosed in the body through phenol include indigestion such as vomiting, difficulty swallowing, increased secretion of saliva, diarrhea and anorexia, nervous disorders such as headache, dizziness, brain disorders, and destruction of skin tissue. The Environmental Protection Agency has determined the permissible amount of phenol in wastewater at 0.1 mg/L, and the World Health Organization has set the amount of this substance at 0.001 mg/L in drinking water [6]. Therefore, removing this organic substance or reducing its concentration to reach the permissible limits before discharge is a challenging issue.

Various physical and chemical methods have been proposed for wastewater treatment, including wastewater containing phenolic compounds, and the selection of these methods depends on the characteristics of the wastewater, such as phenol concentration, pH, temperature, flow intensity, biological oxygen level, and compliance with the standard set by the agency. Among these methods, we can mention separation processes (adsorption, membrane processes, etc.), physical-chemical purification processes, and thermal processes. Currently, there are various methods such as chemical and electrochemical oxidation [7], chemical coagulation [8], solvent extraction [9], membrane separation [10], purification using biological materials [11], and reverse catalytic degradation [12]. The use of absorbents based on biological substrates is one of the technologies that can be used to reduce problems related to environmental pollutants. Among the potential absorbent materials in this field are carbon-based compounds such as activated carbon (AC), carbon nanotubes, and carbon nanofibers, which are hydrophobic and non-polar. ACs are known as effective adsorbents due to developed porosity, large specific surface area, chemical characteristics, and high degree of surface reactivity. AC can be obtained from various sources of carbonaceous materials as a raw material, such as wood, coal, walnut shell, palm kernel, olive kernel, lignin, and many other sources [13]. Currently, in the process of producing kraft pulp and paper, lignin is removed from black liquor. The main use of this residual lignin is as a renewable fuel to supply the energy needed by pulp and paper factories in the form of heat and electricity [14].

About 78 million tons of lignin kraft are produced worldwide every year, and only 2 percent of it, is industrially converted into various products. Planning for the applications of lignin as the third most abundant natural polymer has been going on for several decades [15]. Black liquor of kraft is an aqueous solution that includes the remains of lignin (25-35%), hemicelluloses and other chemicals. This substance is strongly alkaline and its pH value is approximately 13. Its chemical composition depends on the type of wood and the treatment conditions used [16].

Sawdust was used to remove phenol. Four main factors of adsorption processes, i.e. initial concentration of phenol, amount of adsorbent, pH and contact time were investigated. The Box-

Wilson test design method was adopted to find a useful relationship between four variables and removal efficiency. The optimal conditions for removing phenol in the experimental range of variables studies were 130 mg/L initial concentration of phenol, 0.82 g adsorbent amount, natural pH value 6.7 and contact time 120 minutes. Under these conditions, the removal efficiency was 91.6% [17]. Activated carbon was prepared using the leaves of the Ashurak plant and was used to remove phenol. The leaves of this plant were first dried and powdered, and then they were exposed to 25% sulfuric acid for 5 days. After drying, it was placed at a temperature of 600 °C for 2 hours. The highest amount of phenol removal was achieved by 85% at pH = 3 and a temperature of 45 °C [18]. Activated carbon obtained from Banyan tree root waste was used to remove phenol. Banyan root activated carbon (BRAC) was chemically modified using potassium hydroxide. Morphological studies showed a very porous structure for BRAC with a significant amount of functional groups on its surface. Specific surface area and average pore radius were 988 m²/g (BET method), 24 nm (BJH method). BRAC has the maximum phenol removal efficiency of 89.2%. The adsorption process is spontaneous and exothermic in nature [19]. The removal of phenol from wastewater using a biochar (BC) adsorbent was investigated and compared with activated carbon. The main parameters affecting the adsorption process were initial concentration, contact time, pH, and temperature. The maximum removal percentage when using AC and BC was 95% and 55%, respectively. The removal of phenol has fast kinetics and reaches equilibrium within 5 minutes, and the optimum pH was found to be 7. Langmuir and Freundlich isotherm models were used to fit the experimental data of adsorption and it was found that the adsorption process in the used adsorbent follows both mechanisms well [20].

The adsorption of phenol through double modification of starch was investigated. In the first step, phosphate groups were coded on the main chain of starch. Since the phosphate groups were able to form hydrogen bonds with the hydroxyl group of phenol, the modified starch adsorption efficiency for phenol adsorption increased. Then, the second step was done by creating a bond of methacrylic acid on the starch phosphate backbone. Methacrylic acid grafting increased the density of carboxylic groups on starch phosphate. These carboxylic groups created more hydrogen bonds with phenol and caused higher adsorption of phenol. Therefore, double modification increased the adsorption efficiency of ordinary starch compared to phenol, so that the adsorption efficiency improved to 0.151 g/g [21].

