Disperse orange 30 dye removal with H₂SO₄-functionalized activated carbon: adsorption isotherms and kinetics

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Disperse orange 30 dye (DO-30) is a mono azo dye used for coloring of polyesters, nylon, natural fibres, and acetate in the textile sector. In the physicochemical treatment process known as adsorption, dissolved molecules in contaminated water form a chemical and physical bond with the surface of the adsorbent. Various synthetic and natural materials worked well as adsorbents to remove color from soiled textile effluents.

In the present study, H₂SO₄-functionalized activated carbon was synthesized and used for the adsorption of DO-30 dye from synthetic waste water. The effects of different reaction parameters such as adsorbent dosage, initial DO concentration, contact time and temperature on the adsorption of DO-30 onto activated carbon and H₂SO₄-functionalized activated carbon were investigated. To determine the best adsorption equilibrium and adsorption kinetic data of DO-30 adsorption on activated carbon and H₂SO₄-functionalized activated carbon different models for equilibrium and kinetics were applied.

Keywords: Disperse orange 30 dye; acid-activated carbon; dye removal; adsorption isotherms; kinetic and thermodynamic parameters

INTRODUCTION

As industrialization has increased, environmental contamination has emerged as a global issue. The ecosystem and the public health are seriously threatened by water resource pollution. Because of the different compounds it contains, wastewater produced by residential and commercial operations can have permanent impacts when released into the environment. Due to the high concentration of chemicals and dyestuffs in industrial waste, the textile industry currently contributes significantly to environmental contamination [1]. In terms of their molecular makeup, dyes employed in the textile industry are typically water soluble and resistant to biodegradation. Because of this, it is challenging to eliminate these chemicals using traditional therapy techniques, so additional approaches must be used. Because of their hydrophobic nature, dyes with azo groups, such disperse orange 30 (DO-30), can linger in aqueous conditions for extended periods of time and harm living things [2].

Adsorption techniques are used for eliminating these contaminants because of their ease of use, affordability, and high removal effectiveness.

Activated carbon is a popular adsorbent in adsorption processes because of its large surface area and porous structure, which allow it to bind contaminants to its surface and remove them from water [3]. Activated carbon can be functionalized using chemical techniques to improve its qualities [4]. Functionalization with sulfuric acid (H₂SO₄) by adding acidic functional groups to its surface boosts the adsorption ability of activated carbon. Activated carbon's surface becomes more polar as a result of this process, allowing for stronger interactions with dye molecules through hydrogen bonds and electrostatic forces [1]. When compared to pure activated carbon, studies reveal that H2SO4functionalized activated carbon exhibits superior adsorption capabilities for hydrophobic dyes like disperse orange 30 [4].

This study aimed to compare the efficacy of activated carbon chemically functionalized with H₂SO₄ in the removal of disperse orange 30 dyestuff from aqueous solutions and assess the adsorption performance of activated carbon in this procedure. This was accomplished by conducting adsorption studies with both pure and H₂SO₄-modified activated carbon under various conditions, including

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temperature, initial dye concentration, contact time, and adsorbent dosage (0.1 g and 0.4 g). The study examined how both adsorbents affected the removal of dyestuffs and how the modification method affected the adsorption capacity. Furthermore, the system's applicability for isotherm and kinetic models was assessed in accordance with the experimental data acquired, and conclusions on the adsorption mechanism were drawn.

EXPERIMENTAL

The disperse orange 30 dyestuff (Fig. 1) was supplied by SETAŞ, activated carbon was taken from Fluka. H₂SO₄ was purchased from Sigma-Aldrich. 30 ml of concentrated H₂SO₄ was added to 6 g of powdered pure activated carbon (PAC). The mixture was kept at 600 rpm for 6 h at approximately 80 °C. At the end of the process, the mixture was diluted and washed with distilled water. The mixture was filtered using a Nuche flask under vacuum. The H₂SO₄-functionalized activated carbon (AAC) remaining on the filter paper was kept in an oven at 70 °C for 1 night to dry completely. Sigma brand 3-18K model ultracentrifuge device, Shimadzu UV/VIS 2600 and Daihan scientific multi-heat mixer were used.

