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Equilibrium and kinetic mechanism for Reactive Black 5 sorption onto high lime Soma fly ash

Zeynep Eren*, Filiz Nuran Acar

Department of Environmental Engineering, Ataturk University, 25240 Erzurum, Turkey Received 22 May 2006; received in revised form 6 September 2006; accepted 6 September 2006 Available online 10 September 2006

Abstract

Batch adsorption studies were carried out for the sorption of C.I. Reactive Black 5, a reactive dye, onto high lime fly ash, obtained from Soma Thermal Power Plant (Turkey), to be low cost adsorbent. The effect of various experimental parameters such as contact time, adsorbent dose and initial dye concentration were investigated. Determination of the adsorption equilibrium concentrations was determined by UV–vis spectrophotometry analytical method. Equilibrium data were fitted to the Freundlich and Langmuir isotherm equations and the equilibrium data were found to be well represented by the Freundlich isotherm equation. The adsorption kinetics of C.I. Reactive Black 5 onto high lime fly ash were also studied to characterize of the surface complexation reaction. A pseudo-second-order mechanism has been developed to predict the rate constant of the adsorption, the equilibrium capacity and initial adsorption rate with the effect of initial concentration. A single-stage batch adsorber design of the adsorption of C.I. Reactive Black 5 onto high lime fly ash has been studied based on the Freundlich isotherm equation. © 2006 Elsevier B.V. All rights reserved.

Keywords: High lime fly ash; Reactive dye; Adsorption isotherms; Adsorption kinetics; Pseudo-first-order kinetics; Pseudo-second-order kinetics; Intraparticle diffusion

1. Introduction

Fly ash is a waste material originating in great amounts in combustion processes. Although fly ash utilization in construction and other civil engineering applications is high, research is needed to develop new alternative environmental friendly applications. Potential environmental impacts of fly ash utilization have been extensively studied and are well understood. It has been demonstrated in the literature that fly ash can remove cations and anions from water [1,2].

Dye compounds are widely used for textiles, printing, and dyeing, as well as in the food and paper-making industries. Consequently, the effluents of these industries are highly colored. Color is aesthetically objectionable and it also reduces light penetration into water decreasing the efficiency of photosynthesis in aquatic plants, thereby, having adverse impact on their growth [3,4]. Because of higher organic concentration, particular toxicity, complex composition and poor degradability, dyes are the

0304-3894/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2006.09.017 most noticeable contaminant even at very low concentrations, and they need to be removed or decolorized before the wastewater can be discharged [5,6]. Due to the low biodegradability of dyes, the wastewater with dye is usually treated by physical or chemical treatment processes [7]. Currently the sorption technique is proven to be effective and attractive processes for the treatment of these wastewaters. Also this method will become inexpensive if the adsorbent material used is of cheaper cost and does not require any expensive additional pretreatment step [8]. Various low cost adsorbents such as dried activated sludge [9], shale oil ash [10], orange peel [11], waste red mud [12], fly ash [13] have been used as low cost alternatives in color removal processes.

In this paper, we used a low cost material, high lime fly ash, to remove a reactive dye, C.I. Reactive Black 5 from aqueous solutions. The influences on the adsorption of C.I. Reactive Black 5 were investigated in terms of equilibrium time, initial dye concentration and fly ash dose. Fly ash has been studied for removing acid dyes such as Acid Black 1 [14], basic dyes such as Methyl Violet [15], direct dyes such as Congo Red [16]. But there is a limited study for reactive dye by fly ash adsorption. Reactive dyes are typically azo-based chro-

^{*} Corresponding author. Tel.: +90 4422314821; fax: +90 4422360957. *E-mail address:* zeren@atanui.edu.tr (Z. Eren).

Table 1The results of sieve analysis for high lime fly ash

Differential particle size (µm)	% weight			
-355 +212	6.3			
-212 +180	3.5			
-180 +125	4.3			
-125 +90	12.4			
-90 +63	34.5			
-63	39.0			

mophores combined with different types of reactive groups, e.g., vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. They differ from all other classes of dyes in that they bind to the textile fibres such as cotton to through covalent bonds. They are used extensively in textile industries regarding favourable characteristics of bright color, water-fast, simple application techniques with low energy consumption [17].

