Specific features of adsorption of azo dyes on fly ash

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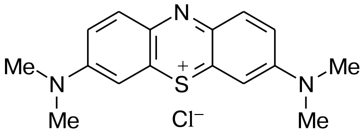
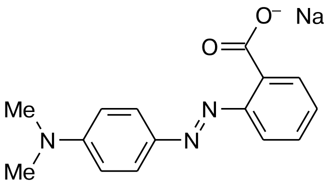
A possibility to utilize fly ash (FA) formed at coal-fired power plants as a cheap adsorbent for the purification of wastewater containing azo dyes methylene blue (MB) and methyl red (MR) was considered. The effect of an FA additive on the adsorption capacity of active carbon was studied. The efficiency of FA as an adsorbent for the purification of aqueous solutions from MB and MR was shown. The adsorption is also fairly efficient when active carbon is partially replaced by FA.

Key words: adsorption, azo dyes, fly ash, X-ray diffraction analysis, wastewater.

Over 700 000 tons of dyes are produced annually worldwide.[1] Acidic, basic, neutral, disperse, direct, reactive, and azo dyes are distinguished among different classes of dyes.[2]. The syntheses of azo dyes are versatile and easy and, therefore, their fraction among synthetic dyes presently exceeds 90%. However, many azo dyes are toxic, potentially carcinogenic, and capable of causing genetic mutations.[3] Approximately 15% of the total worldwide dye production are lost in wastewater during synthesis or processing. Therefore, a decrease in the dye concentration in industrial wastewater to appropriate values is an urgent task all over the world.[4] Methylene blue (MB) and methyl red (MR) are industrial non-biodegradable azo compounds used as paper, textile, and leather dyes and acid-base indicators.



Methylene blue



Methyl red

A simple and efficient method of adsorption by active carbon (AC) is often used for water purification from detrimental impurities. However, high cost of AC and difficulties related to the regeneration and disposal of the adsorbent restrict the application of the adsorption method.[5]

In the recent years, solid industrial wastes of some industrial branches were attempted to utilize for the purification of wastewater from other industrial enterprises. Fly ash (FA) is a product of combustion of coal formed at coal-fired plants. One coal-fired plant with a productivity of 100 MW annually forms about 5660 tons of FA.[6] One of the most efficient methods for FA utilization can be the production of a cheap adsorbent for gaseous outburst and wastewater treatment at various industrial enterprises.[5,7—14]

Fly ash consists mainly of silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) and contains different amounts of carbon, calcium oxide, magnesium oxide, and sulfur. The minerals in coal are fused during combustion and transformed into amorphous solids, which are removed with exhaust gases in the form of suspensions. The amorphous component of FA has a porous structure with nonequilibrated charges formed upon chemical bond cleavage on the surface of ash particles. Thus, fly ash is a tuff-like material (pozzolan) and an efficient adsorbent. The chemical properties of the FA components depend, to a great extent, on the chemical composition of the initial coal.[15,16] It has been shown in many works that FA is an efficient adsorbent for dye removal. However, few investigations have compared the adsorption properties of FA and commercial AC under the same conditions.[17]

The utilization of waste FA represents a great challenge for Turkey.[18,19] At the same time, dyes are produced in Turkey in large amounts.[20] Therefore, contamination control of wastewater formed upon dye production is a very important problem.

The purpose of this study is to investigate the possibility of utilizing FA as a cheap adsorbent for the treatment

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of wastewater containing azo dyes MB and MR. It was also of interest to study the effect of an FA additive on the adsorption capacity of AC.

Experimental

Samples of FA were supplied by the Yatagan coal-fired power plant in the Mugla province (Turkey). Commercial AC samples were available from Merck (Darmstadt, Germany). Adsorbents were dried at 378 K for 1 h, kept in a desiccator, and then mixed with dye solutions. The types of adsorbents used are presented in Table 1.