In the present study, lignin will be extracted from kraft black liquor using appropriate chemical and smoothing operations, and after preparation of activated carbon and its modification by copper ions, the obtained product will be identified by different methods and the capability of this adsorbent in the removal of phenol from the water environment will be investigated.

Activated carbon can adsorb many organic materials with a high adsorption capacity, but its adsorption efficiency is low. To overcome these disadvantages, Cu/AC as a potential high-efficiency adsorbent was studied for treating wastewater with organic in this paper. Although before, activated carbon adsorbent was prepared from lignin, but so far it has been chemically activated with copper ion [22, 23]. The aim of this paper is to modify activated carbon with copper nitrate in order to increase the amount of phenol removal. Lignin has been used to improve properties in terms of phenol adsorption, biodegradability of adsorbents, and recyclability of lignin-based adsorbents.

Materials and Methods

All chemicals were purchased from Merck. Phenol with a purity of more than 99% was distilled before use. Chemical substances soda (99.6%), ethanol (96%), ammonia (25%), and copper sulfate (CuSO₄.5H₂O) were also used. The concentration of phenolic pollutants was measured in adsorption studies using UV-vis spectrometer NANOCOLOR II in 1 cm cell. Black

liquor from Iran's Chuka Wood and Paper Industry Factory located in Guilan province was used to prepare activated carbon.

A Metrohm pH meter (model 827) with a glass composite electrode. Also, the structural and morphological characteristics of the samples were studied using BET equipment (II BELSORP mini, Japan), scanning electron microscope (SEM; Model LEO 1430VP, Germany), and Fourier-transform infrared spectroscopy (FTIR; ALPHA FT-IR Spectrometer Bruker, Germany).

Lignin Extraction from Liquor and Preparation of Activated Carbon

The black liquor of kraft paper baking with an efficiency of 25% was calculated. Then, the extraction of lignin from the cooking black liquor was done by lignin precipitation method by acidifying with 37% hydrochloric acid [24]. In this way, black liquor with 37% HCl was placed on a heater stirrer for one hour at 90 °C, the pH of the solution was adjusted to 2, and then it was placed at room temperature for one hour. Next, a two-phase solution was obtained, which was collected on the Buchner funnel with the help of a strainer and under vacuum, and after repeated washing with double distilled water with pH adjustment under the strainer in the neutral range. The prepared lignin was overnight at a temperature of 90 °C. Then, chemical activation was started with a 2:1 ratio of 85% phosphoric acid to lignin, and the prepared sample was placed in an oven at a temperature of 110 °C for one night, then a relatively hard and sticky solid was prepared. The sample prepared by setting the temperature at 500 °C (with a heating rate of 10 °C/min and gas flow of argon at the rate of 150 mL/min) was placed for 1 hour, and after this period, the sample was also placed at ambient temperature to cool down. Increasing the temperature above 500 °C is not effective, the surface and volume of pores decrease due to thermal contraction and the carbon structure accumulates [25]. Then the sample was washed many times with distilled water to reach the neutral pH range and dried at 90 °C. At the end, the sample was passed through a sieve with 80 mesh, and activated carbon powder was collected.

AC Adsorber Modification Method and Preparation of AC/Cu Approved Adsorber

The prepared AC was washed with distilled water until the color of the effluent became clear. The washed carbon was soaked in distilled water for 24 h and then filtered and placed in an aqueous (5%) HCl solution with stirring for 2 h to remove other impurities. Then the AC was filtered with filter paper and washed with distilled water. In the next step, the desired modifications were made. Therefore, 200 mL of 0.5 M copper sulfate solution was added to 10 g of adsorbent and the pH was adjusted to 8.5 by adding 0.1 M NaOH solution. The modified adsorbent was washed 5 times with 50 mL of distilled water by filtering the separated solution, and the amount of copper ions in the solution was measured under the filter and then placed in an oven at a temperature of 105 °C to dry. BET analysis and scanning electron microscope (SEM) were used to investigate the characteristics of the modified adsorbent.

In order to ensure the amount of copper ion adsorption, the concentration of the copper solution after contact with the modified adsorbent and filtering with filter paper was measured through the atomic adsorption test method [26]. There was 6.3 g of copper in the initial solution, and 1122 mg of this amount was detected in the filtered water. So, 5117 mg of copper nitrate has been absorbed by the adsorbent, which is equivalent to 82% of the copper nitrate in feed.

