Modification of Lignin-derived Activated Carbon with Surfactants for Removal of Phenol

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Activated carbon (AC) was prepared from kraft lignin and was modified with four surfactants, namely sodium lauryl ether sulfate (SLES), dodecyl benzenesulfonic acid (LABSA), cetyltrimethylammonium bromide (CTAB), and cocoamidopropyl betaine (CAPB). The structures of the modified ACs were characterized with various spectroscopic methods. Then, the effects of pH, initial concentration, adsorbent dosage, and contact time on adsorption of phenol from aqueous solutions were evaluated. The adsorption data fitted well with the isotherm and kinetic models, with the Langmuir isotherm and pseudo-second-order kinetics describing this process. The results showed that the highest percentage of adsorption and resistance to saturation was achieved using batch and continuous systems for AC/CAPB at the optimum pH of 8.0. High recovery percentage was also observed for AC/CAPB when ethanol was used as a regeneration solvent. It was also found that adsorption/desorption of phenol is a pH-dependent process. Its superior performance was attributed to the fact that AC/CAPB is zwitterionic in nature and, hence, offers effective adsorption sites within a wide range of pH through combined electrostatic and π-π interactions. It is concluded that lignin-derived AC modified with CAPB as an amphoteric surfactant performs well in removing phenol from aqueous solution in comparison with pure AC and ACs treated with cationic and anionic surfactants.

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INTRODUCTION

Today, the development of various industries has led to an increase in the amount of production and use of chemical compounds, which causes an elevated amount of various pollutants in the effluents. Among the most important of these pollutants are aromatic organic compounds (Rosas *et al.* 2014). Phenol and its derivatives are used in large quantities in petrochemical, pharmaceutical, and chemical industries (paints, chemical fertilizers, oil, grease, pesticide compounds, *etc.*). It can also be present in pulp and paper mill effluents as degradation products of lignin (Biglari *et al.* 2017; Yeber and Silva 2022). For this reason, the amount of phenol pollutant in the effluents of these industries is a critical issue. A significant point in the contamination of the environment with phenolic compounds is associated to its good solubility in water (8.3 g/100 mL) and its relative low vapor pressure at room temperature. Therefore, it is easily transferred to soil and water and will remain in the aqueous phase in a large amount.

Progress has been made in the recent years on developing sustainable materials based on lignin. Around the world, researchers have been investigating ways of producing activated carbon from lignin as a by-product of the pulp industry (Brazil *et al.* 2022; Tang *et al.* 2023). The transformation of kraft lignin into activated carbon is an excellent example of how a waste product can become a resource, supporting the growth of a circular economy. One of the biggest challenges is creating activated carbons that have increased selectivity and holding capacity of the desired pollutants such as phenol. Researchers have performed various alteration techniques, such as chemical activation and surface functionalization (Jjagwe *et al.* 2021; Bidaei *et al.* 2024). One of the newest methods to modify activated carbon is by using the surfactant method, which simultaneously changes the surface chemistry and the way the activated carbon is structured (Ntakirutimana *et al.* 2019). Although there are a number of studies that have tested the effectiveness of ionic surfactant modification on activated carbon, there are very few comparative studies available that evaluate the differences between various surfactants used, especially zwitterionic surfactants. The goal of the present work was to fill that gap by comparing the performances of three surfactant types (anionic, cationic, and amphoteric) in their ability to remove phenol. Emphasis in this work was placed on the zwitterionic surface active agent cocamidopropyl betaine (CAPB) because it has pH-dependent behavior that may increase the likelihood of adsorbing pollutants in a wider range of environmental conditions.

The Environmental Protection Agency has set the permissible amount of phenol in wastewater at 0.1 mg/L, and the World Health Organization (WHO) has set the amount of this substance in drinking water at 0.001 mg/L (Goud *et al.* 2005). Therefore, removing these organic substances or reducing their concentration to reach the permissible limits before discharging is considered a challenging issue.

Phenol is a serious environmental contaminant because, even in trace amounts, it jeopardizes the health of ecosystems and humans over both short and long periods (Chan and Lim 2007). Its danger is attributed to its ability to cross cell membranes and cause neurotoxicity (Mohanty *et al.* 2008). Currently, there are various methods for removing phenolic compounds from the wastewater of various industries, including separation processes such as sorption by activated carbon, membrane processes, *etc*. (Juttner *et al*. 2000; Marrot *et al*. 2006), physio-chemical purification processes (Naguib and Badawy 2020) *via* chemical oxidation and electrochemical (Mukherjee *et al*. 2007), chemical coagulation (Abarbot *et al*. 2006), and reverse catalytic degradation (Tomaszewska *et al*. 2004) methods.

Activated carbons (AC) are known as effective adsorbents because of the developed porosity, large specific surface area, variable chemical properties of the surface, and high degree of surface reactivity. Several sources of carbonaceous materials can be used as raw materials for the production of AC, from materials such as wood, coal, walnut shell, date kernel, olive kernel, and many other sources (Bidaei *et al.* 2024).

Lignin is considered as a biomass derived carbon-rich material from an abundant renewable resource, with potential applications in modern society. It is possible to modify the lignin molecule extracted from different industrial sources as a macromolecule and produce various compounds such as sorbents to be used in wastewater treatment (Mollaei *et al*. 2020; Stanisz *et al.* 2021).

Kraft pulp production generates lignin as a by-product from black liquor. Although the pulp and paper industry currently use this lignin predominantly as an on-site renewable energy source (Kugge and Deuss 2021), its conversion into commercial products is minimal. Annually, only about 2% of the 78 million tons of kraft lignin produced globally is valorized industrially. This is despite longstanding research initiatives aimed at developing applications for this abundant natural polymer (Saito *et al*. 2012; Tang *et al.* 2023).

Kraft black liquor is an aqueous solution that contains lignin residues, hemicelluloses, and other chemicals. This substance is strongly alkaline and its pH value is approximately 13. Lignin can be recovered from this alkaline stream through acid precipitation (Hubbe *et al.* 2019; Brazil *et al.* 2022; Mohammadpour *et al.* 2024).

In this study, reuse potential and valorization of lignin in fabricating activated carbon in line with sustainable development goals was investigated. In addition, the modification of this AC was performed with different surfactants to enhance the removal of phenol from aqueous solution. This comprehensive study addresses the need for comparative evaluation of different surfactant types and provides mechanistic insights into the superior performance of zwitterionic surfactant-modified AC. The performance of the adsorbents was evaluated at different conditions with batch and continuous systems.

EXPERIMENTAL

All chemicals used were of analytical reagents grade and prepared in deionized water. Phenol (≥ 99.0%) was obtained from Merck and distilled before use. Black liquor was prepared from the Chuka-Iran wood. The paper mill is located in Gilan province, Iran, to extract lignin for manufacturing activated carbon.