Figure 1. Chemical structure of disperse orange 30 dyestuff

Disperse orange 30 dyestuff solutions were prepared successively at concentrations of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg/L with the aim to create calibration curves. To prepare the solutions, distilled water was utilized. The absorbance of the solutions at a wavelength of 450 nm was measured using a Shimadzu UV-Vis instrument. The DO-30 calibration curve is shown in Figure 2.

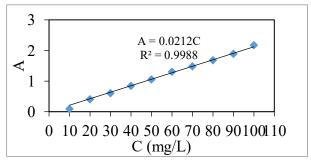


Figure 2. Calibration curve of disperse orange 30 in pure water at different concentrations obtained from absorbance changes at 450 nm wavelength

The equation A=0.0212C was used for the calibration curve. This linear equation's formulation is essential for computing modifications in the experiment's later stages.

RESULTS AND DISCUSSION

The pure activated carbon (PAC) and H₂SO₄-functionalized activated carbon (AAC) were used to remove disperse orange 30 dyestuff from synthetic waste water solutions *via* adsorption process. The parameters such as contact time (10–30-60-90-120-150 min), temperature (25-30-40-50-60 °C), initial dye concentration (50-100-150-200-250-300 mg/L), and adsorbent dosage (0.1 and 0.4 g) were examined.

The percent dye removal (DR, %) of DO was calculated using Eq. 1:

$$\%DR = \frac{(Co - Ce).100}{Co} \tag{1}$$

where Co(mg/L) and Ce(mg/L) are DO-30 dye solution concentrations at the initial and equilibrium stage, respectively.

To determine the optimal adsorption time and adsorbent dosage, 100 mg/L DO solutions at 700 rpm on PAC and AAC adsorbents were measured for 10-30-60-90-120-150 min, 0.1 and 0.4 g adsorbents, respectively. Centrifugation was carried out after sample collection, and absorbance measurements were taken to ascertain the removal effectiveness. *Ce* values were calculated from the calibration curve according to their absorbance at 450 nm, and dye removal percent (DR, %) of PAC and AAC adsorbents was calculated according to Eq. 1 and the results are given in Table 1.

Table 1. Contact time and adsorbent dosage of DO-30 dye removal with PAC and AAC adsorbents as 0.1 and 0.4 g.

	P	AC	AAC			
t (min)	A	Ce (mg/L)	DR (%)	A	Ce (mg/L)	DR (%)
10	0.94	44.37	55.63	0.74	34.80	65.19
10*	0.36	16.85	83.15	0.41	19.24	80.76
30	0.96	45.21	54.79	0.75	35.46	64.54
30*	0.35	16.55	83.44	0.39	18.70	81.29
60	0.99	46.73	53.26	0.86	40.35	59.65
60*	0.44	20.85	81.58	0.38	18.07	81.93
90	1.12	53.03	46.97	0.89	42.32	57.68
90*	0.44	20.85	79.15	0.39	18.83	81.17
120	1.00	47.18	52.82	0.92	43.43	56.57
120*	0.49	23.33	76.67	0.39	18.46	81.54
150	0.98	46.59	53.41	0.98	46.29	53.71
150*	0.52	24.47	75.53	0.38	18.06	81.94

*0.4 g adsorbent results

As the adsorbent amount and the contact time increased, the removal of DO-30 dye increased as well.

The temperature effect on DO-30 dye removal from synthetic waste water was examined on 0.1 and 0.4 g of PAC and AAC adsorbents with 10, 60 and 90 min at 25, 30, 40, 50 and 60 °C. The highest DO-30 dye removal results were obtained with 0.4 g adsorbent at 90 min and are given in Table 2.