Adsorption Tests and Investigation of Effective Factors

In a series of batch experiments, certain amounts of adsorbents (AC and AC/Cu) were contacted with solutions containing phenol with different concentrations (0-100 mg/L) at room temperature and were stirred. The pH of the solutions was adjusted using solutions of NaOH and HCl. An adsorbent dosage of 0.1 g in a 50 mL solution was chosen as the consumed adsorbent dose for all experiments (except for dosage investigation experiments). The parameters investigated in this study included contact time, initial pH of the solution, initial concentration of the drug solution, consumed adsorbent dosage, and temperature. The method used in the experiments was the classical approach, which involved altering one parameter while keeping other parameters constant.

To investigate the studies in the continuous system, a glass column with a diameter of 1 cm and a length of 25 cm was used to perform column tests. 0.1 g of each adsorbent was filled in a column (with a height of 5 cm) and then the phenol solution with a certain concentration (100 mg/L) was passed through the column at a flow rate of 3 mL/min. The column outlet solution was analyzed to determine the amount of unabsorbed phenol after every 10 ml. To calculate the percentage and capacity of adsorption, as well as the percentage of desorption in the discontinuous system, Eqs. 1-4 were used, respectively:

$$\% Sorption = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q_t = \frac{(C_0 - C_t) \times V}{w} \quad (2)$$

$$\% Desorption = \frac{m^*}{m_0} \times 100 \quad (3)$$

$$m^* = C_e \times V' \quad (4)$$

$$m_0 = (C_0 - C_e)V \quad (5)$$

where C_0 and C_t are the initial and the unabsorbed concentration (mg/L) at time t , respectively. At equilibrium, C_t becomes C_e and q_t becomes q_e . q_t is the adsorption capacity (mg/g), V and w are the initial volume of the sample solution (L) and the weight of the adsorbent (g), respectively. m (mg) and m^* (mg) are the mass of the adsorbent before exposure to the adsorbent and the mass of phenol remaining in the desorption solution. To calculate the adsorption capacity in the column system, the amount of phenol absorbed on the adsorbent was used from Eq. 6:

$$q_{b\&c} = \frac{\Sigma(C_0 - C_t)V_{elu}}{w} \quad (6)$$

where C_t is the concentration of the solution exiting the column (mg/L), V_{elu} is the volume of the desorption solution (L), q_b and q_c are the adsorption capacity at the breaking point, the adsorption capacity of the entire column, and the adsorption capacity of the recovered column (mg/g), respectively.

For the desorption studies, 0.1 g of the adsorbent used in the phenol adsorption process for 30 minutes in contact with the desorption solvents (soda solutions and Ammonia 0.1 M and ethanol) was placed and then filtered through filter paper, and the amount of desorbed phenol was measured.

Measurement of Phenol

Phenol was determined based on Hach Company's method (Method 8047), standard methods for water and wastewater testing, and using the USEPA 420.1 method for wastewater [27]. Quantitative analysis of phenol was performed using the calibration curve obtained using standard solutions of phenol prepared in deionized water in the range of 0.2-0.005 ppm. All experiments were performed with at least three replicates. The results were reported as the average of these measurements. Linear regression analysis was used to process the data. The relative standard deviation (RSD) was less than 0.1% and the detection limit was 0.02 ppm based on three times the standard deviation of the blank.

Desorption Studies

In order to check the desorption rate of phenol absorbed by AC and AC/Cu, after washing the saturated adsorbent with distilled water, these adsorbents were put in contact with solutions such as NaOH, NH₃, ethanol, and the performance of each of them for better desorption of phenol from the adsorbents was investigated.

Results and Discussion

Examining the Effect of pH

The pH of the phenol solution is effective for controlling the adsorption capacity of adsorbents. The results show (Fig. 1) that the amount of adsorption in AC/Cu has increased compared to AC, and the highest amount of phenol adsorption has occurred at a pH of 8. The adsorption percentage increased with increasing pH from 2 to 8, but when the pH value increased from 8 to 10, the phenol adsorption decreased. The reason for the drop in phenol adsorption at alkaline pHs is that the sites of reactive functional groups on the surface of AC, such as OH or COOH, are deactivated at pH values above 8 [28]. The adsorption of phenol at high pH values is reduced by the conversion of phenol from molecular to ionic state, which in turn causes repulsion between phenol ions and the adsorbent surface.