The kinetic and the mechanistics steps involved in the sorption processes were evaluated at different initial dye concentrations. A single-stage batch sorber has been designed for the removal of C.I. Reactive Black 5 by high lime fly ash based on the equilibrium data obtained.

2. Materials and methods

2.1. Fly ash

The high lime fly ash used in this study was obtained from Thermal Power Plant of Soma, Turkey. The surface area of fly ash determined by the BET method (Quantasorb Surface Area Analyser, Model QS-17) was $5.35 \text{ m}^2/\text{g}$. The fly ash was sieved to obtain various size fractions using sieves and the results are given in Table 1. It was used without any pretreatment in the adsorption studies. According to ASTM C 618 standard, the fly ash is divided into two types namely C type fly ash and F type fly ash. F type fly ash is named low lime fly ash because the quantity of CaO is below 10%. Also, the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is more than 70% in F type fly ash. C type fly ash is named high lime fly ash because the quantity of CaO is more than 10% and the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is more than 50% in this type fly ash. Hence, Soma fly ash is C type fly ash due to the quantity of CaO is more than 10% (23.45%) and the sum of $SiO_2 + Al_2O_3 + Fe_2O_3$ is more than 50% (70.48%) [18]. Its constitution has been presented in Table 2.

Table 2	
Chemical composition of Soma fly ash [18]	

Constituent	% weight
SiO ₂	42.82
Al ₂ O ₃	20.82
Fe ₂ O ₃	4.57
CaO	23.45
MgO	1.74
SO ₃	1.47
K ₂ O	1.31
Na ₂ O	0.32
Cl	0.01

2.2. Reactive Black 5 (RB5)

C.I. Reactive Black 5 was obtained a textile firm in Turkey. Its visible absorbance was 598 nm. General structure "vinyl sulfone-azo" dye was given in Fig. 1. A stock solution of 1000 mg/L of RB5 was prepared by dissolving 1 g of dye in 1 L distillated water and used for further studies by diluting as concentrations desired.

2.3. Method

Batch adsorption experiments were carried out at room temperature (20 °C) and at natural pH. The dye solution with fly ash were stirred in the closed glass flask using a horizontal shaker (Thermolyn Rosi 1000) at a 200 rpm constant agitation speed for an hour. Samples were withdrawn at suitable time intervals and were filtered and their concentrations determined by UV-vis Spectrophotometer (Shimadzu-160A). For the preventing the loss of dye in filtration test, the filtration performance was examined before the experiments were started up. So, both filtered dye solution and not filtered dye solution were analyzed. There was too small difference to negligible between two solutions. Then, the filtered dye solution was used to measure of color. The operating parameters were contact time, initial dye concentration and fly ash dose. The effect of contact time was studied for an hour. The effect of initial dye concentration was studied in a range of concentration (5-100 mg/L). The effect of fly ash dose on adsorption was studied at a range of fly ash dose (2.5–15 g/L).

3. Results and discussion

3.1.1. Effect of contact time and initial concentration

The effect of contact time on the RB5 adsorption by the fly ash was investigated for an hour. The adsorption rate was very



Fig. 1. Chemical structure of Reactive Black 5.



Fig. 2. The effect of initial dye concentration on adsorption efficiency (—) and equilibrium dye concentration (...) (10 g/L of fly ash, 200 rpm agitation speed and room temperature, 20° C). (**I**) Co = 5 mg/L; (**A**) Co = 25 mg/L; (**X**) Co = 50 mg/L; (×) Co = 100 mg/L.

high in 5 min for all experiments. Thereafter a gradual increase in adsorption occurred with increasing contact time up to 40 min and then the adsorption rate was nearly stable up to 60 min. So, the period of 60 min was fixed as the equilibrium contact time the following studies. The effect of initial concentration of RB5 on the extent of adsorption by fly ash was studied and the relevant data are given in Fig. 2. When the RB5 concentration was increased from 5 to 100 mg/L; the adsorption efficiency decreased from 100% to 72.62%, while the adsorption capacity (q_e) increased from 0.5 to 7.262 mg/g. Fig. 2 shows that the adsorption efficiency to be highly dependent on the initial RB5 concentration.

