

Absorption of Phenol and Methylene Blue by Activated Carbon from Pecan Shells¹

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Abstract—Activated carbon is produced from pecan shells by chemical activation using phosphoric acid. This activation is followed by the treatment with sodium dodecyl sulfate to prepare the surface for the adsorption of phenol and methylene blue from aqueous solution. The results showed a great ability for methylene blue removal with sorption capacity of 410 mg/g at pH 9 and solution concentration of 35 mg/L, while moderate adsorption was obtained for phenol with a capacity of 18 mg/g at pH 11 and the same solution concentration. The increase or decrease in solution pH has a favorable effect on the sorption of both adsorbates. Langmuir and Freundlich models were used to fit the experimental data.

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INTRODUCTION

Activated carbon is known to be an effective adsorbent for the removal of solutes from fluids. The choice of this carbon in environmental remediation depends on its surface area, adsorption capacity and non-reactivity with the target solute. Previously, a new active carbon from pecan shell was prepared as an adsorbent for the removal of metal ions, radioactive isotopes and organics from aqueous solutions [1]. This work involved the activation of the pecan shell with phosphoric acid while air is injected during the activation process [2]. Then, several attempts were performed on this carbon either through study of its active surface functional groups, enhancement of the carbon's surface area, or utilization of carbon for the adsorption of different solutes from aqueous solutions.

Toles et al. [3] studied the effect of functional groups on the surface capacity of this carbon. They proved that the wet activation process with air gives the greatest quantity of surface functional groups and the highest metal uptake. Ahmedna et al. [4] compared the properties of activated carbon from pecan shells with those of carbons from rice straw, rice hulls, and sugarcane baagasse and showed that the types of shells and binder, as well as the activation method, determine the properties of the carbon. Dastgheib and Rockstraw [5] studied the functional groups of the activated carbon from pecan shells and proposed that the acidic groups detected using the Boehm titration method not only be considered as oxygen-containing acidic groups, but also as oxygen/phosphorus groups. Ng et al. [6]

reported that steam activation of pecan shells produced carbon which has the potential to replace Filtrasorb 400 in applications involving the removal of geosmin from aqueous media. They developed process flow diagrams for the large-scale production of this carbon derived from steam or phosphoric acid activation and carried out an economic evaluation to estimate the cost of manufacturing these carbons [7].

Although this carbon was extensively studied, there were no attempts to utilize different activation techniques to enhance its capacity and selectivity for target solute(s).

This study is attempted to improve the surface properties of the activated carbon synthesized from pecan shells through the modification with sodium dodecyl sulfate surfactant. The obtained activated carbon will be tested for the removal of phenol and methylene blue (**MB**) from aqueous solutions.

EXPERIMENTAL

Pecan shells were brought from Las Cruces area, New Mexico, USA. Sodium dodecyl sulfate (**SDS**) was provided from Mallinckrodt Co. Methylene blue and phenol were analytical grade supplied by Merck. Hydrochloric, nitric, and *o*-phosphoric acids were analytical grade supplied by Sigma Chemical Company.

The activation procedure was performed by mixing 30 g of powdered pecan shells (the particle size is less than 45 μm) with excess hot *o*-phosphoric acid and boiling over Bunsen burner. Meanwhile, air was injected through the paddles of a glass stirrer into the solution at a flow rate of 1.5 l/min until the mixture

¹ The text was submitted by the authors in English.

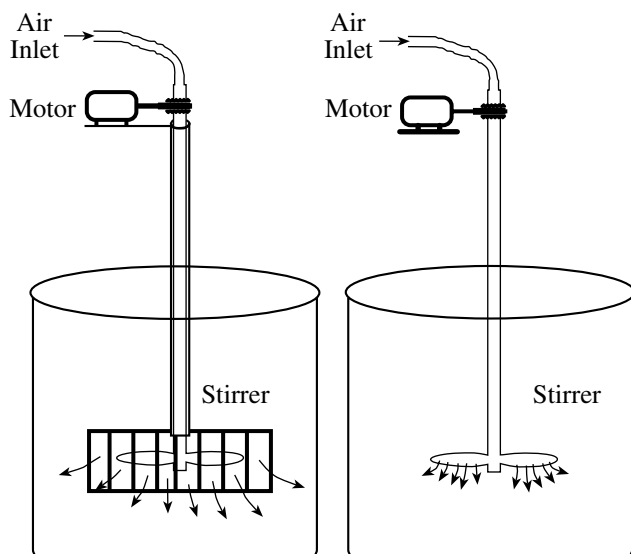


Fig. 1. Schematic diagrams for the reaction apparatus.