The following dyes were used to prepare adsorbates: MB (3,7-bis(dimethylamino)phenothiazinium chloride, $C_{16}H_{18}ClN_3S \cdot 3H_2O$, 373.91 g mol^{-1}, m.p. 453 K, solubility in water 50 g L^{-1}, pH 3) and MR (2-[(4 dimethylamino)phenylazo]benzoic acid sodium salt, $C_{15}H_{14}N_3NaO_2$, 291.29 g mol^{-1}, m.p. 448 K, solubility in water 800 g L^{-1}, pH 4.4—6.0) (Merck).

Six solutions of MB in distilled water with concentrations of 0.05, 0.10, 0.20, 0.30, 0.60, and 1.00 mg L^{-1} and six solutions of MR in distilled water with concentrations of 10.00, 15.00, 20.00, 25.00, 30.00, and 40.00 mg L^{-1} were used as adsorbates. Concentration intervals of solutions of MB (0.05—1.00 mg L^{-1}) and MR (10.00—40.00 mg L^{-1}) differ noticeably, which allows one to study the behavior of the adsorbents during adsorption at different concentrations. The contents of MB and MR in solutions before and after adsorption were measured spectrophotometrically using a PG T80 UV-Visible double beam spectrophotometer at 663 and 430 nm, respectively. The initial and final concentrations of the adsorbates were determined from the calibration curves of the transmittance *vs.* concentration plotted for standard solutions of MB and MR with concentrations of 0.01—1.00 and 0.01—40.00 mg L^{-1}, respectively.

In each series of experiments, a weighed sample of the adsorbent and an adsorbate solution (20 mL) with a known concentration were placed in a 50-mL colored-glass bottle with a sealing plug at ~20 °C. The pH values of solutions of MB and MR were maintained constant: 3.0 and 4.4, respectively. In all experiments, ash samples were used after sieving through a 0.710-mm mesh. Adsorbate—adsorbent mixtures were thoroughly stirred (300 rpm) for 15 min. Then the samples were left in the dark for 1 h to complete the adsorption process. Control samples were prepared in the same way but without adsorbent addition.

It has previously[21] been shown that on contact of solutions with the adsorbents prepared from FA the optimum absorption of the adsorbate was achieved within 30—40 min. Based on this, adsorption experiments were continued for 1 h, and spectrophotometric analysis of all samples was carried out in 1 h after the onset of the adsorption process.

Table 1. Used adsorbents and their content in 1 L of the solution (*m*)

Adsorbent	Sample	*m*/g
Yatagan fly ash (FA)	FA-1	5.0
	FA-2	15.0
Yatagan fly ash + active carbon (YFA)	YFA-1	2.5 (FA) + 2.5 (AC)
	YFA-2	10.0 (FA) + 5.0 (AC)
Active carbon (AC)	AC-1	5.0
	AC-2	15.0

Results and Discussion

Dry sieve analysis of the original ash sample showed that all particles were ≤2.00 mm in size. The hydrometrically determined particle size distribution below 2.00 mm shows that 21, 50, and 93% fall per fractions of particles 25, 31, and 150 μm, respectively. The maximum and average sizes are 282 and 55 μm. Thus, the particle size is small, and the ash material can be used in adsorption without grinding into finer particles.

X-ray diffraction of ash samples before and after MR adsorption. The X-ray diffraction pattern of the initial ash exhibits a series of intense diffraction peaks, revealing the presence of the following phases: quartz (SiO_2), cristobalite (SiO_2), anorthite ($CaAl_2Si_2O_8$), albite ($NaAlSi_3O_8$), anhydrite ($CaSO_4$), lime (CaO), and hematite (Fe_2O_3).[22]. The mineral composition is characteristic of the high-calcium FA obtained from lignite coal combustion.[23]

The X-ray diffraction pattern also shows a pronounced broad peak at 2θ = 17—48°, which can be attributed to diffuse scattering of X-rays by amorphous silica. Similar features were reported in other works.[15,24]

Comparison of three most strong lines in the X-ray diffraction patterns of the samples before and after adsorption shows that after adsorption the anhydrite and calcium oxide phases virtually disappear. These changes can be explained by the hydration of $CaSO_4$ and CaO that occurs on contact of the ash with water during adsorption

$$CaSO_4 + 2\,H_2O \longrightarrow CaSO_4 \cdot 2H_2O, \qquad (1)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2. \qquad (2)$$

