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ORIGINAL PAPER

Kinetic and equilibrium studies of methylene blue adsorption on functionalized polymethyl methacrylate in polyvinylidene fluoride–hexafluoropolypropylene matrix

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Abstract
Herein a novel polymeric adsorbent composite material was introduced for the adsorption of methylene blue from aqueous solutions for the purpose of water treatment. Adsorption process was examined by using Langmuir and Freundlich isotherm models together with pseudo-first and second order kinetic analysis. It was found that characteristic of the adsorption process was well described by Langmuir isotherm following pseudo-first order kinetic route. The maximum monolayer adsorption capacity was determined as 49.04 mg g^{-1}. In light of thermodynamic parameters of the adsorption and removal of MB from the composite in acidic solution suggested that the process was based on ion-exchange mechanism. Negative values of Gibbs free energies changing from − 5.41 to − 15.99 kJ mol^{-1} with increasing temperature demonstrated that adsorption process occurs spontaneously. Heat of adsorption and entropy values were found as 58.30 kJ mol^{-1} and 0.23 kJ mol K^{-1}, respectively. Therefore, adsorption process was endothermic in nature without noticeable disorder. The material consisting of functionalized poly(methyl methactrylate) in the polyvinylidene fluoride–hexafluoropolypropylene matrix is considered to be a potential adsorbent material for the treatment of polluted waters.

Keywords Langmuir · pseudo-first order kinetic · Polymer composite · Waste water

Introduction

Increasing water pollution due to the discharges of textiles or other sectors who are intensively dealing with toxic dyes increased the severity of environmental problems and accelerated the researches to eliminate these organic molecules by economically and environmentally-friendly processes. Approximately 40 g of textile dyes are consumed for dyeing 1000 g of cotton fabric on average, and 20–30% of these dyes are released into the ecosystem. (Allègre et al. 2006). These dye effluents carried by water accumulate in the aquatic environment and have a detrimental effect due to toxicity (Walsh et al. 1980). These pollutions have to be removed with efficient and clean technologies. In the literature biological treatment processes (Holkar et al. 2016); coagulation/flocculation (Liang et al. 2014), membrane separation (Wang et al. 2019a, b) chemical oxidation (Cheng et al. 2016) and adsorption (Sheng et al. 2018) are frequently used methods for this purpose. Among these methods, adsorption process is the most commonly preferred one for its low cost. Polymeric adsorbents constitute an interesting category among the adsorbent materials because of their variable chemical structure and abundance (Jianwei et al. 2015; Auta and Hameed 2014). Also strong binding affinities, high adsorption capacity, superior mechanical, chemical and thermal stability puts the polymer-based adsorbents into a special place (Bingjun et al. 2009; Liu et al. 2018). In particular, chemically modified polymeric materials are considered to be very effective adsorbents for removing dye molecules from aqueous solutions without leaving any adsorbent residue (Pan et al. 2009). Various kinds of polymeric materials such as polyaniline (Kanwal et al. 2018; Wang et al. 2019a, b), chitosan (Vilela et al. 2019), polyvinyl alcohol (Sanchez et al. 2019; Dai et al. 2018), polystyrene (Al-Sabagh et al. 2018; Wen et al. 2015), polyacrylamide (Zhang et al. 2018), polyurethane (Lefebvre et al. 2018; Kumari et al. 2016) and cellulose (Tong et al. 2018; Varghese et al. 2019) are

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currently being researched for the use in the treatment waste waters. However, these polymers are used as a matrix of a composite in which the adsorption is realized by the additives of the composite such as bentonite, montmorillonite, silica, zirconium oxide, alumina, iron oxide, etc. (Nasar and Mashkoor 2019). The main disadvantages of the composite adsorbents are the decrease in the adsorption power of the additives due to the difficulty in homogeneous distribution of the additives in the polymer, the indifference of the pure polymer to the dye molecules, and the low resistance to strong acidic and alkaline conditions. In this point of view, an ideal polymeric adsorbent material should have self-adsorption properties and chemical inertness.