becomes solidified, as shown in Fig. 1. At this moment, the temperature of the mixture was equal to 270°C. Then, the activated shells were directly put into cold 0.5 M SDS solution ($4 \pm 1^\circ\text{C}$). The mixture was stirred at 500 rpm for 5 h. Afterward, the modified carbon was filtered, washed with 1 l of deionized water five times, dried at 105°C, and stored in a desiccator for further use.

Adsorption was carried out in a set of Erlenmeyer flasks (250 mL). Solutions of phenol and methylene blue with different initial concentrations were prepared from corresponding fresh stock solutions. These samples were mixed with fixed mass of 0.1 g of the prepared activated carbon and allowed to equilibrate in an isothermal shaker ($22 \pm 1^\circ\text{C}$) for 48 h. Blank samples containing either activated carbon mixed with deionized water or target solute solution alone with different initial concentrations were prepared in a similar manner for comparison. After equilibration, the samples were allowed to settle, then centrifuged and analyzed using a UV-1601 Shimadzu spectrophotometer.

All Pyrex glassware was soaked in 0.1 M solution containing 75 wt % hydrochloric acid and 25 wt % nitric acid, then washed with soap and deionized water to remove any adhered impurities.

THEORY

Several isotherm models can express the variations in the target solute concentration at the surface of adsorbent at equilibrium. The most popular model is the Langmuir model, which relates the rates of adsorption and desorption of a solute at equilibrium by the equation [8]

$$k_{\text{ads}} C_e N (1 - \theta_e) = k_{\text{des}} N \theta_e, \quad (1)$$

where k_{ads} and k_{des} are the rate constants of adsorption and desorption at the surface of the adsorbent, respectively. N is the maximum number of the sites occupied by the solute of interest at the equilibrium solute concentration C_e , and θ_e is the ratio of adsorption capacity at specific solute concentration to its limiting value. The above equation is rearranged to

$$q_e = \frac{K_L Q C_e}{1 + K_L C_e}, \quad (2)$$

where Q is the maximum solute uptake by the adsorbent surface at equilibrium and K_L is the Langmuir constant which represents the ratio of adsorption and desorption rate constants.

On the other hand, the Freundlich model was used (to make allowance for the effect of surface energy heterogeneity) in which the energy term, K_L , in the Langmuir model varies as a function of surface coverage owing to the heat of adsorption [9]. The Freundlich equation has the form

$$q_e = \alpha C_e^\beta, \quad (3)$$

where α and β are constants. The index β is the adsorption intensity and the coefficient α can be related to the surface energy by the proportionality relation

$$\alpha \propto RTnK_L e^{\Delta H/RT}. \quad (4)$$

RESULTS AND DISCUSSION

Chemical activation of pecan shells was carried out in two different stages. The first stage involved the oxidation of the shells with the acid at elevated temperature using a newly developed glass impeller. Two different impellers were used in the activation step in order to obtain the best shear and minimal foam formation. The first one was rounded by four glass windows to allow the slurry pass through during the rotation. Once the carbonaceous slurry gets solidified, the second impeller was used in order to avoid the blockage of impeller windows. The completion of the activation experiment is identified by the transformation of the pasty carbon into dry char.

At the second activation step, the hot solid carbonaceous material was quenched with cold solution of aerated surfactant. Continuous mixing of the mixture was performed in a beaker while air was passed during the mixing process for 2 h.

The use of these new impellers has the advantage that air or water can be injected in the solution continuously while they rotate at high speed.

The produced carbon was analyzed for ash content, moisture content, pH, and density. Table 1 shows the results obtained using the corresponding ASTM methods. It is obvious that the produced carbon has high density and ash content. In comparison with the results

obtained previously [10], the ash content increased from 4 to 13.2 wt % and the pH from 6.5 to 7.5.