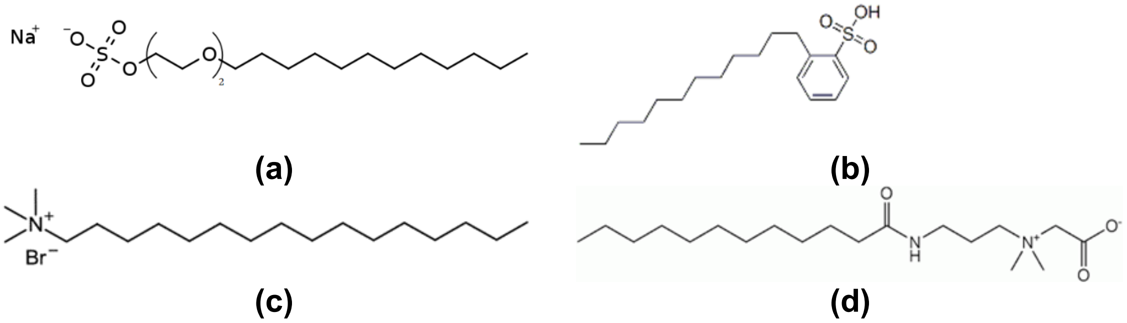

Fig. 1. Chemical structure of surfactants (a) SLES, b) LABSA, c) CTAB, and d) CAPB

The surfactants, including sodium lauryl ether sulfate (SLES) and dodecylbenzene-sulfonic acid (LABSA) as anionic surfactants, cetyltrimethyl ammonium bromide (CTAB) as cationic surfactant, and cocamidopropyl betaine (CAPB) as amphoteric surfactant (Fig. 1) were supplied from Merck.

Absorbance measurements were carried out using a Nanocolor-II UV–Vis spectrophotometer with a 1-cm cell.

A Metrohm pH meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for determining the pH. The characteristic properties of samples were studied using Fourier transform infrared (FT-IR) (Bruker-Alpha, Germany), nitrogen gas adsorption (BET) (II Belsorp mini, Japan), and scanning electron microscopic (SEM; Model LEO 1430VP, Germany) instruments.

Preparation of activated carbon

Extraction of lignin from the black liquor was done by acidifying the black liquor with 37% hydrochloric acid (Mussatto *et al.* 2007). The extent of precipitation of lignin was evaluated in terms of the effect of pH. After reaching the desired pH, the solution was stirred for 1 h at a temperature of 90 °C. Then, the solution was placed at room temperature for 1 h to obtain a completely biphasic solution. A filter paper (on the Buchner funnel under vacuum) was used to separate the formed sediment and the sediment was completely separated. After this step, the precipitate was washed well with an aqueous solution (with pH = 2) several times, and the separated lignin on filter paper was washed again with distilled water until reaching neutral pH. In the next step, kraft lignin was collected, dried in an oven at 90 °C for 24 h, and the solid material was ground as a control sample. Impregnation of dried matter was conducted at a 2:1 ratio of 85% phosphoric acid to lignin, and the prepared sample was placed in an oven over night at a temperature of 110 °C. The preparation of activated carbon was then proceeded using an electric furnace under argon atmosphere at 500 °C.

Modification of AC by surfactants

In order to carry out the modification, the activated carbon (AC) was washed with distilled water repeatedly until the color of the effluent became clear. The washed carbon was soaked in distilled water for 24 h and then filtered and after that placed in 5% HCl aqueous solution with continuous shaking for 2 more hours to remove other impurities and dust particles. Then the AC was filtered and then washed with distilled water. In the next step, the desired modifications were made according to the following protocol.

Solutions with various concentrations of surfactants (SLES, LABSA, CTAB, and CAPB) were prepared (concentration of 500 mg/L to prevent foaming of the solution) and a certain volume of these solutions (100 mL of surfactant solution) was placed in contact with a desired amount of AC for 12 h and mixed at a speed of 200 rpm (by a shaker) to absorb onto the sorbent. The concentration of the surfactant solution after contact with the sorbent and was measured to ensure the amount of surfactant sorption.

Then, the modified sorbent is separated from the solution by filtering, washed 5 times with distilled water, and dried overnight in an oven at 90 °C.

Sorption experiments and investigation of effective factors for phenol removal

In a batch experiment, known amounts of adsorbents (AC/SLES, AC/CTAB, AC/LABSA, and AC/CAPB) were treated with solutions spiked by phenol with different concentrations (0 to 100 mg/L) at room temperature while being stirred by a mechanical shaker. For column investigation, a glass column with a diameter of 1 cm and a length of 25 cm was used (to draw the breakthrough curve to check the resistance of sorbents against pollutant saturation in the flow system). About 1.0 g of each adsorbent was packed in a column (with a height of 5 cm) and then a 50 mg/L phenol solution was passed through the column at a flow rate of 3 mL/min at room temperature. The eluted solution from the column was analyzed for determining the amount of unabsorbed phenol after every 10 mL.

The adsorption percentage was calculated using the following relationships. In order to calculate the percentage and capacity of adsorption as well as the percentage of desorption in the batch system Eqs.1 to 4 were used, respectively:

$$\%Sorption = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

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

$$\%Desorption = \frac{m^{*}}{m_0} \times 100 \tag{3}$$

$$m^{*} = Ce * V^{/} \quad \text{and} \quad m_0 = (C_0 - Ce)V \tag{4}$$

In Eqs. 1 to 4, C_0 and C_t are the initial and the residual concentrations (mg/L) at time t, respectively. At equilibrium, C_t becomes C_e and q_t becomes q_e. The q_t denotes the adsorption capacity (mg/g), whereas V and w, are the initial volume of the sample solution (L) and the weight of the adsorbent (g), respectively. M_0 (mg) and m* (mg) are the masses of the sorbate before exposing to the adsorbent and the phenol mass remaining in the desorption solution. V is the volume of the desorption solution (L). The absorption capacity in the column system *i.e.*, the amount of phenol absorbed on the adsorbent surface was calculated using Eq. 5,

$$q_{b\&C} = \frac{\Sigma(C_0 - C_t)V_{elu}}{w} \tag{5}$$

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

For desorption studies, 1.0 of adsorbent used in the phenol absorption process was placed in contact with desorption solvents (NaOH and ammonia solutions with concentrations of 0.1 M and ethanol) for 30 min and then filtered through filter paper, and the amount of absorbed phenol was measured.