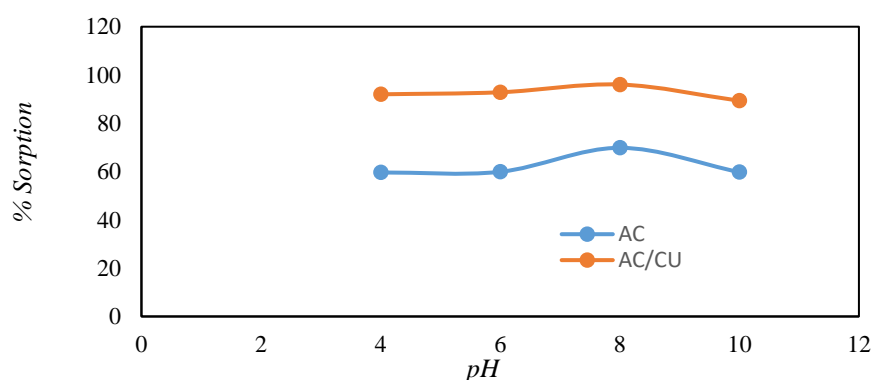


Fig. 1. Effect of phenol pH on its adsorption by AC and AC/Cu

While the percentage removal at pH less than 8 will be higher due to the non-dissociation of phenol molecules and the dominance of dispersion interactions. That is, at a not very alkaline pH, negatively charged phenol ions will have the ability to establish an electrostatic bond with the adsorbent due to the low concentration of hydroxyl ions and the lack of negative competitive effect of these ions with phenolate. At pH above 8, the presence of hydroxyl ions with a higher concentration prevents the establishment of an electrostatic bond between positively charged

copper ions on the adsorbent with phenol in the solution, and the percentage of adsorption decreases.

Effect of Phenol Initial Concentration

The results of the adsorption capacity are summarized in Fig. 2. An increase in phenol adsorption capacity was observed in the modified AC/Cu adsorbent compared to unmodified AC.

Effect of Amount of Adsorbent

In order to investigate the effect of the adsorbent amount in phenol adsorption, solutions of phenol with a volume of 50 mL and a concentration of 100 mg/L at optimal pH were separately exposed to two adsorbents with different amounts from 0.1 to 1 g. After filtration, the amount of unabsorbed phenol was calculated. The results show that (Fig. 3) the amount of adsorption has increased with the increase in the amount of adsorbent, because as the amount of adsorbent surface increases, more adsorption sites are available to phenol.

When the amount of adsorbent used decreases and goes to 0.1 g, despite the fact that the percentage of adsorbed phenol decreases, the value of q_e increases. The maximum adsorption capacity occurs in the early stages due to the availability of a larger surface area of the adsorbent, which provides free binding sites for the adsorption of phenol by the adsorbent. After reaching a certain level of use, carbon reaches the saturation point and loses its adsorption efficiency.

Impact of Contact Time

Increasing the contact time has increased the amount of phenol adsorbed on AC/Cu, and the highest amount of adsorption was achieved after 60 minutes (more than 96%). The results (Table 1) show that the adsorption process can be considered fast because a large amount of phenol is adsorbed by AC and modified AC in the first 30 minutes. The amount of phenol adsorption increased at a high speed in the first half an hour of the adsorption process, and after that, the change in the percentage of adsorption in the case of AC was almost significant, because the adsorption sites was more at the beginning of the adsorption process and the phenol molecules easily have been attracted to these places. The optimum adsorption time for activated carbon is one hour. In the case of AC/Cu, after half an hour, the increase in the percentage of phenol adsorption were more minor, because there were more adsorption sites at the beginning of the adsorption process and phenol molecules were easily absorbed in these sites. On the other hand, the presence of copper ions in the modified adsorption structure has caused a greater tendency of the adsorbent to establish an electrostatic interaction with phenol and a greater intensity of phenol adsorption by this adsorbent.

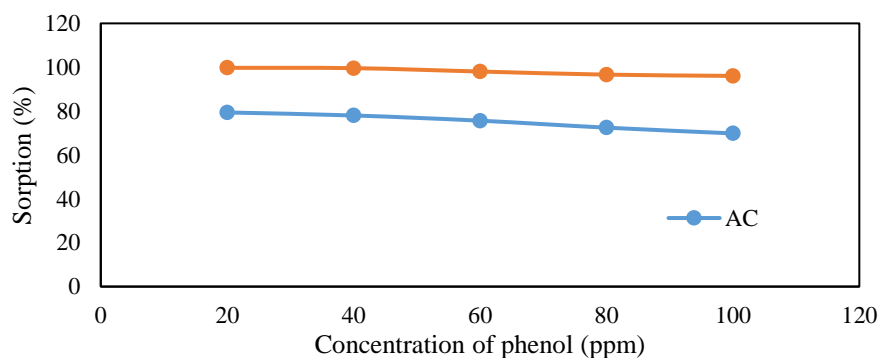


Fig. 2. The effect of the initial concentration of phenol on its adsorption by AC and AC/Cu