Adsorption isotherms of methylene blue and phenol for the produced carbon are shown in Figs. 2 and 3, respectively. These isotherms were measured at different solution pH values ranging from 4 to 11 in order to obtain the maximum uptake for both adsorbates at specific pH values. It was shown that, both at pH values lower and higher than pH 7, the adsorption of methylene blue and phenol increase (Fig. 4). The values of MB uptake obtained at pH 4 and pH 9 were 285 and 410 mg/g, respectively, when the concentration of MB in solution was 35 mg/l. Conversely, the maximum removal for MB obtained at pH 11 and the same solution concentration was 18 mg/g. Higher solution concentration yields larger removal capacity for both adsorbates.

To predict whether the presence of H⁺/OH⁻ has an effect on the stability of the MB in solution, five blank MB solutions were prepared with variable pH values and left to stand for different periods of time. Figure 5 shows the variations in color intensity (concentration) of MB with time. It is clear that there is no change in MB concentration within a period of 48 h during which the adsorption isotherm was measured. After that, the intensity of the MB solution color decreased with time for the samples that had pH values higher than 7, which is associated with either dimerization of MB or its reaction with OH⁻ ions [11].

SDS molecules dissolve the lipophilic part of MB molecule through London interactions with its carbon-chain moiety and, hence, increase the MB uptake by the carbon surface. This was expected as the charged nitrogen in MB molecule may interact with the negative charge of SDS, which may lower the solubility of MB in water. Such interaction depends on the pK_a values of

Table 1. Physical properties of activated carbon prepared from pecan shells

Test type	Standard	AC treated with SDS	AC without treatment with SDS
Ash content, wt. %	D 2866-94	13.2	4
Moisture content, wt. %	D 2867-95	17.8	2
Apparent density, g/L	D 2854-96	490	495
pH	D 3838-80	7.5	6.5

both MB and SDS and the pH of the medium [12, 13]. On the other hand, at pH 7, the lipophilic part of SDS may interact with the uncharged MB and, hence, increase the solubility of MB in solution, which decreases its adsorption at the surface of the carbon.

Adsorption isotherms of phenol show similar trend as in the case of MB (Figs. 6, 7). The amount of phenol uptake is 18 mg/g at pH 11 when the initial solution concentration is 35 mg/l. The carbon capacity decreases to an approximate value of 4 mg/l with decreasing in the pH value to 4 or 8.5 at the same initial solution concentration. This was expected because for phenol, the charged species would be present in the basic medium and the uncharged species exist in the acidic medium depending on the pK_a value. In basic solutions, the phenol is attracted by the surface of carbon, as well as the lipophilic part of SDS molecule. However, in the case of acidic solutions, it is expected that the interaction of SDS with phenol would also increase the phenol uptake by the carbon, because the lipophilic part of SDS may interact with the uncharged

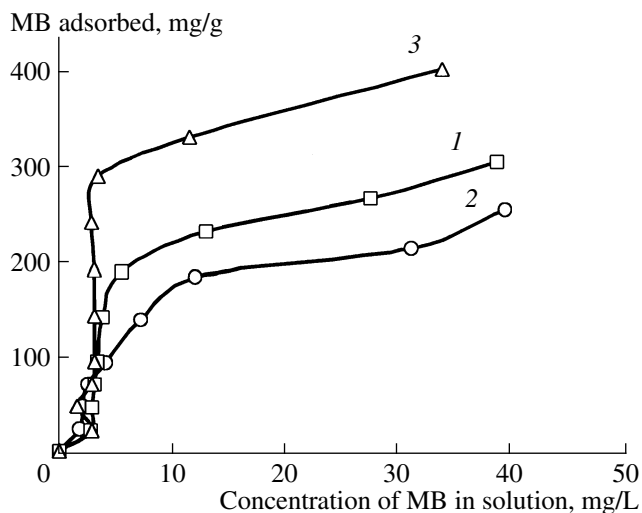


Fig. 2. Isotherms of methylene blue adsorption on the surface of activated carbon for solution pH (1) 4, (2) 7, and (3) 9.

