COMPARISON OF ACTIVATED CARBON PRODUCED FROM CAROB STONES WITH 4A ZEOLITE FOR ALLURA RED AC DYE ADSORPTION

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Abstract: The objective of the study was to prepare low-cost activated carbon from carob stones (Ceratonia siliqua) and compaire its adsorption behavior for allura red dye with that of a commercial 4A zeolite. The carob stones activated carbon (AC) and commercial 4A zeolite (4AZ) were characterized BET surface area, micropore volume, total pore volume, average pore size. Adsorption of a food dye, allura red, by AC and 4AZ was examined. The experimental adsorption equilibrium data were compared with the Langmuir and Freundlich isotherm models and the isotherm model parameters were determined. Pseudo-first-order and pseudo-second-order equations were fitted to the kinetic data, and the rate constants were evaluated. Results showed that activated carbon produced from carob stones is suitable for the adsorption of allura red food dye and could be used as a low cost effective adsorbent in the treatment of the industrial wastewater.
Keywords: Carob stones, 4A zeolite, activated carbon, allura red, food dye.

Introduction

Activated carbon is one of the widely used adsorbents in removal of food dyes because of its large surface area, pore size distribution and high adsorption capacities. Activated carbon is produced from variety of raw materials such as cherry stones, apricot stones, cornelian cherry stones, olive stones, wood and coal. Activated carbons can be produced by chemical activation. Chemical activation is a single step method for the preparation of raw material in the presence of chemical agent such as KOH, NaOH, LiOH, $ZnCl_2$ and H_3PO_4 (Erdogan 2016; Erdogan and Erdogan 2016). Philip (1996) produced activated carbon from apricot stones by activation with H_3PO_4. The highest spesific surface area and micropore volume and mean pore radius were found as 1603 m^2/g, 0.752 cm^3/g, 9.4 Å, respectively. Erdogan (2016) produced activated carbons from cherry stones by KOH and NaOH treatments. The highest specific surface area and micropore volume were found as 1380 m^2/g and 0.630 cm^3/g, respectively. Li et al. (2008) prepared coconut shell based activated carbons at carbonization temperatures ranging from 400-1000 °C. In their study, BET surface area and micropore volume of the sample obtained were 1926 m^2/g and 0.931 cm^3/g, respectively. Erdogan and Erdogan (2016) prepared activated carbon by chemical treatment (H_3PO_4) from cherry stones for dye adsorption. Zeolites are microporous and crystalline silicates commonly used as adsorbents in various chemical reaction. Dyes are widely used in food, textile paper and cosmetic industries. Allura red belongs to the monoazo class of synthetic food colourants. Chemically it is identified as Red No. 40 and this compound is disodium6-hydroxy-5-(2methoxy-5-methyl-4-sulphophenylazo)-2-naphthalenesulphonate (Sánchez-Duarte et al. 2012). The main objects of this study are: (i) to study the feasibility of using the activated carbons produced from carob stones as a low-cost adsorbent for the removal of allura red dye, (ii) to compare its adsorption behavior for food dye to that of a commercial 4A zeolite (iii) to determine the applicability of various isotherm models (Langmuir and Freundlich) to find out the best-fit isotherm equation and (iv) to determine kinetic parameters and explain the nature of the adsorption.

Materials and Methods

In this study, carob stones were obtained from Antalya in Turkey. The precursor, carob stones were first air dried, then crushed. Then, carob stones were contacted with dilute a 15 vol.% sulfuric acid solution for 12 hours and washed with hot distilled water. 4A zeolite (4AZ) was purchased from Sigma-Aldrich.

Preparation of the activated carbon: 20 g of dried carob stones (<2 mm) was mixed in a beaker with 200 mL of LiOH solution which corresponded to an impregnation ratio of 4:1 (weight of impregnation reagent/weight of carob stones) for 10 hours at 65°C. The mixtures were immersed in the ultrasonic bath for 120 minutes at 65°C and then the impregnated sample was then dried over a night in a moisture oven at 120°C. Then, the impregnated sample was carbonized in a tube furnace (Protherm STF) under N_2 flow at a heating rate of 10°C/min up to 700°C for 1 hour. After the activation, the sample was allowed to cool down to the room temperature under N_2 flow before its removal from the furnace. The activated sample was washed several times with HCl and hot distilled water to remove residual chemicals until it did not give chloride reaction with $AgNO_3$. The activated sample was dried for

6 hours at 120ºC. Activated sample was stored in a sealed flask and labelled. The pores of activated carbon were characterized by analysis of N_2 adsorption–desorption isotherms at 77 K using Micromeritics ASAP 2020 (Erdogan 2018a).