Study of kinetics and adsorption isotherm

Pseudo-first-order and pseudo-second-order models were utilized to study phenol adsorption kinetics. All the kinetics tests were performed in a series of 50 mL phenol solutions with concentration of 100 mg/L and 0.1 g of adsorbents at optimal pH for interval times of 15, 30, 45 and 60 min. Solutions with different concentrations of 20, 40, 60, 80 and 100 ppm were prepared to obtain adsorption isotherms of phenol on pure and surfactant modified ACs. All the experiments were conducted at pH 8 and temperature of 25 °C. The equilibrium data were then analyzed using Langmuir and Freundlich isotherm models. To calculate the parameter of models, the formulas mentioned in the literature were used (Ma *et al.* 2013; Mollaei *et al.* 2020; Patil *et al.* 2024).

Determination of phenol

Determination of phenol was carried out according to the Hach company method (method 8047), which conforms to the standard for the examination of water and wastewater, and using procedure of USEPA method 420.1 for wastewater. Quantitative analysis of phenol was carried out using a calibration curve prepared using the phenol standard solutions in deionized water.

All experiments were performed in triplicate. The results used were average of these measurements. The linear regression analysis was used for data processing. The relative standard deviation (RSD) was less than 1.0% and the detection limit value, based on the three times the standard deviation of the blank was 0.02 mg/L.

RESULTS AND DISCUSSION

Sorption of Phenol by AC and Surfactant-Modified AC (Batch System)

Effect of pH

To study the optimal pH in the batch system for four modified sorbents, 50 mL solutions of phenol with an initial concentration of 100 mg/L at different non-buffered pH values (4 to 10) were treated in contact with 1.0 g of the adsorbents for 30 min. It should be noted that regarding AC, the optimum contact time was for one hour, and the results of the pH effect presented in Table 1 correspond to 1.0 h of contact time for adsorbent and phenol solutions at different pH values. The pH of the solutions was adjusted using dilute solutions of NaOH and HCl. Then, after filtering with filter paper, the filtrate was used to measure the amount of unabsorbed phenol using a spectrophotometer. A calibration curve was used to measure the amount of phenol that was not absorbed. The pH of the phenol solution was found to be effective for controlling the sorption capacity of the adsorbents. The results showed (Table 1 and Fig. 2) that the highest amount of adsorption was achieved with AC/CAPB and a pH of the solution equal to 8.0. The sorption percent was increased by increasing the pH from 2 to 8, but when the pH value continued to increase from 8 to 10, the amount of phenol adsorption percent decreased. In fact, the reactive functional groups sites on the surface of modified ACs such as -OH or -COOH groups were passivated at pH values above 8.0. On the other hand, the adsorption of phenol decreased at high pH values due to the ionization of its molecules while the removal percentage at pH values lesser than 8.0 was higher because of non-dissociated form of phenol molecules and predominance of London dispersion interactions.

Table 1. Effect of pH on Adsorption Capacity of Phenol by Adsorbents

q_e (mg/g)					
		pH 4	**pH 6**	**pH 8**	**pH 10**
AC		2.98	3.0	3.49	2.99
AC/SLES		4.50	4.53	4.76	4.50
AC/LABSA		4.56	4.57	4.87	4.39
AC/CTAB		4.47	4.51	4.89	4.61
AC/CAPB		4.64	4.46	4.94	4.54

The ideal pH value of 8.0 for AC/CAPB can be explained by analyzing the zwitterion character of the CAPB molecule. As the pK_a value of phenol is 9.99, at pH 8.0 the vast majority of phenol molecules are still neutral. At this same pH, CAPB contains a positively charged quaternary ammonium group and a deprotonated carboxyl group, resulting in balance across both of these groups when CAPB progressively interacts with neutral phenol molecules *via* hydrogen bonding, π-π stacking and hydrophobic attractions, while the phenol remains in a neutral state.

At pH values above 8, the proportion of ionized phenol molecules gradually increases according to the Henderson-Hasselbalch equation, leading to increased electrostatic repulsion with the negatively charged AC surface and deprotonated carboxyl groups of CAPB.

The opposite effect occurs at lower pH due to the increased protonation on the CAPB molecules resulting in a decrease in the availability of diverse interactions for the phenol to bind to.

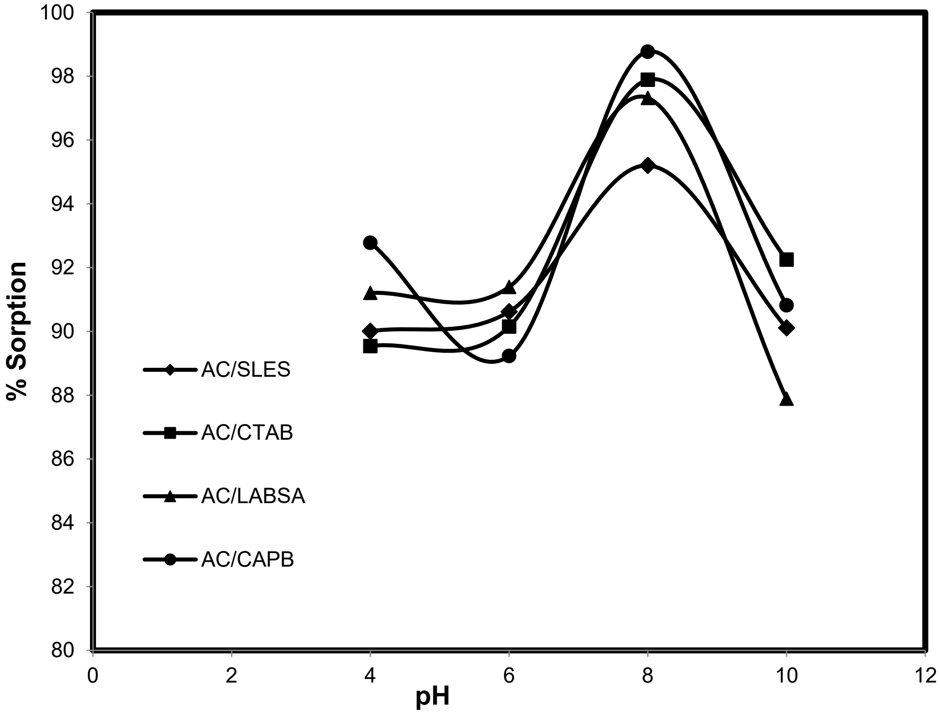

Fig. 2. Effect of pH on sorption of phenol by AC/SLES, AC/LABSA, AC/CTAB, and AC/CAPB

Aqueous solutions of phenol are weakly acidic with a dissociation constant (pK_a) of 10.0. As the pH approaches and exceeds the pKa, the proportion of phenol molecules existing as anions increases.