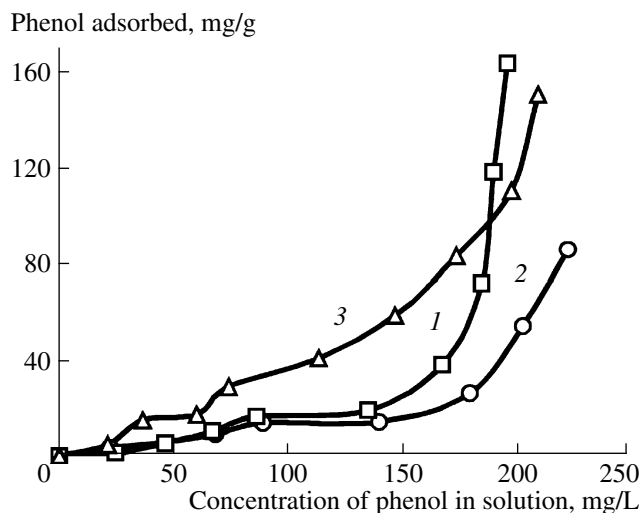


Fig. 3. Isotherms of phenol adsorption on the surface of activated carbon for solution pH (1) 4, (2) 8.5, and (3) 11.

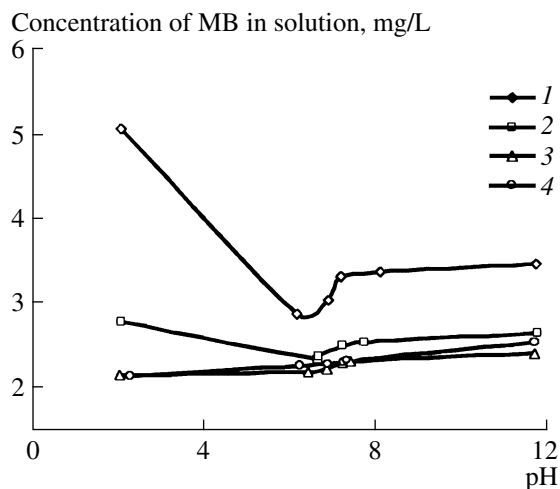


Fig. 4. Effect of solution pH on the adsorption of methylene blue on activated carbon surface. The curves correspond to (1) 1, (2) 2, (3) 5, and (4) 9 days.

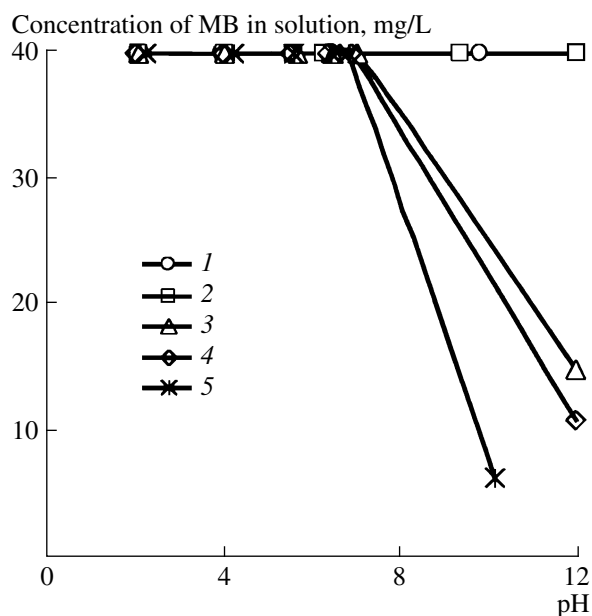


Fig. 5. Effect of solution pH on the change in the color intensity of methylene blue. The curves correspond to (1) 1, (2) 2, (3) 5, (4) 6, and (5) 9 days.

phenol and, hence, increase its interaction with the charged surface of the carbon.

Leng and Pinto [14] found that the uptake of phenol is a combined effect of physisorption and surface polymerization, where the functional groups on the activated carbon take part in both the electrostatic and dispersive interactions. They concluded that the phenol uptake increases upon the removal of the carboxylic functional groups from the carbon surface as a result of decreased competitive adsorption of water molecules on the basal planes of the carbon.