Adsorbate

The commercial food dye FD&C Red 40 ($C_{18}H_{14}N_2O_8S_2Na_2$, molecular weight 496.4 g/mol, C.I. 16045, λmax=500 nm, pKa= 11.4, chemical structure shown in figure 1) was supplied by Sigma-Aldrich. Distilled water was used to prepare all solutions.

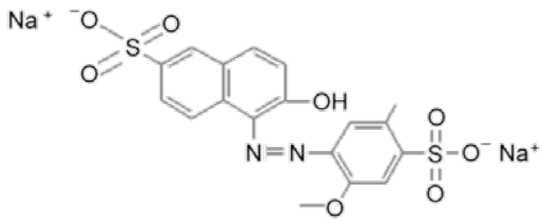

Figure 1. Chemical structure of FD&C Red 40.

Results and Discussion

The N_2 adsorption-desorption isotherms of the activated carbon (AC) is shown in Figure 2. It can be seen that, activated carbon possessed a combination of type I and type IV isotherms according to IUPAC classification. Appearance of hysteresis loop indicates the presence of mesopores.

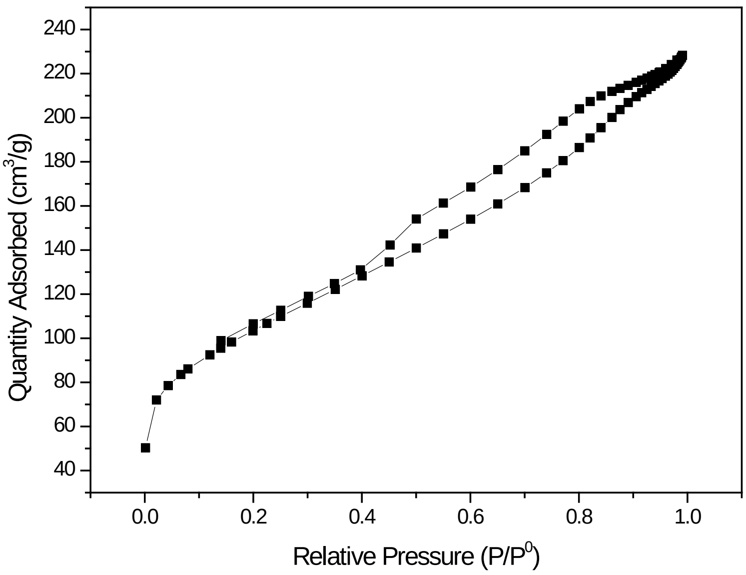

Figure 2. The adsorption-desorption isotherms of activated carbon sample (AC).

Average pore widths and pore volumes were calculated from the nitrogen adsorption isotherm data by t-method analysis. Table 1 gives the values of the BET surface areas, Langmuir surface areas, total pore volumes, micropore volumes and average pore widths which were calculated by using the nitrogen adsorption-desorption data obtained at 77 K. The BET and Langmuir surface areas were found for the AC produced with LiOH activation, as 359.76 and 563.76 m^2/g, respectively. In our previous studies we have reported that the BET surface areas and pore volumes and average pore widths of 4A zeolite (Erdogan 2018b). BET surface area and average pore width of 4AZ adsorbent were found as 18.09 m^2/g and 19.391 nm, respectively.

Table 1: Physical characteristics of the activated carbon sample (AC).

BET surface area (m^2/g)	359.76
Langmuir surface area (m^2/g)	563.76
Total pore volume (cm^3/g)	0.349
Micropore volume (cm^3/g)	0.023
Average Pore Width (nm)	3.880

Allura Red Adsorption:
Figure 3 and 4 present the adsorption isotherms of allura red as the relationship between the amount of dye adsorbed per unit mass of a given porous adsorbents and time. Fig. 3 shows that the adsorption capacities at equilibrium (q_e) decreased with an increase in adsorbent dose from 0.005 to 0.05 g/LThis corroborates the reports of our previous study (Erdogan and Erdogan 2016). Figure 4 showed that the adsorption capacities at equilibrium (q_e) decreased with an increase in adsorbent dose from 0.05 to 0.2 g/L. This is explained as a consequence of partial aggregation, which occurs at high adsorbent amount resulting in decreased active sites. Similar results have been reported for the sorption of various adsorbate onto various adsorbents in literatüre (Erdogan and Erdogan 2016, 2018).