Then $Ca(OH)_2$ can react with silica or alumina

$$Ca^{2+}{}_{aq} + 2\,OH^-{}_{aq} + SiO_2 \longrightarrow Ca(OH)_2 \cdot SiO_2 \cdot H_2O, \qquad (3)$$

$$Ca^{2+}{}_{aq} + 2\,OH^-{}_{aq} + Al_2O_3 \longrightarrow Ca(OH)_2 \cdot Al_2O_3 \cdot H_2O. \qquad (4)$$

The formation of calcium silicate and calcium aluminate hydrogels improves the adsorption capacity of FA.

Adsorption and adsorption isotherms from solution. The curves of adsorption isotherms were obtained by plotting the dependences of the amount adsorbed on the MB or MR concentration in the initial solution (mol L^{-1}). The amount adsorbed is measured in moles of adsorbate per gram of adsorbent ($n_0\Delta x_1/m$). Here n_0 is the total number of dye moles in the initial solution, Δx_1 is the change in the molar fraction of the dye in solution during adsorption, and m is the weight of the adsorbent.[25] The steep rise of the isotherm of FA (Fig. 1) characteristic of the ad-

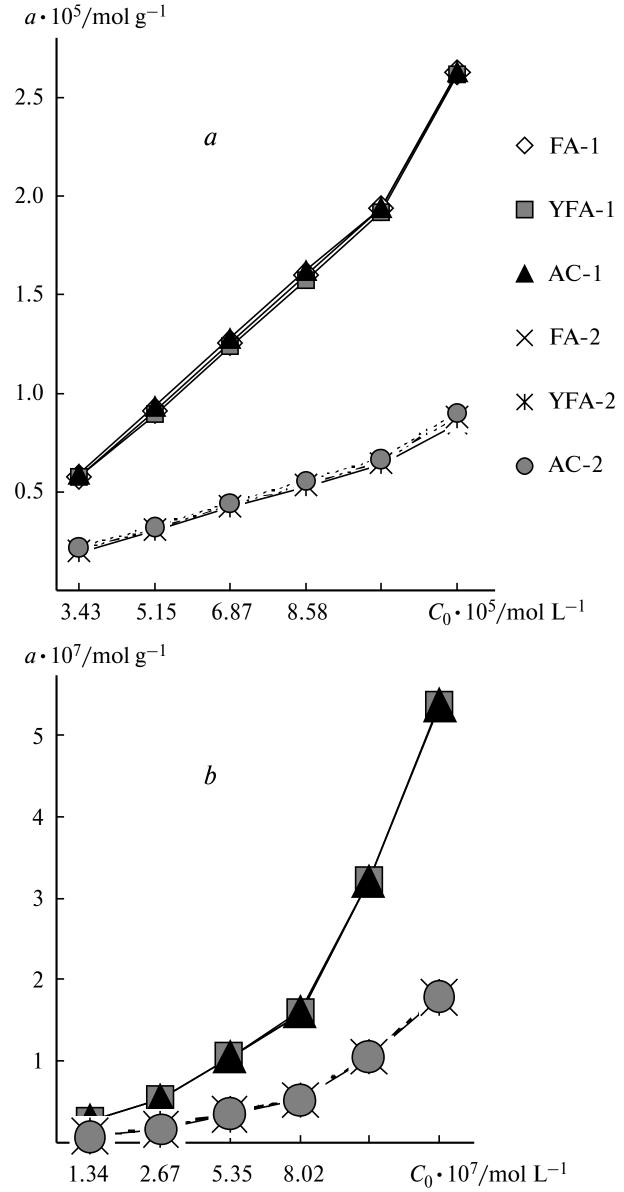

Fig. 1. Adsorption isotherms from solutions of MR (*a*) and MB (*b*) in the logarithmic scale.

sorption of substances with high affinity of the adsorbent indicates that water in a dilute solution does not compete with the dye for sites on the adsorbent surface.[26] The smooth (without sharp inflections) shape of the isotherms suggests that a monolayer coating is formed on the adsorbent surface, which is caused, most likely, by the strong attraction of dye molecules to the adsorbent surface. It is clearly seen that the amount of the adsorbed substance increases with an increase in the dye concentration in the initial solution.