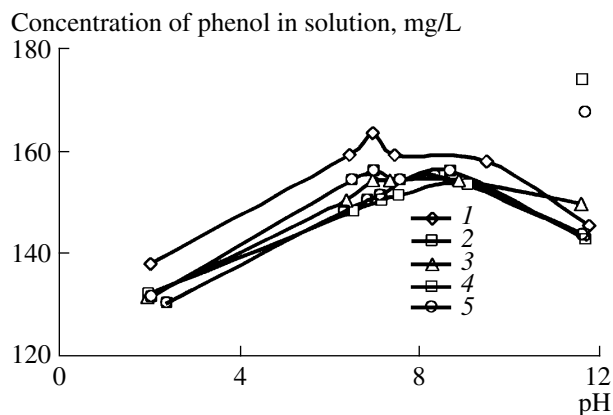


Fig. 6. Effect of solution pH on the adsorption of phenol on activated carbon surface. The curves correspond to (1) 1, (2) 4, (3) 5, (4) 8, and (5) 11 days.

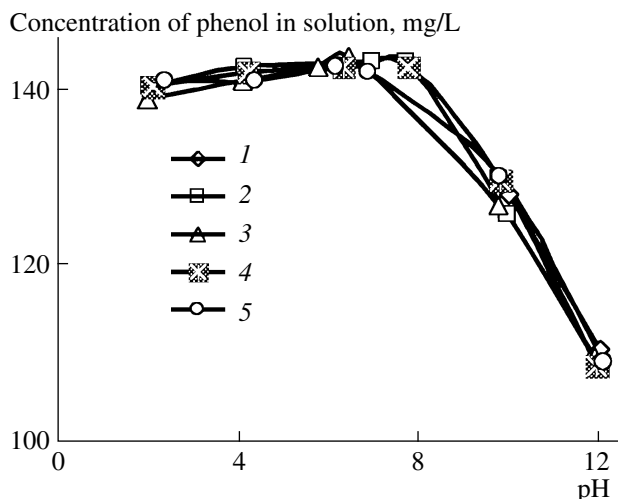


Fig. 7. Effect of solution pH on the change in the color intensity of phenol. The curves correspond to (1) 1, (2) 4, (3) 5, (4) 8, and (5) 11 days.

To model the adsorption data for both phenol and MB, Langmuir and Freundlich equations were tested. It is shown that the Langmuir equation best fits the MB adsorption isotherm obtained at pH 7, with a regression coefficient of 0.975 and $\sum (error)^2 = 1633$. Alternatively, phenol isotherm measured at pH 11 was best fitted by the Freundlich equation with a regression coefficient of 0.964 and $\sum (error)^2$. The corresponding parameters of a model are shown in Tables 2 and 3.

CONCLUSIONS

Activated carbon from pecan shells was treated with anionic surfactant (SDS) in order to enhance its sorp-

Table 2. Isotherm model's parameters and correlation coefficients calculated for the experimental data for methylene blue adsorption at different pH values

Solution pH	Langmuir model				Freundlich model			
	Q	K_L	$\sum(errors)^2$	R^2	α	β	$\sum(errors)^2$	R^2
4	392.2	9.61×10^{-2}	11203	0.895	55.18	48.32×10^{-2}	16075	0.850
7	309.2	10.32×10^{-2}	1633	0.975	46.54	46.69×10^{-2}	4179	0.936
9	516.5	13.28×10^{-2}	55865	0.705	0.214	5.64	36748	0.571

Table 3. Parameters of isotherm model and correlation coefficients calculated for the experimental data for phenol adsorption at different pH values

Solution pH	Langmuir model				Freundlich model			
	Q	K_L	$\sum(errors)^2$	R^2	α	β	$\sum(errors)^2$	R^2
4	20.47×10^4	2.21×10^{-6}	11394	0.576	3.03×10^{-11}	5.54	2435	0.909
8.5	46.84×10^4	5.21×10^{-7}	1777	0.708	1.51×10^{-8}	4.16	311	0.949
11	13.20×10^4	4.02×10^{-6}	2591	0.876	3.47×10^{-3}	1.98	751	0.964

tion capacity for methylene blue and phenol. It was found that this treatment has a positive effect on methylene blue removal but slight effect on phenol. The utilization of pecan shells as a raw material to produce this activated carbon has advantages of low cost, minimum energy requirement, and high carbon selectivity for dyes.

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SPELL: 1. baagasse