Treatment of lab-scale factory wastewater including disperse orange 30 dye with low cost H₂SO₄-activated rubber particle adsorbent obtained from waste tyre

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In this study, disperse orange 30 dye (DO-30) was removed from a liquid solution using cheap adsorbents made from rubber particles obtained from scrap waste tyre (WTRP) and H₂SO₄-activated rubber particles obtained from waste scrap tyre (AF-WTRP) *via* adsorption process. Adsorption isotherms and adsorption kinetics of DO-30 dye removal from synthetic wastewater by adsorption technique were investigated by changing the adsorbent dosage, contact time, dye concentration and temperature. The DO-30 dye removal from labscale factory waste water was investigated according to optimization results of synthetic waste water.

Keywords: H₂SO₄-activated rubber particles obtained from scrap waste tyre; disperse orange 30 dye; dye removal; adsorption kinetics and adsorption isotherms

INTRODUCTION

For many years, water pollution caused by textile industry dyeing processes has been one of the environmental problems. The textile industry's effluent is generally dense in mordants, surfactants, and inorganic dyes. Some textile dyes that are released into water have a severe impact on aquatic life because they are poisonous and carcinogenic. Disperse orange 30 is an azo dye that is highly soluble in organic solvents. DO-30 is used for dyeing synthetic textiles like polyester, nylon, and acrylic. Its azo structure can degrade into hazardous compounds throughout the dyeing and wastewater treatment processes [1]. These contaminants can be removed from water using physical, chemical, and biological treatments. Each approach has limits; thus, treatment processes can be combined based on the content and density of pollutant chemicals. [2] Treatment by physical methods maintains its place as a frequently preferred method from past to present with the advantage of minimum need for chemical substances in the removal process. Its simplicity, flexibility, high efficiency and the ability to recycle pollutants are among the advantages that increase its uptake [3]. Adsorption which is a surface-based process in which charged ions or molecules are attracted to the adsorbent's solid surface and adsorbed there, has recently emerged as one of the most common physical dye removal procedures [4].

In this research, DO-30 dye was removed from synthetic and labscale factory waste water solutions *via* adsorption on acid-functionalized and non acid-functionalized waste scrap tyre rubber particles. And also, to understand the adsorption process of DO-30 dye removal from waste water *via* WTRP and AF-WTRP adsorbents, the adsorption kinetics for the rate of solute adsorption and the duration of adsorbate residence at the solid-liquid interface and isotherms for figuring out how the adsorbent and adsorbate interact, as well as the adsorbent's ideal adsorption capacity, were investigated.

EXPERIMENTAL

The dispersed orange 30 dye which is (4-((2,6-dichloro-4-nitrophenyl)azo)-N-(cyanoethyl)-N-(acetoxyethyl)) (Fig. 1), has a chemical formula of C₁₉H₁₇Cl₂N₅O₄, with molecular weight of 450.27 g/mol is provided as solid form by the SETAŞ Company, H₂SO₄ is supplied by Sigma-Aldrich. The used devices in the experiments were Sigma brand 3-18K model ultracentrifuge device, UV-2600 Shimadzu UV/Vis spectrophotometer and Daihan Scientific multi-heat mixer.

Submicron particle size rubber particles ($<300~\mu$) obtained from scrap waste tyres were used successfully for methyl violet dye removal from synthetic waste water [5]. 12 g of rubber powder was mixed with 60 ml of H₂SO at 1000 rpm. The acid-functionalized rubber powder was separated using a pressurized filtration technique. It was left to dry in

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a 70 °C oven for 24 h. During the experiment, both rubber powder and rubber powder functionalized with sulfuric acid (H₂SO₄) were used as adsorbents to remove dispersed orange dye 30 from synthetic and labscale factory waste water solutions.

The calibration curve was drawn between 10 mg/L and 100 mg/L DO-30 solution concentration absorbances. The obtained calibration equation is given in Figure 1 with chemical formula of DO-30 dye and UV absorbances of solutions at 450 nm.