Table 2. Temperature effect on DO-30 dye (100 mg/L) removal with 0.4 g of PAC and AAC adsorbents for 60 and 90 min

PAC				AAC		
T (°C)	A	C _e (mg/L	DR (%)	A (1	C _e mg/L)	DR (%)
25	0.56	26.34	73.66	0.72	34.18	65.82
25*	0.58	27.39	72.61	0.54	25.34	74.66
30	0.46	21.77	78.23	0.89	41.84	58.16
30*	0.50	23.71	76.29	0.55	25.79	74.21
40	0.53	24.90	75.09	0.75	35.55	64.45
40*	0.54	25.61	74.39	0.47	22.02	77.98
50	0.31	14.82	85.18	0.63	29.49	70.51
50*	0.37	17.38	82.62	0.42	19.62	80.38
60	0.14	6.47	93.53	0.39	18.43	81.57
60*	0.10	4.72	95.28	0.12	5.45	94.55

^{*}These results refer to 90 min.

The highest DO-30 dye removal was 95% obtained with 0.4 g adsorbent at 90 min with increasing temperature at 60 °C.

Adsorption isotherms are crucial for maximizing the utilization of any adsorbent because they explain how the adsorbate and adsorbent interact. The stability of the contacts between the adsorbent and the adsorbate, as well as the adsorption affinity of molecules, are revealed by the shape of the isotherm. Adsorption isotherms can be expressed mathematically in a variety of ways; some are empirical and require the correlation of experimental data, while others are based on a simplified physical description of adsorption [5].

In this study, the Freundlich and Temkin adsorption isotherms were applied for DO-30 adsorption on 0.4 g of PAC and AAC for 90 min at room temperature for 50, 100, 150, 200, 250 and 300 mg/L DO-30 initial concentrations. The Temkin isotherm states that because of interactions between the adsorbent and adsorbate, the heat of sorption should decrease linearly with sorption coverage on the adsorbent [6, 7].

The linear q_e vs lnC_e plot was created for the Temkin adsorption isotherm, and the slope and intersection point of this linear plot were used to determine the Temkin adsorption isotherm parameters, lnA and b, respectively. For Freundlich

adsorption isotherm, the linear log qe vs log Ce plot was drawn and the kinetic parameters, n and K_F , were obtained from the slope and the intersection point of this linear plot, respectively. The results are displayed in Table 3. Figures 3 and 4 show the Temkin isotherms for PAC and AAC, respectively. The Freundlich isotherms for PAC and AAC are given in Figs. 5 and 6.

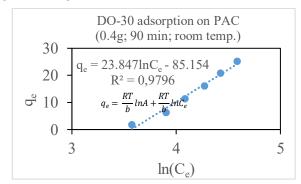


Figure 3. Temkin adsorption isotherm: DO-30 dye adsorption on PAC

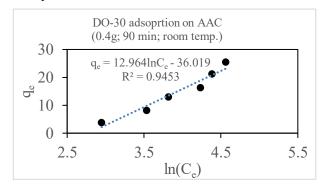


Figure 4. Temkin adsorption isotherm:DO-30 dye adsorption on AAC

It was found that the experimental adsorption data of DO-30 dye adsorption suited the Freundlich and Temkin isotherm models well based on the regression coefficients of these two isotherms (Table 3).

The rate at which a sorbate is retained or released from an aqueous solution to a solid-phase interface is referred to as adsorption kinetics. The pseudofirst, pseudo-second order and Webber-Morris intraparticle diffusion models (WM-ID) kinetic analysis was applied to determine the kinetics of DO-30 adsorption from synthetic waste water solutions by 0.4 g PAC and AAC adsorbents between 20 to 160 min time period and the results are given in Table 4.