3.2. Effect of fly ash dose

To determine the effect of fly ash dose on the adsorption efficiency, the range between 2.5 and 15 g/L of fly ash dose were studied at a fixed RB5 concentration (50 mg/L, its pH 5.64). Fig. 3 shows the effect of fly ash dose on adsorption efficiency, % and equilibrium RB5 concentration, C_e . The amount of dye adsorbed increased from 2.964 to 4.368 mg/g for an increase in fly ash dose from 2.5 to 15 g/L. Similarly the adsorption efficiency increased from 59.28% to 87.36% as the fly ash dose increased from 2.5 to 15 g/L. This may be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increasing dose of the adsorbent. At higher fly ash to dye concentration ratios, there was a very fast superficial sorption onto the adsorbent surface that produces a lower dye concentration in the equilibrium solution than when the fly ash to dye concentration ratio was lower [8]. This indicates that the more surface area is available, therefore the number of sites increases.

3.3. Adsorption isotherms

The adsorption isotherms were measured in order to evaluate the discrepancy between the experimental data and the theoretical equilibrium capacity predicted from the kinetic equations [19]. In addition, the equation parameters and the underlaying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanisms and the surface properties and affinities of the sorbents [20]. In this study, the two most common isotherms were used to describe the experimental adsorption data, Langmuir and Freundlich model.

The theoretical Langmuir isotherm often used to describe sorption of a solute from a liquid solution as

$$q_{\rm e} = \frac{x}{m} = \frac{q_{\rm max}bC_{\rm e}}{1+bC_{\rm e}} \tag{1}$$



Fig. 3. The effect of fly ash dose on adsorption efficiency (—) and equilibrium dye concentration (...) (50 mg/L of dye concentration, 200 rpm agitation speed, natural pH 5.64 and room temperature, 20 °C). (\blacksquare) M = 2.5 mg/L; (\blacklozenge) M = 5 mg/L; (\bigstar) M = 10 mg/L; (\bigstar) M = 15 mg/L.

The constants q_{max} and b are characteristics of the Langmuir equation and can be determined from a linearized form of Eq. (1), represented by

$$\frac{C_{\rm e}}{x/m} = \frac{1}{bq_{\rm max}} + \left(\frac{1}{q_{\rm max}}\right)C_{\rm e} \tag{2}$$

which will have a straight line with a slope of $1/q_{max}$ and an intercept of $1/(bq_{max})$ when C_e/q_e is plotted against C_e , where C_e is the equilibrium concentration (mg/L), q_e the amount of dye sorbed at equilibrium (mg/g), q_{max} the maximum monolayer adsorption capacity (mg/g), and b is the sorption equilibrium constant (L/mg).

The Freundlich isotherm is the earliest known relationship describing the sorption equation. The Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a protein binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. On limitation of the Freundlich model is that the amount of adsorbed solute increases indefinitely with the concentration of solute in the solution [20]. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption and is expressed by the following equation:

$$q_{\rm e} = K_{\rm f} C_{\rm e}^{1/n} \tag{3}$$

The equation may be linearized by taking the logarithm both sides:

$$\log q_{\rm e} = \log K_{\rm f} + \left(\frac{1}{n}\right) \log C_{\rm e} \tag{4}$$

which will have a straight line with a slope of 1/n and an intercept of $\log(K_f)$ when $\log(q_e)$ is plotted against $\log(C_e)$, where K_f and 1/n are empirical constants dependent on several environmental factors. The linear isotherms constants and the coefficient determination, r^2 , are represented in Table 3 for two model.