Based on the phenol dissociation conditions, sorption on modified AC materials is performed more efficiently when phenol is a neutral molecule. In acidic environments, surfactant intercalated in AC pores space provides an effective environment pollution removal due to van der Waals forces and hydrophobic effects. When the solution is alkaline, phenol sorption decreases due to electrostatic repulsion forces between the negatively charged AC particles and phenol anions.

Effect of initial concentration

For performing this stage of experiment, 1.0 g of sorbents were treated with 50 mL of phenol solution with a concentration of 10 to 100 mg/L for 30 min (for AC modified adsorbents) and 1.0 h (for AC) accompanied by mild shaking at room temperature. The obtained results are summarized in Table 2 and Fig. 3.

Table 2. The Effect of the Initial Concentration of Phenol on Adsorption Capacity of Adsorbents

			q_e (mg/g)			
	Conc. of Phenol (ppm)	**20**	**40**	**60**	**80**	**100**
AC		0.79	1.5	2.35	2.89	3.49
AC/SLES		0.95	1.92	2.87	3.84	4.76
AC/LABSA		0.98	1.97	2.95	3.90	4.86
AC/CTAB		1.00	1.98	2.97	3.92	4.89
AC/CAPB		1.00	1.98	2.97	3.95	4.93

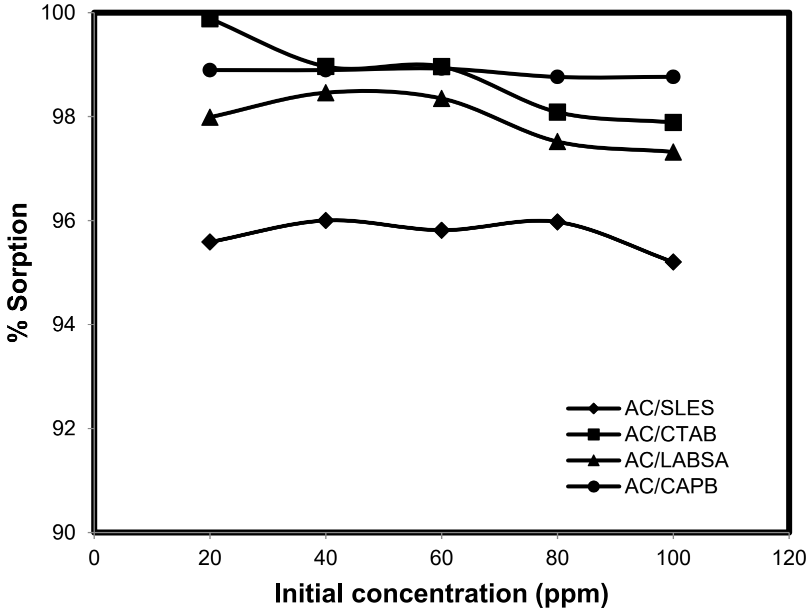

Fig. 3. Effect of initial concentration on percent sorption of phenol by AC/SLES, AC/LABSA, AC/CTAB and AC/CAPB

The results indicated that the adsorption capacity of modified AC was improved in comparison with unmodified AC. The highest adsorption capacity was observed on the AC/CAPB. In fact, the presence of a double bond in the structure of phenol can cause π-π interaction between the double bonds in the structure of CAPB compared to CTAB (the π donor in the aromatic ring of phenol and the π acceptor in CAPB surfactant) and the adsorption capacity of CA/PBAC increased slightly compared to AC/CTAB.

Effect of adsorbent dosage

In order to study the effect of adsorbent dosage, 50 mL of phenol solution with a concentration of 100 mg/L at optimal pH were separately exposed to 0.10 to 1.0 g adsorbents and stirred for 1 h by a mechanical shaker. The results showed (Table 3 and Fig. 4) an increase in the amount of sorption and adsorption capacity by increasing the amount of adsorbent due to the availability of more exchangeable sites or adsorbent surface area.

Table 3. Effect of Adsorbent Dosage on Adsorption Capacity of Phenol

q_e (mg/g)						
	Adsorbent Dosage (g)	**0.1**	**0.3**	**0.5**	**0.8**	**1.0**
AC		19.3	7.05	4.71	3.68	2.99
AC/SLES		37.63	14.97	9.17	5.79	4.76
AC/LABSA		37.93	14.93	9.54	6.01	4.86
AC/CTAB		38.73	15.09	9.47	6.06	6.12
AC/CAPB		38.9	14.92	9.57	6.10	6.17

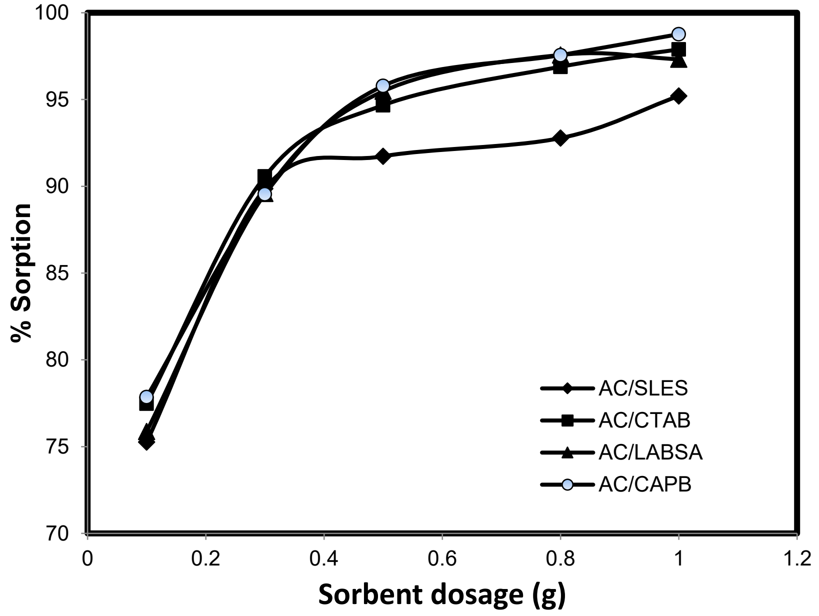

Fig. 4. Effect of adsorbent dosage on percent sorption of phenol by AC/SLES, AC/LABSA, AC/CTAB, and AC/CAPB

Effect of contact time

In order to determine the equilibrium time for the phenol adsorption process, 50 mL solution at optimal pH were mixed with 1.0 g of adsorbent for 15 to 60 min at a speed of 100 rpm. After filtering of solutions, the supernatants were analyzed. It was observed that by increasing the contact time, phenol sorption percentage increased and optimum removal of about 99% was achieved at contact time of 60 min (Table 4 and Fig. 5). However, no significant improvement was observed in preliminary tests extending to 120 minutes.