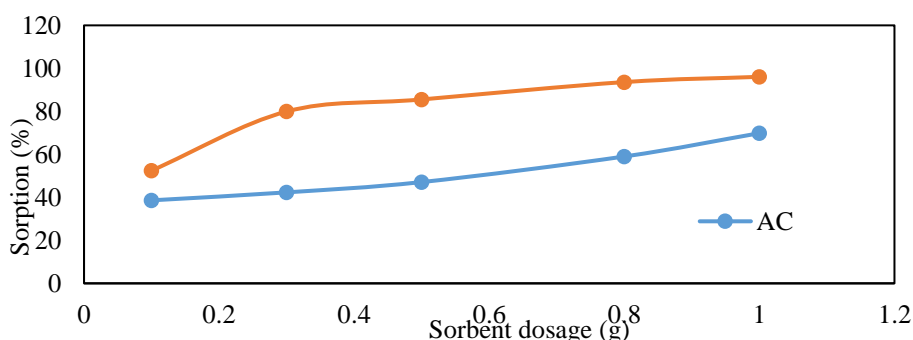


Fig. 3. Effect of adsorbent amount on phenol adsorption by AC and AC/Cu

Table 1. Effect of contact time on phenol adsorption by AC and AC/Cu

60	45	30	15	Time (min)	Absorbent
3.49	3.0	2.49	1.96	q_e (mg/g)	AC
69.8	60.0	49.8	39.2	Adsorption Percentage	
4.83	4.81	4.80	4.0	q_e (mg/g)	AC/Cu
96.6	96.2	96.05	94.1	Adsorption Percentage	

Effect of Temperature

The effect of temperature on surface adsorption of the drug is shown in [Table 2](#).

Table 2. Effect of temperature on phenol adsorption by AC and AC/Cu adsorbents

Temperature (K)				Absorbent
328	318	308	298	
71.6	71.3	70.2	69.8	AC
99.7	99.1	98.8	96.05	AC/Cu

It is clear that the adsorption of phenol by these modified adsorbents is somewhat dependent on temperature, so with the increase in temperature, the percentage of phenol removal increases appropriately. The increase in adsorption with increasing temperature indicates that the adsorption process is endothermic. The increase in adsorption percentage with increasing temperature can be attributed to the effect of swelling in the internal structure of AC, which opens pores that allow the mobility and adsorption of phenol molecules [29].

Adsorption Kinetics

Adsorption kinetics was investigated to examine the factors influencing the rate of the adsorption process. For this purpose, pseudo-first-order and pseudo-second-order models were used in this study to identify the appropriate kinetic model. The adsorption mechanism involved interactions between the organic functional groups on the activated carbon surface and the herbicides, facilitated by hydrogen bonding, electrostatic interactions, and $n-\pi$ interactions. The calculated parameters from each model are reported in [Table 3](#). Based on the results obtained and the comparison of the kinetic equation's correlation coefficients (R^2), it is evident that the pseudo-second-order equation exhibits better conformity. Furthermore, [Table 3](#) shows that the

calculated equilibrium capacities (q_{e2}) from the pseudo-second-order equation show better agreement with the experimentally obtained equilibrium capacities (q_{eexp}). Therefore, the pseudo-first-order equation with higher accuracy can predict the adsorption of drug species on the two adsorbents.

Table 3. Constants of First-Order and Second-Order Equations in all experiments

Pseudo First Order			Pseudo Second Order			
q_{e1} (mg/g)	k_1 (1/min)	R^2	q_{e2} (mg/g)	k_2 (g/mg min)	q_e (exp) (mg/g)	R^2
0.27	0.06	0.92	3.61	0.44	3.58	0.999

Desorption Studies

The obtained results are shown in Table 4. The higher percentage of phenol recovery by the modified AC adsorbent, using ethanol can be indicative of the fact that complex chemical reactions such as complex formation or chelation, oxidation-reduction, and precipitation reactions occur during the removal of phenol by these adsorbents. The higher percentage rate by ethanol compared to the other two solvents indicates the involvement of hydrophobic interactions between phenol and organic compounds (such as carboxylic groups) in the active carbon structure.

Table 4. Investigation of phenol desorption from AC and AC/Cu adsorbents

Solvent and Adsorbent			Solvent
Ethanol	Profit (0.1 M)	Ammonia (0.1 M)	
44.7	24.1	38.2	AC
42.4	23.4	14.7	AC/Cu

There was also some desorption from the adsorbents, which shows that the electrostatic interaction was caused by the tendency to adsorb phenol with a negative charge through the positive charge of the copper ion introduced into the AC structure. Although other mentioned interactions are also involved in the adsorption of phenol by this adsorbent, it seems that electrostatic forces have a greater contribution to this mechanism.