In this study, a novel composite polymeric adsorption material (CPAM) was prepared from polyvinylidene fluoride–hexafluoropolypropylene (PVDF–HFP) and polymethylmetacrylate (PMMA) composite by sulfuric acid hydrolysis method. The resulting composite polymer has carboxylic acid groups demonstrating strong affinity to methylene blue (MB) which is used in this study as a representative cationic dye. The chemical inertness provided by PVDF–HFP and strong affinity caused by oxygen containing groups of the present polymeric adsorbent may suggest a promising alternative for waste water treatment processes. Additionally, this material introduces an advantage of easy removal from waste waters without any residue eliminating the commonly used, high cost filtration steps after adsorption process. The study was carried out between April and August 2019, in the city of Buca, Izmir, Turkey.

Materials and methods

Materials

Poly(methyl methactrylate) (Sigma) with an average molecular weight of 350,000 g mol^{-1}, poly(vinylidene floride-*co*-hexafluoropropylene) with weight average and number average molecular weights of 455,000 g mol^{-1} and 110,000 g mol^{-1}, respectively, were purchased from Sigma. Sulfuric acid (Sigma), tetrahydrofuran (THF) (Sigma) and dimethylformamide (DMF) (Fluka) were used without any purification.

Methods and charaterization

Fourier transform infrared spectra (FTIR) of the adsorbent were recorded with a Perkin Elmer Spectrum BX-II Model Fourier Transform IR spectrometer using ATR module in the range of 4000 and 400 cm^{-1}. MB concentration was followed up by using Perkin Elmer Lambda 950 UV/Vis spectrometer. Batch adsorption experiments were realized using glass bottles in temperature controlled environment.

Preparation of CPAM

PMMA was mixed with PVDF matrix to form a composite with a ratio of 5% in THF/DMF (1:1) solvent mixture, then casted into glass petri dishes and was allowed to dry at ambient temperature. The dried samples were immersed into concentrated sulfuric acid in a round bottom flask and refluxed at 373 K for 8 h. And then the sample (CPAM) was removed, thoroughly washed with deionized water and dried at 343 K for 24 h. CPAM samples were placed into glass petri dishes, sealed with paraffin film and saved for further analysis and experiments. The reaction mechanism of the composite polymer to form CPAM with sulfuric acid takes place on the methacrylate groups in the PMMA backbone, which are hydrolyzed by the removal of methanol. Polyacrylic acid is formed at the end of the reaction. Oxygen containing groups formed in this reaction such as carbonyl, hydroxyl, ether are the main attracting centers for MB molecule.

Adsorption studies

Batch adsorption experiments were performed in 50 mL glass bottles, each of which contained 30 mL of MB solutions with different concentrations at neutral pH (3.0×10^{-5} mg L^{-1}, 1.5×10^{-4} mg L^{-1} and 3.0×10^{-4} mg L^{-1}) by using three different amounts of adsorbent (0.0500 g; 0.0725 g; 0.1000 g) for each concentration. Adsorption processes were carried out at 277 K, 298 K and 323 K. At several intervals, equilibrium concentrations of the MB solutions were determined by UV–vis spectrometer at 664 nm with the aliquots taken from the bottles.

The amount of MB adsorbed on CPAM at equilibrium was calculated by Eq. 1:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg g^{-1}) denotes the equilibrium adsorption capacity for MB adsorbed per gram of the CPAM, C_0 and C_e (mg L^{-1}) are the initial and equilibrium MB concentrations, respectively. V is the volume of the MB solution (L), and m is the mass of CPAM (g).

Theory of adsorption

Langmuir and Freundlich isotherms were employed to study adsorption capacity at equilibrium. The experimental data were plotted according to the linear forms of the Eqs. 2 and 3:

Langmuir isotherm

$$\frac{C_e}{q_e} = \left(\frac{1}{K_a q_m}\right) + \frac{C_e}{q_m} \tag{2}$$

Freundlich isotherm

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{3}$$

where C_e and q_e are concentration (mg L^{-1}) and adsorption capacity (mg g^{-1}) at equilibrium, respectively. Maximum adsorption capacity is represented by q_m (mg g^{-1}). K_a (L mg^{-1}) is the Langmuir adsorption constant, K_f [(mg g^{-1}) (L $mg^{-1})^{1/n}$] is the Freundlich adsorption constant, and n is the Freundlich adsorption intensity.