The comparison was made between the experimental q_e (mg/g) values and the calculated values q_e (mg/g) and the variance between the experimental data and the two model's prediction are also given in Fig. 4. It can be seen from Fig. 4 that Freundlich adsorption isotherm is more suitable than Langmuir adsorption isotherm for removal of RB5 onto fly ash. The high correlation coefficient ($r^2 = 0.955$) indicates that the high affinity between fly ash surface and RB5 plays the major role in the adsorption mechanism in Freundlich model. This suggests that some heterogenity in the surface or pores of the fly ash will play a role in dye adsorption [21].

The slope 1/n, ranging between 0 and 1 is a measure of adsorption intensity or surface heterogenity, becoming more heterogeneous as its value gets closer to zero [22]. In this study, the



Fig. 4. Comparison of Langmuir and Freundlich isotherms for adsorption of RB5 onto high lime fly ash. (\blacklozenge) q_e experimental; (\blacksquare) q_e Langmuir (obtained from Eq. (2)); (\blacktriangle) q_e Freundlich (obtained from Eq. (4)).



Fig. 5. A single-stage batch adsorber.

value of 1/n was found to be 0.321 which indicates favourable adsorption.

3.4. Design batch adsorption from isotherm data

Adsorption is a well-known equilibrium separation process for wastewater treatment containing organics. Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems and provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. Assuming the batch adsorption to be a single-stage equilibrium operation, the separation process can be defined mathematically using these isotherm constants to estimate the residual concentration of dye or amount of adsorbent for desired purification [23].

Adsorption isotherm relations are used to predict the design of single-stage batch sorption systems. A schematic diagram is shown in Fig. 5. The solution to be treated contains V sol-

Table 3 Equilibrium constants for RB5 onto high lime fly ash

Langmuir isotherm $(y=0.1392x+0.2649)$			Freundlich isotherm ($y = 0.3209x + 0.3625$)				
q_{\max}	b	r^2	$K_{ m f}$	п	r^2		
7.184	0.526	0.922	2.304	3.116	0.955		



Fig. 6. Volume of effluent (V) treated against adsorbent mass (M) for different percentages of RB5 removal. (\blacklozenge) 90%; (\blacksquare) 80%; (\blacktriangle) 70%; (\times) 60%; (\bigstar) 50%.

vent (L), and the initial concentration is reduced from C_0 to C_1 (mg/L). The amount of adsorbent is M and the solute concentration increases from q_0 to q_1 (mg/g). If fresh adsorbent is used, $q_0 = 0$. As the proceeds, the mass balance equates the solute removed from liquid to that picked up by the adsorbent. The mass balance equation for the sorption system can be written as [8,22]:

$$V(C_0 - C_1) = M(q_0 - q_1)$$
(5)

Under equilibrium conditions:

$$C_1 \to C_e \quad \text{and} \quad q_1 \to q_e \tag{6}$$

For the sorption isotherm studies confirm that the equilibrium data for RB5 adsorption onto fly ash best fitted in Freundlich isotherm, the Freundlich data may now be applied Eq. (5) and substituting for q_1 from Eq. (2) and rearranging gives

$$\frac{M}{V} = \frac{C_0 - C_1}{q_e} = \frac{C_0 - C_e}{K_f C_e^{1/n}}$$
(7)

Eq. (7) permits analytical calculation of the adsorbent solution ratio for a given change in solution concentration, C_0 to C_e . Fig. 6 shows a series of plots (90%, 80%, 70%, 60% and 50% color removal at different solution volumes, i.e., 1, 2, 3, 4, 5, 6, 7 and 8 L) derived from Eq. (7) for the adsorption of 50 mg/L of RB5 onto fly ash. The amount of fly ash required for the 90% removal of RB5 solution of concentration 50 mg/L was 18.657, 37.314, 55.972 and 74.629 g for dye solution volumes of 1, 2, 3 and 4 L, respectively.