In the case of 4 modified AC sorbents, with the increase of contact time from 0.5 to 1.0 h, the amount of phenol absorption increased, although compared to the absorption of phenol by AC, the extent of increase in absorption after 0.5 h was not so high. So, the sorption process can be considered fast because of the large amount of phenol adsorbed by the modified adsorbents within the first 30 min of sorption. In other words, the amount of phenol adsorption increased at a high speed in the first 0.5 h of the absorption process, and after that the change in the percentage of adsorption was negligible. This can be attributed to the fact that the sorption sites were initially abundant and phenol molecules were easily adsorbed at these sites. As a result, the selected time to achieve the highest adsorption by these four modified AC adsorbents was determined to be 30 min.

Table 4. Effect of Contact Time on Adsorption Capacity of Phenol by Adsorbents

		***q*e (mg/g)**			
	Contact Time (min)	**15**	**30**	**45**	**60**
AC		1.96	2.49	3.0	3.49
AC/SLES		4.64	4.76	4.77	4.78
AC/LABSA		4.64	4.87	4.875	4.88
AC/CTAB		4.70	4.89	4.90	4.90
AC/CAPB		4.73	4.94	4.945	4.95

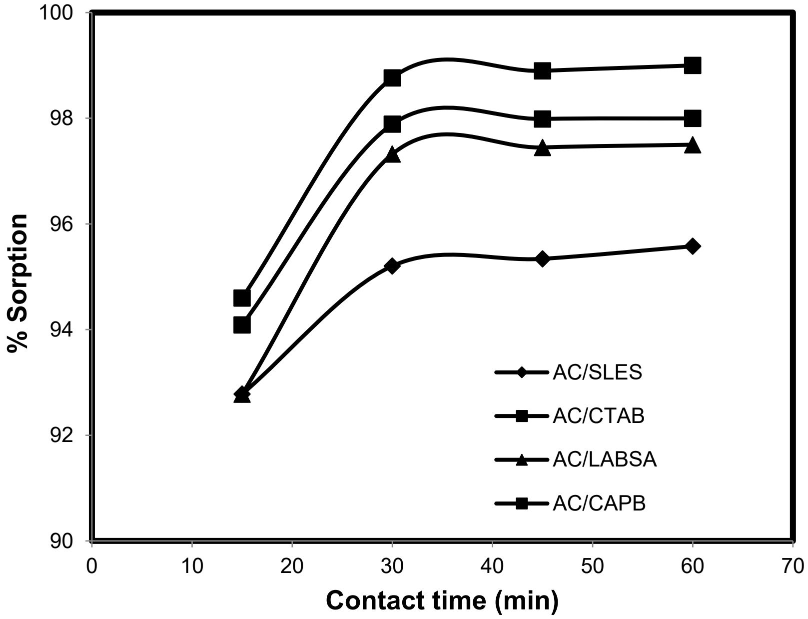

Fig. 5. Effect of contact time on percent sorption of phenol by AC/SLES, AC/LABSA, AC/CTAB, and AC/CAPB

Effect of temperature

Industrial wastes are usually discharged into the sewers with temperatures higher than the ambient temperature. Therefore, temperature is an important parameter that affects the adsorption capacity and provides important information about the thermodynamics of the adsorption process and standard enthalpy change. The results of the effect of temperature are given in Table 5.

It is clear that the adsorption of phenol by these modified adsorbents is slightly dependent on temperature, so with increasing temperature, the percentage of phenol removal increased slightly. The increase in sorption with increasing temperature indicates that the adsorption process was weakly endothermic.

Table 5. Effect of Temperature on the Phenol Sorption Percentage by Adsorbents

	Temperature (K)			
	298	308	318	328
AC	69.8	70.2	71.3	71.6
AC/SLES	97.3	97.9	98.5	99.3
AC/LABSA	97.3	98.0	98.5	99.3
AC/CTAB	97.9	98.2	99.0	99.5
AC/CAPB	98.7	98.8	99.0	99.6

Desorption Studies

To study the desorption rate of phenol, the saturated adsorbent was washed with distilled water. It was then placed in contact with desorption solutions such as NaOH, NH_3, and ethanol. Then, the efficiency of phenol desorption from adsorbents was assessed. The results are shown in Table 6.

Table 6. Effect of Different Eluents on Desorption Percentage of Phenol

Eluent Solutions			
	NH_3 (0.1 M)	NaOH (0.1M)	Ethanol
AC	38.2	24.1	44.7
AC/SLES	25.3	10.3	32.6
AC/LBSA	27.8	13.2	38.1
AC/CTAB	29.9	16.3	39.8
AC/CAPB	30.4	19.9	40.2

The desorption percentages in Table 6 represent the fraction of adsorbed phenol that was recovered from the adsorbent surface into the eluent solution. Higher recovery percentage of phenol by modified AC adsorbents (modified by anionic and amphoteric surfactants), using ethanol may indicate complex chemical reactions such as complex or chelate formation, redox and precipitation, that have occurred during phenol removal by these adsorbents. However, the higher desorption percentages by ethanol compared to the other two desorption solvents indicates the involvement of hydrophobic interactions between phenol and surfactants placed on the AC adsorbent. Generally, surfactants are amphiphilic molecules that have a hydrophilic head (carboxyl group, ethylene oxide, amino group *etc*.) and a hydrophobic head (alkyl chain), which affects their arrangement in the solution or adsorption process on the surface of adsorbent. Since AC also has a low degree of polarity, the interaction of surfactants with AC surface can be affected by thermodynamic factors such as enthalpy and entropy levels (Ntakirutimana *et al.* 2019). Meanwhile, when the NaOH solution was used, less desorption occurred compared to other eluents. This suggests that while electrostatic interactions may play some role, the dominant adsorption mechanism for phenol on surfactant-modified ACs likely involves partitioning into the surfactant monolayer rather than strong ionic binding. This is analogous to gas-liquid chromatography where analytes partition into a liquid stationary phase coated on a solid support.

On the other hand, the reason for higher desorption in the default AC compared to modified sorbents is that phenol sorption in AC is mostly due to physical interactions and the dominant type of sorption can be described as physical adsorption. But in surfactant-modified ACs, since these modifiers have entered in the structure of AC, they mostly trap phenol with the help of their functional groups and establish a stronger bond that reduces the desorption to some extent compared to AC.

Adsorption of Phenol in the Column System

After conditioning of column as earlier mentioned, a solution of phenol with an initial concentration of 100 mg/L with the optimal pH obtained from the tests of the batch experiments and a flow rate of 5 mL/min was passed through the column contains one gram of adsorbent. To draw the breakthrough curve, 10 mL samples were taken from the output solution at regular volume intervals from the column and the amount of phenol was measured spectrophotometrically. Finally, the breakthrough curve was drawn as C_e/C_0 (the ratio of the unabsorbed concentration of the phenol to its initial concentration) *versus* output volume (V_e) of the solution. The results are shown in Fig. 6.