To describe the adsorption mechanism, the process was evaluated in light of so-called first order and second order kinetic models (Eqs. 4, 5).

Pseudo-first order model;

$$\log\left(q_e - q_t\right) = \log q_e - k_1 t \tag{4}$$

Pseudo-second order model;

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{5}$$

where k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants of first and second order kinetic models, respectively (Junlapong et al. 2020).

Thermodynamics of adsorption

Thermodynamic parameters of adsorption such as Gibbs free energy ($\Delta G°$), enthalpy of adsorption ($\Delta H°$) and the entropy ($\Delta S°$) are important for illuminating the mechanism of adsorption. These thermodynamic parameters can be calculated with Eqs. 6 and 7 (Arias and Sen 2009):

$$\Delta G° = \Delta H° - T\Delta S° \tag{6}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303RT} \tag{7}$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}), C_e is the equilibrium concentration (mg L^{-1}), T is temperature (Kelvin), and R is the gas constant (8.314 J mol^{-1} K^{-1}). To find the thermodynamic parameters, a linear graph of ($1/T$) against log (q_e/C_e) is plotted. From the slope, enthalpy of adsorption can be calculated. Entropy of adsorption can be determined from the intercept of the plot (where R is equal to 8.314 J mol^{-1} K^{-1}). By using these enthalpy and entropy values, Gibbs free energies of the adsorption are calculated for each desired temperature values by using Eq. 6. Gibbs free energy is an important parameter for explaining the spontaneity of the adsorption. If the adsorption spontaneous, MB molecules are self-driven to the polymeric matrix where attraction groups are available. Enthalpy of reaction gives clues about the nature of the adsorption, and whether physical or chemical bond is formed during the adsorption process. It is generally assumed that the physical bond is less than 200 kJ, and that the chemical bond occurs above this value. Entropy value shows the disorder of the system. If the entropy is high enough, the molecules are randomly distributed to the adsorption sites where multiple adsorption layers are possible.

Results and discussion

FTIR results

The FTIR spectra of CPAM is given in Fig. 1a. The peak at 1706 cm^{-1} and its shoulder at 1757 cm^{-1} appeared due to the presence of ester carbonyl group stretching vibration belongs to the PMMA. The part of this peak at 1805 cm^{-1} is the proof for creation of carbonyl groups in PMMA backbone by the sulfuric acid catalyzed carboxylization. The broad peak ranging from 3700 to 3100 cm^{-1} can be attributed to hydrogen bonded hydroxyl groups of the polymer. As to the PVDF–HFP part of the composite, the bands at 1402 and 1187 cm^{-1} are stretching of –C–F– and symmetrical stretching of $–CF_3$ groups, respectively. Stretching at 1074 and 1024 cm^{-1} can be assigned to –CO groups. The bands at 881 and 848 cm^{-1} correspond to the C–C skeletal vibration. The adsorption at 512 cm^{-1} refers to the symmetrical stretching vibration of $–CF_2$ groups (Selvi and Hema 2014). For the immobilization of the methylene blue, oxygen containing groups detected from FTIR interact with the positively charged sulfur atoms on the MB molecule as depicted in Fig. 1b.