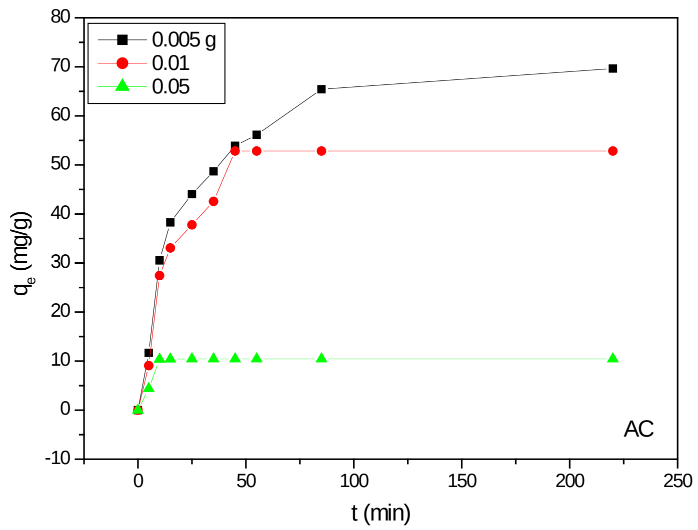

Figure 3. Effects of adsorbent dosage and contact time on the adsorptive uptake of allura red dye onto the carob stones-derived adsorbent (conditions: C_0=20 mg/L; temperature=30 °C).

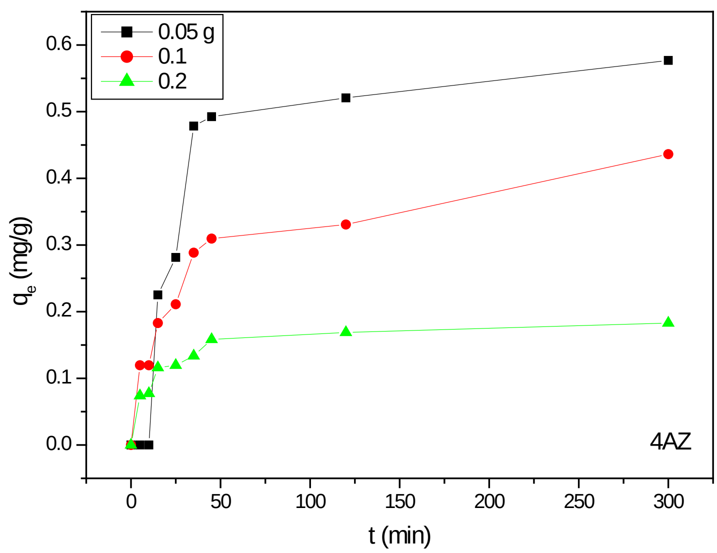

Figure 4. Effects of adsorbent dosage and contact time on the adsorptive uptake of allura red dye onto 4A zeolite adsorbent (conditions: C_0=20 mg/L; temperature=30 °C).

The equilibrium adsorption isotherms are essential to the practical design and optimization of adsorption process. The adsorption isotherm describes how adsorbates interact with adsorbents. The equilibrium data of allura red dye adsorption onto activated carbon and 4A zeolite were explored using the isotherm model of Langmuir and Freundlich. The parameters obtained of the two isotherm models were calculated and represented in Table 2. The correlation coefficients descended in the order of: Langmuir> Freundlich for AC. Langmuir adsorption isotherms constants related to adsorption capacity, Q_0 were found as 94.877 and 0.048 mg/g for AC and 4AZ, respectively. The relatively large adsorption capacity for AC could be attributed to its relatively large surface area (359.76 m^2/g) and total pore volume (0.349 cm^3/g). The results revealed that the adsorption of food dye on carob stones-based activated carbon was best described by the Langmuir isotherm, indicating the adsorption was homogeneous and a monolayer was present.