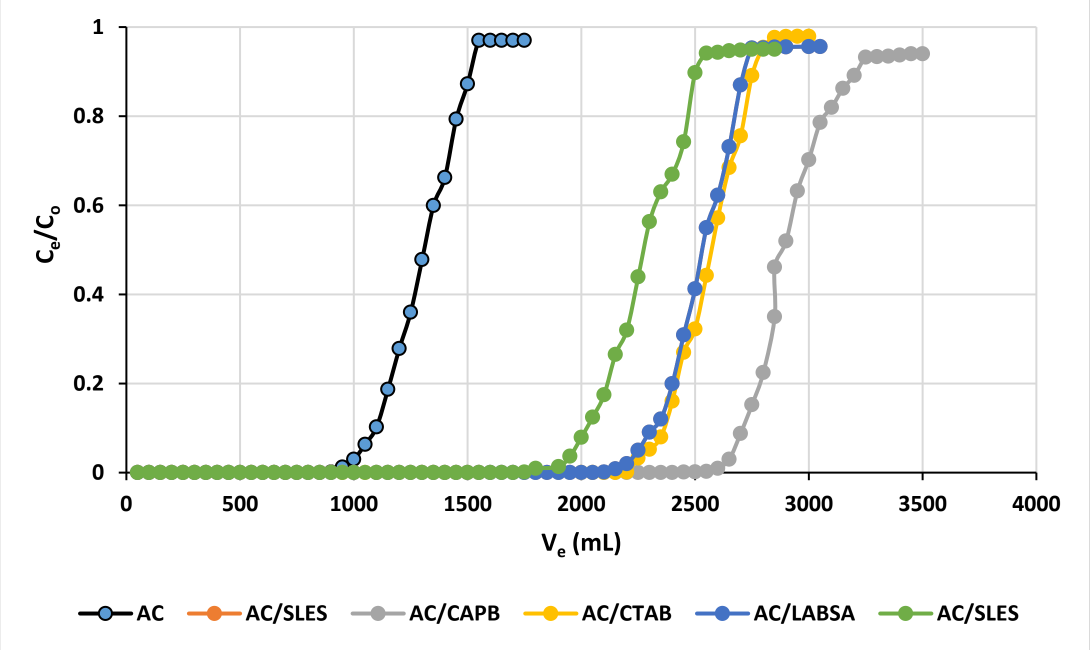

Fig. 6. Breakthrough curves for the removal of phenol by AC, AC/SLES, AC/LABSA, AC/CTAB, and AC/CAPB

As can be seen from the experimental results, the highest breaking point and the highest resistance were observed in the AC/CAPB sorbent. In fact, the obtained curve shows that the breaking point for AC/CAPB was after treatment of above 3000 mL of 100 mg/L phenol solution. Based on the results, AC/CAPB seemed to be much more effective adsorbent compared with other modified adsorbents for removal of phenol in column/ flow systems.

Adsorption Kinetics and Isotherm Modeling

Initially, the rate of adsorption was determined using two models; pseudo-first order and pseudo-second order. Both model equations were fitted well with the collected kinetic data (Table 7). The pseudo-second order model was shown to have the highest overall correlation to the experimental data ($R^2>0.99$). However, it is important to note that good fit to pseudo-second-order kinetics does not necessarily demonstrate a chemical reaction mechanism, as such fits are commonly observed for adsorption onto porous materials due to their complex diffusion pathways into a network of tiny pores (Hubbe *et al.* 2019).

Table 7. Kinetic Parameters of Pseudo First- and Pseudo Second-order Models for the Adsorption of Phenol by AC and AC/CAPB at 25 °C

Adsorbent type	**First-order kinetic model**			**Pseudo-second-order kinetic model**			
	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**
AC	0.271	0.06	0.9231	3.61	0.44	3.58	0.9999
AC/CAPB	0.47	0.093	0.8291	5.02	0.261	4.94	0.9999

After determining the kinetics of the process; next, the data evaluation of the equilibrated adsorption on AC and AC/CAPB was performed through the Langmuir and Freundlich sorption isotherm models. The Langmuir model was shown to produce higher coefficients of determination (R^2>0.99). This is indicative of equal, non-interacting sites of adsorption (Table 8), as assumed in the derivation of that isotherm model. By comparison of the Q_{max} values, as determined from the Langmuir model, it was demonstrated that the AC-CAPB with 22.0 mg/g performed about three times better than unmodified AC (7.88 mg/g).

Table 8. Langmuir and Freundlich Isotherm Model Parameters for the Adsorption of phenol by AC and AC/CAPB

Sample	**Langmuir**			**Freundlich**		
	K_L	Q_{max}	R^2	K_f	n	R^2
AC	0.027	7.88	0.985	0.28	1.32	0.966
AC/CAPB	0.237	21.97	0.998	0.241	1.155	0.955

Characterization of Adsorbents

The modified and untreated AC samples were characterized in terms of morphological and functional groups using nitrogen adsorption (BET), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR).

Specific surface area measurements

Brunauer-Emmert-Teller (BET) analyses were conducted to determine the specific surface area and pore volumes of solid sorbents based on the physical adsorption of inert N_2 gas. The results demonstrated that the specific surface area and pore volume of AC were increased after modification process (Table 9).

Table 9. Parameters of BET Analyses for AC and Modified AC Adsorbents

	Specific Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size Average (nm)
AC	283.2	0.190	2.75
AC/LABSA	1331.1	0.973	2.95
AC/ SLES	940.1	0.695	2.92
AC/CTAB	929.2	0.693	2.98
AC/CAPB	930.7	0.692	2.97

Surfactant modification likely creates a monolayer on the AC surface, which may alter the accessibility of nitrogen molecules to the pore structure during BET measurements. However, among these modified ACs, the highest gain in the specific surface area is related to the modification of AC with smaller molecular size surfactant, LABSA. The relative low values in specific surface area of other modified ACs can be attributed to exchange sites which were satisfied by surfactants with large molecular size, resulting in inaccessibility of the internal surface to nitrogen gas and blocking of the some micropores in the AC structure.

An alternative interpretation is that surfactant treatment provides a liquid-like layer covering the AC surface, creating an environment where phenol can partition into this layer. This partitioning mechanism could explain the enhanced adsorption despite modest changes in measured surface area. Although the specific surface area of the adsorbent and the volume of cavities inside the adsorbent are lower in the case of AC/CAPB, it shows a higher adsorption rate to phenol. The reason for this result is that in addition to the *π-π* dispersion interactions through delocalized electrons in the aromatic rings of surfactants (though such π-π interactions typically contribute only modestly to the total binding energy), electrostatic attraction also increases the adsorption power in the case of this adsorbent (Jjagwe *et al.* 2021).