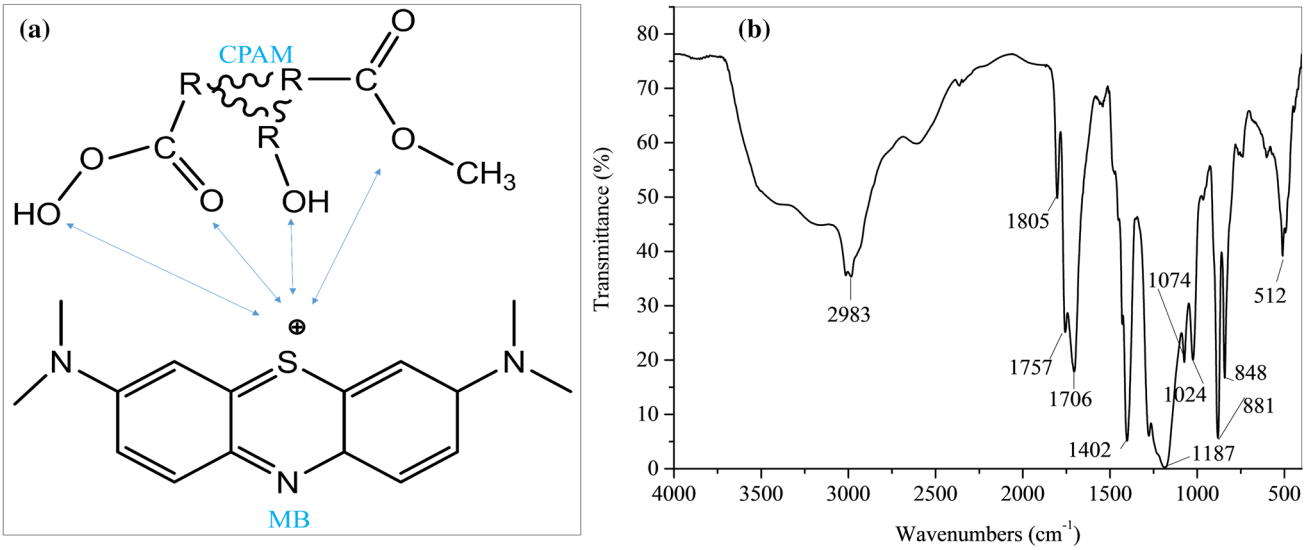

Fig. 1 **a** Interactions of the functional groups with MB, **b** FTIR spectrum of CPAM