Table 4
Effect of initial RB5 concentration

3.5. Adsorption kinetics

In order to examine the controlling mechanism of sorption process such as chemical reaction, diffusion control and mass transfer, several kinetic models are used to test experimental data. The prediction of batch sorption kinetics is necessary for the design of industrial sorption columns. The nature of the sorption process will depend on physical or chemical characteristics of the adsorbent system and also on the system conditions. Lagergren pseudo-first-order, pseudo-second-order, Elovich kinetic equation and parabolic diffusion model were previously used in literature in order to predict the mechanism involved in the sorption process. In this study, the applicability of the pseudo-first-order model, the pseudo-second-order model and intraparticle diffusion model were tested for the sorption of RB5 onto high lime fly ash. The best fit model was selected based on the correlation coefficient, r^2 values.

3.5.1. The pseudo-first-order model

A simple kinetic of sorption is the pseudo-first-order equation in the form [24]:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_1(q_\mathrm{e} - q_t) \tag{8}$$

Integrating Eq. (8) and applying the boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t, gives

$$\log(q_{\rm e} - q) = \log q_{\rm e} - \left(\frac{k_1}{2.303}\right)t$$
(9)

where q_e and q_t are the amounts of dye sorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order sorption (min⁻¹). The pseudo-first-order rate constants, k_1 , calculated q_e and the linear correlation coefficient values, r_1^2 are given in Table 4, it was seen that the pseudofirst-order model was not fit very well. The adsorption reached equilibrium fast in 5 min and the experimental data for kinetic calculation are not good enough in the first-order kinetic model. The results of 5 and 10 mg/L of initial dye concentrations were stable during 60 min treatment period. So, these values were not used for first-order kinetic model calculation. Only, the results of 25, 50 and 100 mg/L of initial dye concentrations were used for the first-order kinetic model calculation (even, 50 mg/L of initial dye concentration have two data in first-order model). So, the adsorption of RB5 onto high lime fly ash is not well represented

Experimental		First-order kinetic model		Second-order kinetic model				Intraparticle diffusion model		
<i>C</i> ₀ (mg/L)	$q_{\rm e} \ ({\rm mg/g})$	$q_{\rm e} \ ({\rm mg/g})$	$k_1 ({\rm min}^{-1})$	r_1^2	r_2^2	$q_{\rm e} \; ({\rm mg/g})$	k_2 (g/(mg min))	h (mg/(g min))	$\overline{k_{\rm i}({\rm mg/}({\rm gmin^{0.5}}))}$	r_i^2
RB5										
5	0.500	_	_	_	1.000	0.500	_	_	_	_
10	0.990	_	_	_	0.999	0.993	8.236	8.123	0.001	0.316
25	2.438	0.218	0.079	0.81	1.000	2.461	0.787	4.766	0.027	0.864
50	4.000	0.225	0.081	1.00	1.000	4.014	1.595	25.707	0.023	0.571
100	7.262	2.011	0.061	0.73	0.997	7.402	0.067	3.659	0.201	0.936



Fig. 7. Pseudo-first-order kinetic for adsorption of RB5 on fly ash. (\blacklozenge) Co = 25 mg/L; (\blacksquare) Co = 50 mg/L; (\blacktriangle) Co = 100 mg/L.

first-order kinetic model. Fig. 7 shows the pseudo-first-order plot for RB5 onto high lime fly ash.

3.5.2. The pseudo-second-order model

The pseudo-second-order rate expression was used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces. The advantage of using this model is that there is no need to know the equilibrium capacity from the experiments, as it can be calculated from the model. In addition, the initial adsorption rate can also be obtained from the model [24,25]. The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of adsorbent and the amount sorbed at equilibrium. The sorption equilibrium, q_e , is a function of, e.g., the temperature, the initial metal ion concentration, the sorbent dose, particle size and the nature of solute–sorbent interaction. The kinetic rate equations can be rewritten as follows:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k(q_\mathrm{e} - q_t)^2 \tag{10}$$

where k is the rate constant of sorption (g/(mg min)), q_e the amount of dye sorbed at equilibrium (mg/g) and q_t is the amount of dye on the surface of the sorbent at any time t (mg/g).