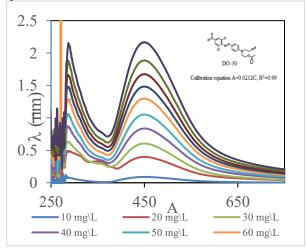


Figure 1. UV spectra of DO-30 dye solutions at different concentrations

RESULTS AND DISCUSSION

The DO-30 dye adsorption activation time on WTRP and AF-WTRP adsorbents was determined 0.4 g adsorbent 100 mg/L DO-30 solution in 10, 30, 60, 90, 120 and 150 min at room temperature. The adsorption spectra of the solutions were obtained with a UV-VIS spectrophotometer after adsorption activation time passed, the solutions were centrifuged for 10 min, the solution concentrations at equilibrium, *Ce* were calculated from the calibration curve according to their absorbance at 450 nm, and dye removal yield percentages (RY%) of WTRP and AF-WTRP adsorbents were given at Table 1.

Table 1 Adsorption activation time effect on DO-30 removal yield with WTRP and AF-WTRP adsorbents

WTRP				AF-WTRP			
t		C_{e}	RY		Ce	RY	
(min)	Α	(mg/	(%)	A	(mg/	(%)	
		L)			L)		
10	0.48	22.60	77.40	0.39	18.62	81.38	
30	0.50	23.59	76.41	0.39	18.26	81.74	
60	0.61	28.64	71.36	0.39	18.56	81.44	
90	0.51	24.09	75.91	0.36	16.98	83.02	
120	0.56	26.40	73.60	0.35	16.67	83.33	
150	0.54	25.60	74.40	0.51	23.92	76.08	

The best DO-30 dye removal yield was obtained with AF-WTRP due to the acidic functions of the adsorbent. The activation time increase did not affect the dye removal yield of DO-30 with WTRP and AF-WTRP according to Table 1.

The temperature effect on dye removal percent of WTRP and AF-WTRP adsorbents was studied in the temperature range of 25-30-40-50-60 °C in a 100 mg/L DO-30 solution for 90 min.

Table 2. Temperature effect on the adsorption of DO-30 on WTRP and AA-WTRP adsorbent

WTRP				AF-WTRP		
T		C_{e}	RY		Ce	RY
(°C)	A	(mg/L)	(%)	A	(mg/L)	(%)
25	0.66	31.10	68.90	0.59	27.77	72.23
30	0.67	31.76	68.24	0.69	32.61	67.39
40	0.58	27.52	72.48	0.61	28.56	71.44
50	0.69	32.50	67.50	0.62	29.33	70.67
60	0.38	17.92	82.08	0.33	15.68	84.32

The temperature affected the adsorption of DO-30 dye on WTRP and AF-WTRP adsorbents. It is seen from Table 2 that the dye removal yield increased from 60 % to 80 % with increasing temperature.

Adsorption isotherms such as Freundlich [6] and Temkin [7] were applied for the adsorption of DO-30 dye on WTRP and AF-WTRP adsorbents with 0.4 g adsorbents at room temperature for 10 min and intial DO-30 dye concentrations as 50-100-150-200-250-300 mg/L. The results are given in Table 3.

Table 3. Concentration effect on the adsorption of DO-30 on WTRP and AF-WTRP

WTRP				AF-WTRP		
C_{DO}	A	C_{e}	RY	Α	Ce	RY
(mg/L)		(mg/L)	(%)		(mg/L)	(%)
50	0.58	27.33	45.34	0.64	30.32	39.35
100	0.94	44.41	55.59	1.08	51.03	48.97
150	1.27	59.75	60.17	1.46	69.03	53.98
200	1.63	77.05	61.47	1.81	85.19	57.40
250	1.93	90.90	63.64	2.12	100.21	59.92
300	2.28	107.44	64.19	2.58	121.86	59.38

The Freundlich adsorption isotherm of $logQ_e$ and $logC_e$ was plotted and Temkin adsorption isotherm was plotted linear q_e versus lnC_e adsorption of DO-30 with WTRP and AF-WTRP adsorbents. The adsorption isotherms were given in Figs. 2 and 3 for DO-30 dye adsorption during 10 min at room temperature with WTRP and AF-WTRP, respectively.