The reason for the greater desorption of AC compared to the modified adsorbent is that the adsorption of phenol in AC is mostly through physical bonds and the dominant type of adsorption is surface adsorption. But in AC modified with copper ions, since the copper ions enter the AC structure, in addition to the hydrophobic interactions of the compounds in the active carbon structure, also traps phenol through electrostatic interaction and creates a stronger bond that reduces the amount of desorption to some extent compared to AC [30]. HCl was not used, because the acidification of the adsorbents causes the adsorbent particles to dissolve from its surface. An acidic environment is favorable for phenol adsorption; successful desorption of phenol is more likely in an alkaline environment.

Break Curve

The breakdown curve is a plot of phenol concentration versus time, which is usually in the form of an S-shaped curve, and where the concentration of the phenol reaches 95% of its initial concentration, the breakpoint is called the saturation point of the adsorbent. To perform this test, a phenol solution with an initial concentration of 100 mg/L, an optimal pH of 8, and a flow rate of 5 mL/min was passed through a column containing 1 g of adsorbent. Next, during a certain period of time, the solution is collected from the end of the column and the concentration of the pollutant is measured to measure the amount of pollutant absorbed and as a result, the amount of adsorption is determined. The results are presented in Fig. 4.

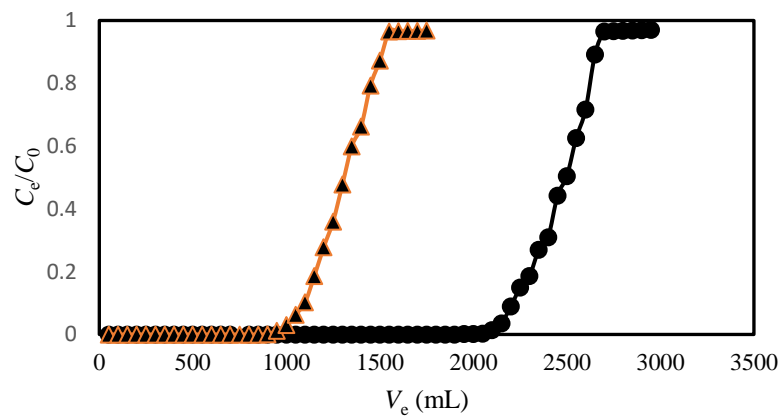
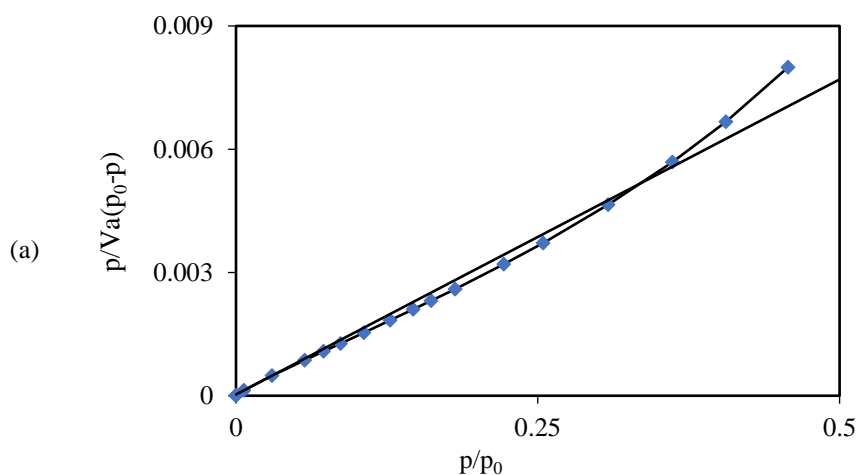


Fig. 4. Phenol adsorption failure curve by AC (\blacktriangle) and (\bullet) AC/Cu

Breakpoint and saturation resistance for AC/Cu adsorbent are much better than AC. The breakpoint of AC/Cu after contact with about 2700 mL of phenol solution is 100 mg/L (that is, AC/Cu can remove more than 95% of phenol in the said volume). AC/Cu is a much more effective adsorbent compared to AC adsorbent for phenol removal in column systems.