Table 2: Freundlich and Langmuir isotherm constants for the adsorption allura red onto AC and 4AZ at 30 °C

Isotherms	**Parameters**		
Freundlich	**K_F** $(mg/g)(L/mg)^{1/n}$	**1/n**	**R^2**
AC	32.926	0.321	0.236
4AZ	6.2E-14	10.43	0.066
Langmuir	**Q_0** (mg/g)	**K_L** (L/mg)	**R^2**
AC	94.877	0.421	0.718
4AZ	0.048	0.052	0.023

Langmuir adsorption isotherm constant related to adsorption capacity, Q_0 were found as 94.877 mg/g. To confirm the favorability of the adsorption, the separation factor R_L was calculated by the following equation;

$$R_L = \frac{1}{1 + K_L C_0}$$

where the adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Here, the value of R_L was found to be 0.106 and 0.490 for AC and 4AZ, respectively, which further confirmed that the Langmuir isotherm was favorable for of food dye on two adsorbents.

Adsorption kinetics provides an understanding of the mechanism of adsorption, which in turn governs mass transfer and the equilibrium time. Allura red was adsorbed on adsorbents as a function of time. Pseudo-first-order and pseudo-second-order models have been obtained at the temperatures of 30 °C for the various adsorbent amount (0.005, 0.01 and 0.05 g for AC and 0.05, 0.1 and 0.2 g for 4AZ). The regression coefficients (R^2) were evaluated for all models. The results are shown in Table 3. As shown in Table 3, the highest R^2 values were obtained for the pseudo-second order kinetic model and the experimental q_e values matched well with the calculated data. The higher regression coefficients indicated that the pseudo-second-order model was a better fit than the pseudo-first-order model. Therefore, it can be said that the pseudo-first-order model is not suitable to explain the adsorption process accurately. Similar results have been found for the our previous study (Erdogan and Erdogan 2016).

Table 3: Kinetic model parameters for the adsorption of allura red dye onto AC at different adsorbent dosage.

			Pseudo first order			Pseudo second order		
T(°C)	m_{ads}(g/L)	$q_{e,exp}$(mg/g)	k_1(min^{-1})	$q_{e,cal}$(mg/g)	R^2	k_2(g/mgmin)	$q_{e,cal}$(mg/g)	R^2
30	0.005	69.653	0.0305	60.218	0.977	8.86E-4	74.294	0.990
	0.01	52.838	0.0468	47.913	0.948	1.92E-3	55.928	0.988
	0.05	10.441	0.650	51.395	0.934	0.0858	10.526	0.999

Kinetic parameters for the removal of allura red by 4AZ are represented in Table 4. The results for the 4AZ showed good agreement with the two kinetic models, especially with the pseudo-second order kinetic model except for 0.05 g adsorbent, suggesting the presence of chemisorption for 4AZ.

Table 4: Kinetic model parameters for the adsorption of allura red dye onto 4AZ at different adsorbent dosage.

			Pseudo first order			Pseudo second order		
T(°C)	m_{ads}(g/L)	$q_{e,exp}$(mg/g)	k_1(min)$^{-1}$	$q_{e,cal}$(mg/g)	R^2	k_2(g/mgmin)	$q_{e,cal}$(mg/g)	R^2
30	0.05	0.5769	0.0212	0.4627	0.730	-30.42	1.52E-4	0.086
	0.1	0.4362	0.0421	0.714	0.915	0.106	0.452	0.984
	0.2	0.1829	0.0339	0.163	0.963	0.538	0.188	0.998

Conclusion

The present investigation showed that biowaste carob stones can be effectively used as a raw material for the preparation of activated carbon via chemical activation using LiOH. The BET surface area and total pore volume of produced activated carbon were 359.76 m^2/g and 0.349 cm^3/g, respectively. This activated carbon (AC) and commercial 4A zeolite (4AZ) were used to remove allura red food dye from aqueous solutions at various temperature. In a batch of adsorption studies, the efficiency of allura red dye adsorption by AC or 4AZ increased with adsorbent dosage, but the equilibrium adsorption capacity decreased significantly. Adsorption capacities of allura red dye onto AC and 4AZ were 94.877 and 0.048 mg/g, respectively. The Freundlich and Langmuir isotherm models were used for the mathematical description of the adsorption of allura red dye onto AC or 4AZ at 30 °C and the results suggested that the adsorption equilibrium data fitted well to the Langmuir model for AC. The pseudo-first order and pseudo-second order models were used to analyze the data obtained for allura red dye adsorption onto the prepared activated carbon and 4AZ. The kinetic calculations show that the adsorption followed the pseudo-second order model for AC. This study has revealed that carob stones based activated carbon can be used as a highly efficient and economically viable adsorbent for allura red dye removal from aqueous solutions.

Acknowledgements

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