FT-IR spectroscopy

Functional groups changes of AC after modification were characterized by infrared spectroscopy. FTIR spectra of all unmodified and modified ACs are shown in Fig. 7. A sharp peak appeared at 3440 cm^{-1} is assigned to stretching mode of hydroxyl group in the AC occurring due to the sorption of water molecules within the interlayer space of the AC and formation of hydrogen bonding. These symmetrical stretching vibration bands were shifted from 3433.57 cm^{-1} to 3412.23 cm^{-1}, 3413 cm^{-1}, 3436 cm^{-1}, and 3426 cm^{-1} in AC/LABSA, AC/SLES, AC/CTAB, and AC/CAPB, respectively, owing to vibration bands of hydroxyl (anionic surfactant) or amine groups (cationic and amphoteric surfactant) of surfactants intercalated in the AC structure.

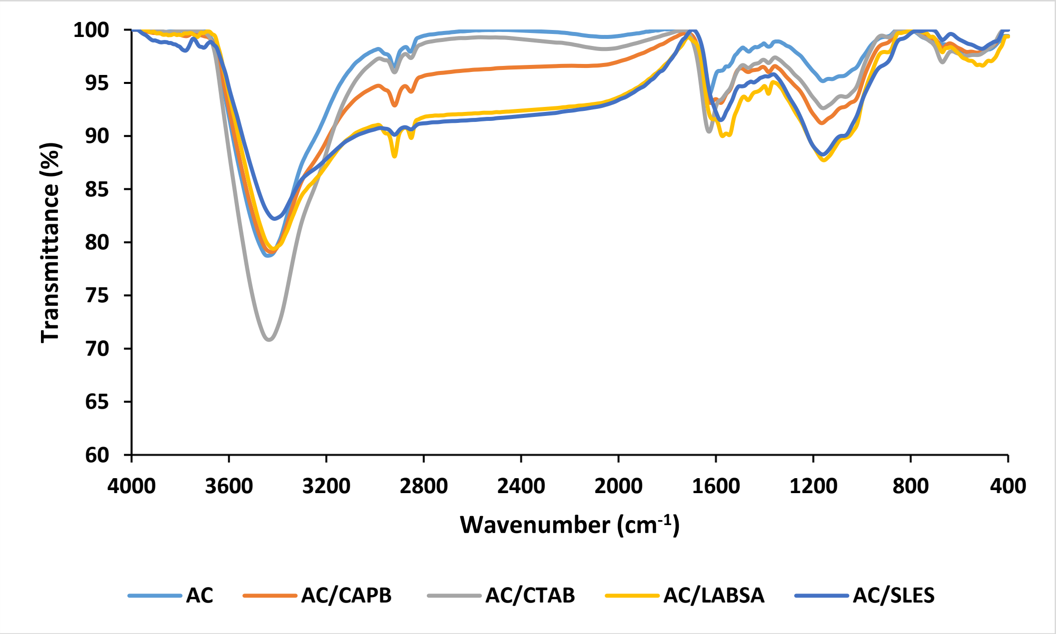

Fig. 7. FTIR spectra of AC, AC/LABSA, AC/SLES, AC/CTAB, and AC/CAPB

After the modification of AC with surfactants, a pair of strong bands at 2920 and 2855 cm^{-1} were observed, which were assigned to the asymmetric and symmetric stretching vibrations of the methylene groups. The peaks in the region 1250 to 1500 cm^{-1} can be assigned to C–H bending of CH_3–R (1385 cm^{-1}) and CH_3–N (1428 cm^{-1}) stretching. The first peak visible in the AC/LABSA, AC/SLES, and AC/CAPB. Second peak is also visible in AC/CTAB sample which is a sign of modification of AC with the desired surfactant. The band at about 1160 cm^{-1} is associated with ether –C–O– symmetric and asymmetric stretching vibration of –C–O–C– ring in the structure of surfactants. These changes in the IR spectra indicate that the interlayer space and pores of AC had been successfully intercalated with LABSA, SLES, CTAB and CAPB.

SEM analyses

Scanning electron microscopy (SEM) was used to analyze changes of the surface morphology and qualitative characteristics of pure and modified AC samples.