Specific Surface Measurement

BET analyses were performed on AC and modified AC. The higher the content of pores with a size larger than the size of the phenol molecule, the higher the specific surface area of the adsorbent, or the more acidic surface groups (carboxylic, phenolic, lactonic, acidic, and basic) there are in an adsorbent. The results of the BET diagram (Figs. 5 & 6 and Table 4) showed that the specific surface area of AC increased from 283.22 m²/g to 517.5 m²/g, after modification with copper ions. The micropore volume of AC was equal to 0.19 cm³/g, which increased to 0.53 cm³/g in the modified AC/Cu adsorbent. Therefore, the results show that the AC modification process with the help of Cu has led to an increase in the reported values of specific surface area and internal pore volume.



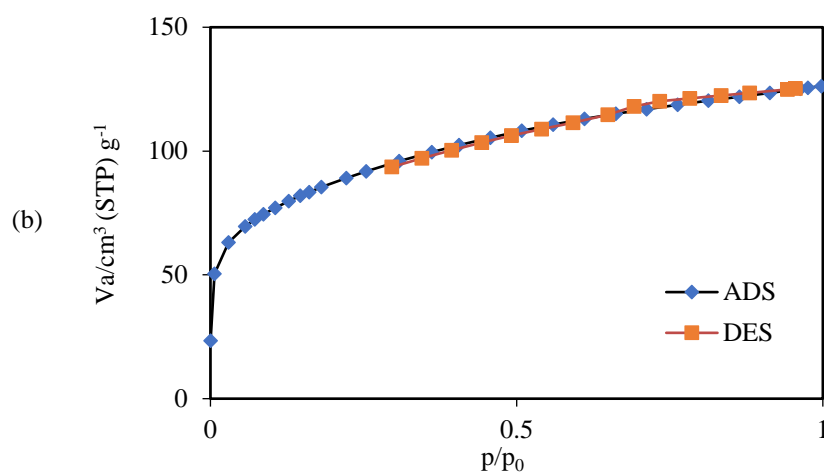


Fig. 5. Plots for BET analysis: (a) plot for surface area, (b) adsorption-desorption CV plot for isotherms

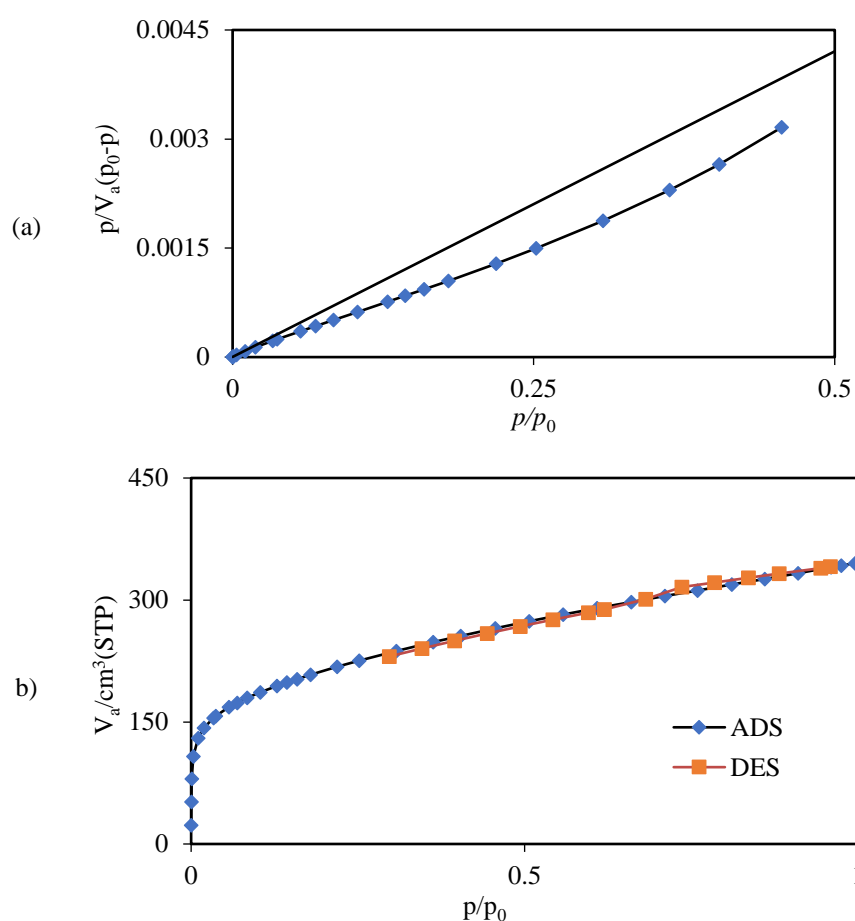


Fig. 6. Plot for BET analysis: (a) plot for surface area and (b) adsorption-desorption CV plot for isotherms for AC/Cu adsorbent