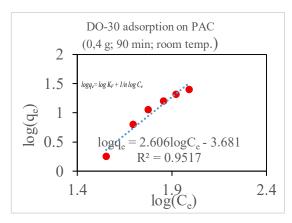


Figure 5. Freundlich adsorption isotherm: DO-30 dye adsorption on PAC

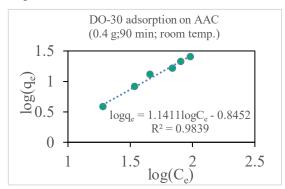


Figure 6. Freundlich adsorption isotherm:DO-30 dye adsorption on AAC

Table 3. Parameter values of the adsorption models for DO-30 adsorption on PAC and AAC adsorbents

Isotherm		PAC	AAC
Freundlich	$\begin{array}{c} logK_F \\ (L.mg^{-1}) \end{array}$	-3.68	-0.84
	n	0.38	0.88
	\mathbb{R}^2	0.95	0.98
Temkin	lnA	-3.57	-2.78
	В	103.9	191.1
	\mathbb{R}^2	0.98	0.95

Table 4. Adsorption kinetic parameters: k_1 (min⁻¹), k_2 (g.mg⁻¹. min⁻¹) and k_3 (mg.g⁻¹. min^{-1/2}), C, R² for DO-30 adsorption on 0.4 g PAC and AAC adsorbents

Kinetic model Parameters PAC			AAC	
Pseudo 1st	k_1	4.10-5	3.10-6	
	\mathbb{R}^2	0.9655	0.4346	
Pseudo	$rac{k_2}{R^2}$	0.035	0.44	
2^{nd}	\mathbb{R}^2	0.999	1	
WM ID	k_3	7.75	41.86	
	C	85.657	79.812	
	\mathbb{R}^2	0.898	0.4952	_

As shown in Table 4, the correlation coefficient of determination of the pseudo-second-order kinetic model exceeded 0.99 and 1 for PAC and AAC. These results indicated that the pseudo-second-order model was more suitable for the adsorption of DO-30 dye onto the PAC and AAC adsorbents.

DO-3 dye adsorption thermodynamic investigation on 0.4 g PAC and AAC adsorbents at 25, 30, 40, 50, 60 °C temperatures at 10, 50 and 90 tim were done and adsorption free energy, adsorption enthalpy and adsorption entropy were calculated. The results are given in Table 5.

adsorption process's viability spontaneous nature without the requirement for an external energy source were demonstrated by the negative ΔG factor. The study's negative ΔG values (Table 4) demonstrated that the adsorption process that eliminated DO-30 happened on its own without the assistance of an outside energy source. The endothermic nature of the process is suggested by the positive values of ΔH° , which also show that the amount adsorbed at equilibrium increases as the temperature rises. When DO-30 dye is adsorbed onto PAC and AAC adsorbents, the solid-solution interface becomes more random, as indicated by the positive values of ΔS° .

Table 5. Thermodynamic parameters in the adsorption of DO-30 on the PAC and AAC adsorbents

PAC				AAC			
t (min)	-ΔG ^{o*} (J/mol)	ΔH° (J/mol)	ΔS° (J/molK)	-ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/molK)	
10	2468.34	3389.04	20.73	2238.73	6574.05	29.07	
60	2548.15	34542.18	123.21	1624.01	21141.67	73.99	
90	2415.43	22611.59	83.41	2677.71	36264.01	128.43	

^{*} ΔG^{o} values refer to 298 K.

CONCLUSION

Acid functionalized and pure activated carbon have been used to produce low-cost adsorbents to remove DO-30 from an aqueous solution. The highest DO-30 dye removal results were obtained as 0.4 g adsorbent at 60 °C during 90 min. The plot of the adsorption isotherms showed that the Temkin model better represents the adsorption of DO-30 on PAC, and Freundlich model - for the AAC adsorbent. The kinetic studies proved that the adsorption of DO-30 on PAC and AAC adsorbents fitted the pseudo-second-order kinetic model with good correlation and this process was spontaneous endothermic according to thermodynamic parameters.

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