Separating the variables in the equation above gives integrating this for the boundary conditions t=0 to t and $q_t=0$ to q_t , gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t\tag{11}$$

which is the integrated rate law for a pseudo-second-order reaction. The kinetics of sorption of RB5 on fly ash were studied on the basis of the pseudo-second-order rate Eq. (11) and

$$h = k_2 q_e^2 \tag{12}$$

where *h* is the initial sorption rate (mg/(g min)) [26]. Fig. 8 shows the pseudo-second-order plot for RB5 onto high lime fly ash. The pseudo-second-order rate constants, k_2 , values of *h* and the linear correlation coefficient values, r_2^2 are given in Table 4, it was seen that at all initial dye concentrations, the linear correlation coefficient r_2^2 values were found to be high.

3.5.3. Intraparticle diffusion model

The intraparticle diffusion is the rate controlling factor, uptake of the sorbate varies with the square root of time. For the rate constant of intraparticle diffusion:

$$q_t = k_i \sqrt{t} \tag{13}$$

where k_i is intraparticle diffusion rate constant (mg/(g min^{0.5})) and q_t is the amount of dye sorbed at any time t (mg/g). The intraparticle diffusion plots are given in Fig. 9 that shows the amount of adsorption against square root of time. Fig. 9 shows a plot of the linearized form of the model in Eq. (13) for the adsorption of RB5 onto high lime fly ash at different initial dye concentrations. The k_i values under different conditions were calculated from the slopes of the straight line portions of the respective plots and are given in Table 4. It can be seen from Table 4, the correlation coefficients, r_2^2 , for the pseudo-second-order kinetic model are much greater than the intraparticle diffusion coefficients and first-order coefficients for the sorption of RB5 onto high lime fly ash, strongly suggesting a chemical reaction mechanism which could occur because of the chemical character of fly ash [27].

The values of the calculated and experimental q_e are represented in Table 4. It can be seen from Table 4 that there is an agreement between q_e experimental and q_e calculated values



Fig. 8. Pseudo-second-order kinetic for adsorption of RB5 on fly ash. (\blacklozenge) Co=5 mg/L experimental data—second-order model; (\blacksquare) Co=10 mg/L experimental data—second-order model; (\checkmark) Co=50 mg/L experimental data—second-order model; (\bigstar) Co=100 mg/L e



Fig. 9. Intraparticle diffusion model for adsorption of RB5 on fly ash. (\blacklozenge) Co=5 mg/L experimental data—interparticle model; (\blacksquare) Co=10 mg/L experimental data—interparticle model; (\blacktriangle) Co=25 mg/L experimental data—interparticle model; (\times) Co=50 mg/L experimental data—interparticle model; (\bigstar) Co=100 mg/L experimental data—interparticle model.

for the pseudo-second-order model. These results based on the assumption that the rate limiting step may be chemical adsorption involving valency forces through sharing or exchange of electrons between dye and the fly ash, provides the best correlation of the data for the RB5 [28].

4. Conclusion

The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. It is therefore important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an appropriate adsorption treatment plant [26]. Generation of thermal and electric energy in the process of solid fuel combustion is inevitably related to production of significant amounts of combustion wastes, fly ashes. The amount of combustion wastes was estimated as million tonnes, including fly ashes. The amount of fly ashes considerably has increased. Combustion wastes are usually left as dumps, which is from an environmentally friendly procedure. However, they can be used as potential adsorbents [29]. In this study, the equilibrium capacity of high lime Soma fly ash was found as 7.184 mg/g dye. Also, the equilibrium and kinetic of adsorption of RB5 on high lime fly ash, obtained from Soma Thermal Power Plant, showed that fly ash can be used as low cost potential adsorbents for dye wastewater. The equilibrium data correlated reasonably well with the Freundlich adsorption isotherm. Intraparticle diffusion and chemical reactions seem significant in the rate controlling step but for the sorption of RB5 onto high lime fly ash the pseudo-second-order chemical reaction kinetics provide the best correlation of the data.

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