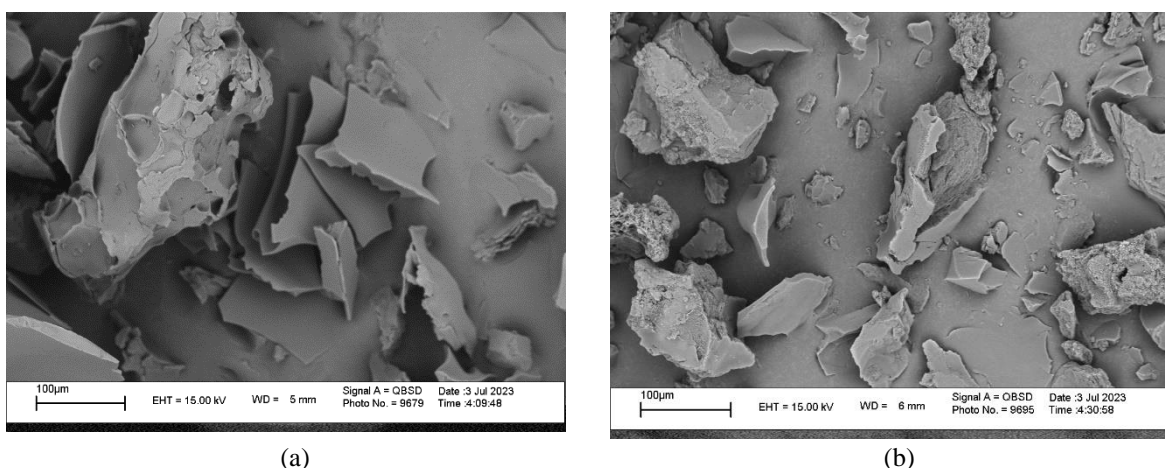
The development of pores in AC occurs during pyrolysis, because this increases the surface and volume of AC pores by expanding the penetration of phosphoric acid molecules in the pores and as a result, increasing the H_3PO_4 -carbon reaction through acid hydrolysis processes, which causes the creation of more pores. The glycosidic bond in hemicellulose and cellulose is hydrolyzed by phosphoric acid along with breaking the aryl bond in lignin [31].

Table 5. BET Analysis Parameters of AC and AC/Cu Adsorbents

Average Pore Diameter (nm)	Pore Volume (cm ³ /g)	Surface Area (m ² /g)	Absorbent
2.75	0.19	283.2	AC
4.12	0.53	517.5	AC/Cu

The Study of Morphology

The morphological characteristics of AC and AC/Cu adsorbents are shown in Fig. 7. The surface of both adsorbents contains particles of different sizes and shapes, which shows that the external surface of these two adsorbents is heterogeneous. This heterogeneity is less visible on the surface of the modified AC. The AC image in Fig. 7a shows roughness and coarser particles on the surface. Modification of AC with copper ion (Fig. 7b) has caused more uniform porosity for the adsorbent. Also, small particles can be seen on the surface, which cannot be seen in Fig. 4, and this can be caused by the adsorption of copper ions on the modified AC. This is proof of the creation of better adsorption active sites for the modified AC compared to AC, that is, these numerous particles provide a sufficient amount of active sites for the adsorption of phenol.

**Fig. 7.** SEM images of (a) AC and (b) AC/Cu

Conclusion

Black liquor is one of the waste products created in the pulp and paper industry. Due to the presence of carbon structure in this waste, it can be used as one of the basic materials for the production of AC using chemical activators. In the present study, AC was prepared with the help of a phosphoric acid activator, from lignin obtained from Kraft black liquor, with a ratio of 2:1 at a temperature of 500 °C. Further, by interacting the resulting active carbon with divalent copper ion, the structure of active carbon was modified and AC/Cu adsorbent was produced. This adsorbent was used to remove phenol from an aqueous medium. The results show that AC/Cu prepared on the basis of lignin can be used well to remove phenol in the range of neutral or weakly alkaline pH (pH = 8). BET and SEM studies also confirm the structural and morphological improvement of AC/Cu compared to the unmodified activated carbon structure. The maximum adsorption capacity (q_m) for phenol removal by the modified adsorbent was found to be 4.80 mg/g, which is much higher than the q_m obtained for AC (1.51 mg/g). On the other hand, investigating the effect of temperature on the amount of adsorption also showed that this adsorbent has a greater effect in removing phenol at higher temperatures. Adsorption

studies in the column system also showed a significant increase in the adsorption capacity of AC/Cu adsorbent (the breakpoint occurred after consuming 2700 mL of 100 ppm phenol solution) compared to unmodified AC in this study.

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