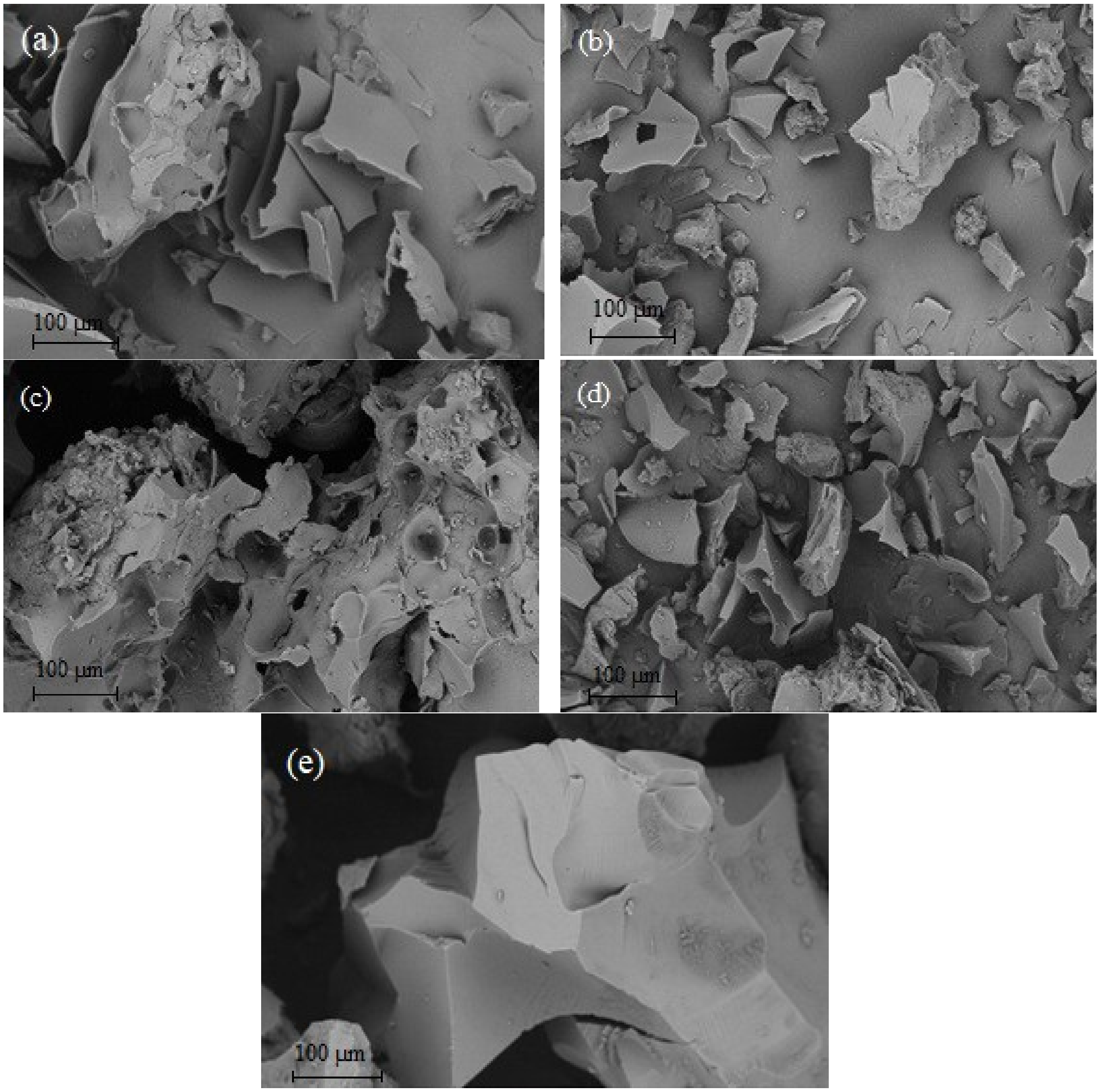

Fig. 8. SEM images of (a) AC; (b) AC/SLES; (c) AC/LABSA; (d) AC/CTAB; and (e) AC/CAPB with 500× magnification

The SEM images of the samples are shown in Figs. 8a-8d. The image of pure AC in Fig. 8a shows roughness and macropores on the surface, whereas modified AC looks much smoother on the surfaces due to deposition of surfactant layer. Furthermore, the AC/CAPB sample in Fig. 8e shows a highly smooth surface that implies highly saturated with surfactants layer than ACs modified by other surfactants. It should be noted that SEM primarily reveals macropores and surface topography; the surfactant molecules themselves are too small to be directly visualized by SEM. The smoother appearance may result from surfactant-assisted cleaning of surface debris during the modification process.

AC modification by CTAB and CAPB (cationic and amphoteric surfactants) caused no change in the granule integrity but resulted in cracking and corrosion on the surface of the particles. In fact, the morphological differences caused by the modification of AC adsorbent with surfactants can be derived from the structural difference between anionic surfactants and the other two surfactants used. All these observations implicate effective interaction between surfactants and AC surface *via* hydrophobic interactions.

Mechanistic Insights into CAPB-Phenol Interactions

The CAPB surfactant modified AC had more favorable characteristics than any other surfactant modified AC. This might be attributed to the interesting structure and pH-responsive zwitterionic nature of CAPB. It is a surfactant that has both positively charged (quaternary ammonium) and negatively charged (carboxylic acid) functional groups that give it dual functionality at pH 8.0, so at that pH the two types of functional groups work together; the quaternary ammonium functional group can form an electrostatic bond with the aromatic ring, and the carboxylic acid functional groups can form hydrogen bonds with the terminal hydroxyl group of phenol (Gerola *et al*. 2017). Furthermore, CAPB, with its long alkyl chain, gives the hydrophobic functional group a good way to adhere to phenol molecules. The performance of AC/CAPB under various conditions is attributable to the fact that AC/CAPB works by multiple modes of interaction, while anionic or cationic surfactant modified ACs work by only one mode of interaction.

Comparison with Other Adsorbents

A comparison of the ability of AC/CAPB to remove phenol was made with other types of adsorbent as presented in the literature (see Table 10).

Table 10. Comparison of Phenol Adsorption Capacity with Various Adsorbents

Adsorbent Type	Q_{max} (mg/g)	Reference
AC/CAPB	22.0	(this study)
Tamarind nut shell AC	3.89	Goud *et al.* 2005
Cherry stone-based AC	20 to 80	Beker *et al.* 2010
Powdered activated carbon (coal, coconut shell and bamboo charcoal)	33 to 59	Ma *et al.* 2013
Banana Peels AC (BPAC)	6.98	Ingole *et al.* 2017
Commercial AC : (coal-derived granular AC, coal-derived powdered AC , and coconut shell-derived powdered AC)	170, 177, and 213	Xie *et al.* 2020
Cassia fistula pod shell AC	184	Patil *et al.* 2024
AC from *Luffa cylindrica*	10 to 55	Belaid *et al.* 2025

The $Q_{\max}$ value for AC/CAPB was 22.0 mg/g, which puts it in the range of some other activated carbon materials made from biomass but shows a substantial increase when compared to unmodified lignin-based ACs. Although some specialized sorbents show better absolute maximum capacities than AC/CAPB, the latter provides benefits such as sustainability due to being produced from a renewable, waste material (lignin), less stringent operational conditions, and its pH responsive properties caused by the zwitterionic nature of the surfactant. Regeneration experiments have shown that AC/CAPB still retained good capacity after completing desorption cycles using ethanol as the regenerant, indicating that it has excellent reusability potential.

CONCLUSIONS

1. Activated carbons were prepared from kraft pulping black liquor and was modified with three types of cationic, anionic, and amphoteric surfactants. The Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), and nitrogen gas adsorption (BET) analyses confirmed the modification of the activated carbon (AC) structure through the adsorption of surfactants.
2. The adsorption of phenol onto activated carbons was best described by using the Langmuir model and pseudo-second-order kinetics. The maximum adsorption capacity of the activated carbon was calculated for the activated carbon modified with the amphoteric surfactant (AC/CAPB), which was approximately 22.0 mg/g.
3. The superior performance of surfactant-modified ACs likely involves partitioning of phenol into a surfactant monolayer on the AC surface, analogous to liquid-phase extraction. This mechanism explains the enhanced adsorption despite sometimes modest changes in measured surface area. The zwitterionic nature of CAPB provides particularly favorable conditions for this partitioning across a range of pH values. The adsorbents also indicated more effectiveness in removing phenol at higher temperatures.
4. Adsorption studies in the column system also showed a significant increase in the adsorption capacity of AC modified with cocamidopropyl betaine as an amphoteric surfactant in comparison with unmodified AC and ACs modified with cationic and anionic surfactants. The AC/CAPB demonstrated good reusability capacity after desorption cycles.
5. This work illustrates that surfactant modification represents a promising strategy toward improving the performance of lignin-derived activated carbons, providing a green approach for wastewater treatment applications while offering new insights into adsorption mechanisms at surfactant-coated interfaces.

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