The amount of the adsorbent used affects the removal of MB and MR from the solution. To study this dependence, we performed a series of experiments in which the content (m) of the adsorbent was 5.0 or 15.0 g in 1 L of the adsorbate. Adsorption on the samples with m = 5.0 g L^{-1} (FA-1, YFA-1) was the same in efficiency as that on the samples with m = 15.0 g L^{-1}. This implies that the number of adsorption sites in the samples with m = 5.0 g L^{-1} is sufficient for the complete absorption of MB and MR. In experiments with m = 15.0 g L^{-1} no expected increase in adsorption of the dyes was observed. Evidently, in these experiments the content of the dyes in the liquid and solid phases achieved equilibrium concentrations (see Fig. 1).[14]

Comparison of the adsorption isotherms for the FA-1, YFA-1, and AC-1 samples (m = 5.0 g L^{-1}) shows that the adsorption capacity of the FA-1 (pure FA) and YFA-1 (mixture of FA and AC) samples is ≥99%, *i.e.*, the value of the same order of magnitude as the capacity of the AC-1 carbon with respect to all solutions of the dyes. This result indicates that FA can be used for the purification of wastewater containing azo dyes with the same efficiency as AC.

To study the adsorption parameters, we used the Langmuir model modified for the processing of results of adsorption of the azo dyes from solutions on FA and AC

$$q_e = (C_e - C_0)V/m, \quad (5)$$

$$C_e/q_e = (1/Q^\circ b) + C_e/Q^\circ, \quad (6)$$

where C_0 and C_e are the initial and equilibrium concentrations of solutions with the adsorbate (mg L^{-1}), V is the solution volume, q_e is the amount of the azo dye adsorbed on the surface unit of the solid adsorbent at equilibrium (mg g^{-1}), and Q^0 and b are the constants in the Langmuir adsorption equation reflecting the adsorption capacity and adsorption parameters, respectively. The parameters of the adsorption isotherm were obtained by plotting the dependence of C_e/q_e on C_e for an equilibrium solution of MB or MR.[11,12,25] As can be seen from the data in Table 2, all adsorption parameters are close and agree with the Langmuir adsorption model (in all cases, the correlation coefficient is $R^2 > 0.9$).

The Q^0 and b values were calculated from the slopes and intersection points of the curves in the corresponding

Table 2. Parameters of the Langmuir equation for the adsorption of MR and MB on the FA, YFA, and AC samples at 298 K

Adsorbent	Q/mg g^{-1}		b/L mg^{-1}		R^2	
	MR	MB	MR	MB	MR	MB
FA-1	5.97	0.19	$9.64 \cdot 10^{-1}$	$2.05 \cdot 10^2$	0.97	0.99
FA-2	2.47	0.06	34.4	$2.98 \cdot 10^2$	0.99	0.98
YFA-1	6.23	0.19	50.2	$1.98 \cdot 10^2$	1.00	0.99
YFA-2	2.70	0.06	$3.37 \cdot 10^2$	$2.23 \cdot 10^2$	0.99	0.99
AC-1	8.14	0.08	$2.46 \cdot 10^3$	$6.36 \cdot 10^6$	0.99	0.99
AC-2	2.67	2.67	$3.74 \cdot 10^4$	$3.74 \cdot 10^4$	0.99	0.99

plots. The Q^0 values for MB and MR adsorption are approximately of the same order of magnitude for all adsorbents. At the same time, the b values for the FA and YFA samples are close but lower than the parameters for AC-1 and AC-2.

Thus, FA can find use as a cheap sorbent instead of expensive AC. Note that the fly ash also decreases the content of suspended impurities, ammonium compounds, and nitrophenol in wastewater, diminishes the chemical consumption of oxygen, and bleaches wastewater.[27,28]

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