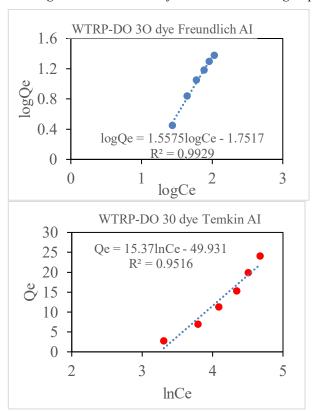


Figure 2. Freundlich and Temkin adsorption sotherms of DO 30 dye on WTRP

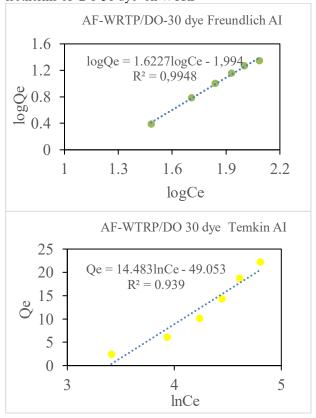


Figure 3. Freundlich and Temkin adsoprtion sotherms of DO-30 dye adsorption on AF-WTRP

The regression coefficients of Freundlich and Temkin adsorption isotherms of DO-30 dye adsorption on WTRP and AF-WTRP adsorbents were determined about 0.99 and 0.94, respectively. The experimental adsorption data fit well the Freundlich isotherm model for adsorbents because of the higher correlation value than Temkin isotherms.

Adsorption kinetics is the study of the amount of adsorbate adsorbed with time, which provides information regarding adsorption speed, mechanism, and adsorbent quality. The pseudo-first [8], pseudo-second order [9], and Webber-Morris intraparticle diffusion models (W-M ID) [10] were applied and detailed results are given in the thesis [11].

The highest correlation coefficients were obtained for pseudo second order for DO-30 dye adsorption with WTRP and AF-WTRP and the second order kinetic model graphics for DO-30 dye adsorption on WTRP and AF-WTRP adsorbents are given in Figure 4.

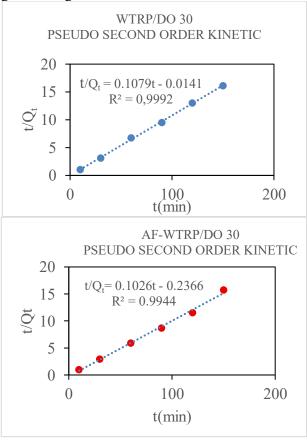


Figure 4. Pseudo second order adsorption kinetic model for DO-30 dye adsorption on WTRP and AF-WTRP adsorbents

Labscale factory waste water was supplied by SETAŞ company. The fabric was dyed in dye bath including DO-30 dye, 0.5 g/L Setalan BKF (egalizator), and Setacid PBS to adjust pH 4 and obtained labscale factory waste water solution was diluted as 10 mg/L (Fig. 5).

S. Karagöz et al.: Treatment of wastewater including disperse orange 30 dye with H2SO4-activated rubber adsorbent...



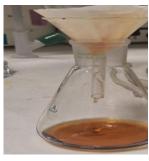


Figure 5 The DO-30 dyed fabric and waste water including DO-30 dye and other dye bath stuffs

The dye removal from 10 mg/L labscale waste water was carried out on 1 g WTRP and AF-WTRP adsorbents. The dye removal yields were obtained as 2.08% with WTRP and 11.31% with AF-WTRP. It was seen that the acid functionalization had positive effect to remove the DO-30 dye with WTRP.

CONCLUSION

In this study, acid-functionalized and non-acid functionalized waste scrap tyre rubber powder adsorbents were used to remove dye from synthetic and labscale waste water solutions. According to the obtained optimization results, dye removal yield of adsorbents was not significantly affected by increasing time due to the active pores adsorbing quickly DO-30 dye and the maximum dye removal yield was obtained at 10 min as 77 % for WTRP and at 90 min as 83 for AF-WTRP. The increasing temperature did significantly affect the removal of DO-30 dye from waste water with WTRP and AF-WTRP from 60 % at 25 °C to 80 % at 60 °C. The adsorption process of DO-30 dye with WTRP and AF-WTRP adsorbents was determined as the Freundlich adsorption isotherm and pseudo-secondorder kinetic model due to the highest regression coefficients.

It was concluded that even 1 g WTRP and AF-WTRP adsorbent was effective to remove DO-30 dye from factory waste water. Hence, WTRP and AF-WTRP adsorbents can be used as cost effective alternative adsorbents for textile companies to remove dye stuffs from waste waters.

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