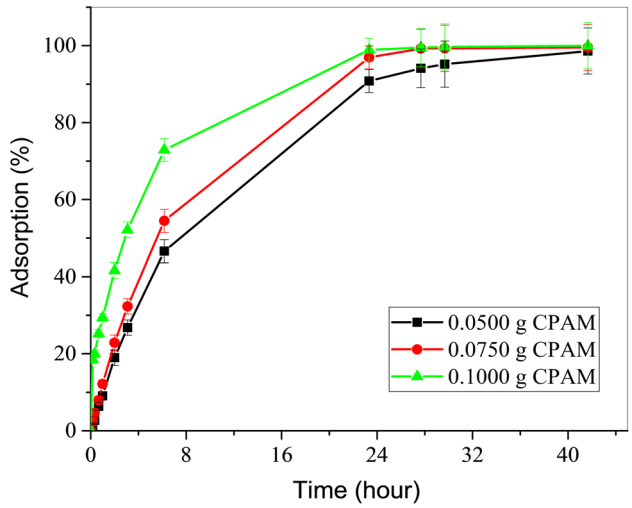

Fig. 2 Effect of adsorbent amount on adsorption

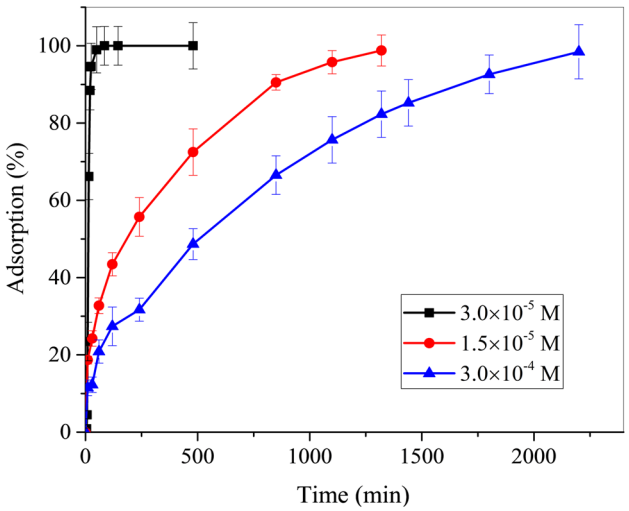

Fig. 3 Effect of MB concentration on adsorption

Adsorption characteristic

Increasing the adsorbent dosage have a positive effect on adsorption amount and rate at the beginning (Fig. 2) due to the plenty of untouched adsorption sites. Adsorption process then slows down and comes to an equilibrium according to the adsorbent dosage with no difference in the adsorbed amount. The effect of MB concentration on adsorption is given in Fig. 3. As expected, the adsorption time increased

Table 1 Isotherm parameters of MB

Models	Parameters	
Langmuir	q_m (mg g^{-1})	49.04
	K_a (L mg^{-1})	1.6936
	R^2	0.9797
Freundlich	N	2.6482
	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	19.7655
	R^2	0.7968

with increasing number of MB molecules. Dye concentration didn't affect the adsorption characteristics. The determination of this property was evaluated by fitting the Langmuir and Freundlich adsorption isotherms, and the relevant parameters are given in Table 1.

From Table 1, it was found that the adsorption process matched perfectly with the Langmuir isotherm model rather than the Freundlich isotherm. This can be inferred from R^2 values that can be calculated from the linear plots of these isotherms. A perfect match to Langmuir isotherm indicates that monolayer surface coverage occurred, and maximum monolayer adsorption was 49.04 mg g^{-1}. In the literature, several polymeric material has been studied recently. In a study carried out by unmodified polyvinyl alcohol for MB removal, adsorption capacity was found as 13.02 mg g^{-1} (Umoren et al. 2013). In another study using polydopamine, an adsorption capacity of 90.70 mg g^{-1} was reached (Fu et al. 2015). Polypyrrole coated Sawdust was used for the MB adsorption by Ansari and Mosayebzadeh yielding an adsorption capacity value of 34.36 mg g^{-1}. Rubber/chitosan blends were also utilized as an polymeric dye adsorbent material with 1.00 mg g^{-1} adsorption capacity (Johns and Rao 2011). Polyethylene-based nanocomposites have also been tried to remove the MB from the water, having adsorption capacity of 48.80 mg g^{-1} (Fagundes et al. 2019). Recently, graphene oxide-based polymeric composites have been the focus of research and have been studied for this type of adsorption, and dye removal capacity was determined as 19.20 mg g^{-1} (El-Sharkaway et al. 2019). The adsorption capacity of CPAM at 49.04 mg g^{-1} appears to be a promising alternative when compared with the adsorbent capacities studied by other researchers mentioned above.

Linear fitting parameters of pseudo-first order and pseudo-second order kinetic models are listed in Table 2. From these parameters, it can be concluded that pseudo-first order kinetic model explains the adsorption process better than pseudo-second order kinetic model. However, by taking into consideration of the R^2 values obtained from the adsorption of MB, it cannot be a wrong assumption to say that both kinetic models are simultaneously correct for the adsorption process. Therefore, MB molecules and water molecules are in a competition during the transfer to the attraction centers of the CPAM (Omer et al. 2018). However, according to the values given in Table 2, q_e for the pseudo-first order kinetic is higher than that of pseudo-second order kinetic. It probably suggests that water molecules are hindered from getting into the matrix by the repulsion of hydrophobic PVDF–HFP polymeric branches. This situation favors the attraction of MB molecules to the centers rather than water molecules. According to the basic theory of the reaction kinetics, If the MB molecules are attracted to the polymer matrix rather than the water molecules, the only changing concentration is to be the MB concentration. Water concentration does not change (due to the excess amount when compared to the MB) during the adsoprtion process which is a sign of pseudo-first order kinetics.

Table 2 Kinetic parameters of MB adsorption on CPAM

Model	Parameters	Methylene blue
Pseudo-first order	q_e (mg g^{-1})	5.0571
	k_1 (min^{-1})	0.0015
	R^2	0.9748
Pseudo-second order	q_e (mg g^{-1})	1.5623
	k_2 (g mg^{-1} min^{-1})	0.0066
	R^2	0.9341

Table 3 Thermodynamic parameters of adsorption

Temperature (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol K^{-1})
277	− 5.41		
298	− 10.24	58.30	0.23
323	− 15.99		

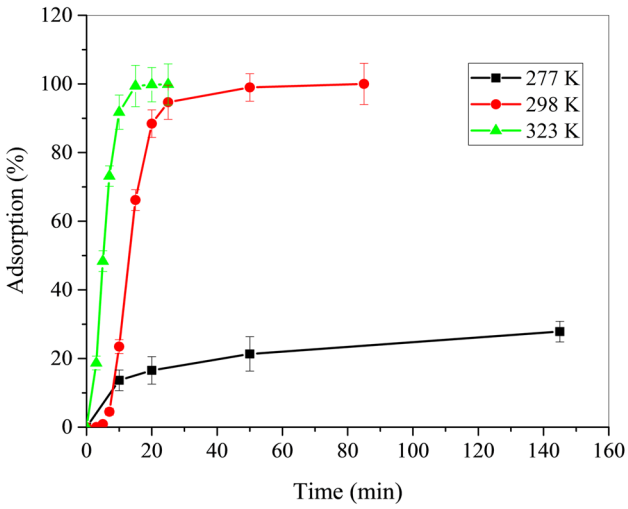

Fig. 4 Effect of temperature on the adsorption yield

Thermodynamic parameters of adsorption are given in Table 3. According to the data, Gibbs free energies of the adsorption ($\Delta G°$) were found as − 5.41, − 10.24 and − 15.99 for 277 K, 298 K and 323 K, respectively. The negative sign showed that adsorption occurs spontaneously due to strong interaction between positively charged MB molecules and carboxylic acid groups.

However, the adsorption temperature ($\Delta H°$) has a positive sign indicating the endothermic nature of the adsorption. MB adsorption begins only after a small heat absorption overcoming the van der Waals forces between polymeric chains. This creates extra surface for the adsorption process. (Holliday and Robinson 1973). This can also be understood from the negatively increasing tendency of Gibbs free energies with increasing temperature. As the temperature of the process increases, chain mobility of the polymeric material (CPAM) increases. Thus, the transfer of MB molecules to the adsorption sites becomes easier. In the Fig. 4, it can be seen that temperature increases the adsorption yield and rate, resulting in fast equilibration. Entropy ($\Delta S°$) change of the process was found very small (0.23 kJ mol K^{-1}) suggesting that adsorption causes no disorder. MB molecules meets the adsorption sites in a regular manner in which one adsorption site is not filled before the previous one is filled completely.

Removal of MB after adsorption was also carried out by immersing into concentrated sulfuric acid to identify the mechanism of adsorption. MB removal from CPAM was successfully observed. Removal of MB in acidic pH proved that adsorption of MB molecules relies on ion-exchange mechanism. In neutral pH, MB molecules replace the hydronium ions on the carboxylic acid groups causing adsorption. On the other hand, in acidic pH values, hydronium ions replace the MB molecules for desorption. By taking into consideration of the above mentioned thermodynamic parameters and ion-exchange mechanism, the adsorption of MB on CPAM can comfortably be claimed to be physical in nature and based on electrostatic attraction.

Conclusion

A novel polymeric composite material (CPAM) was effectively functionalized by sulfuric acid hydrolysis of methacrylate groups on polymethylmetacrylate in polyvinylidene fluoride–hexafluoropolypropylene matrix for the removal of methylene blue from aqueous solutions. The equilibrium data for MB adsorption on CPAM were in agreement with Langmuir isotherm model, and the adsorption onto CPAM was suggested to be an endothermic process (ΔH: 58.30 kJ mol^{-1}). The process was in harmony with pseudo-first order kinetic model with adsorption rate constant (k_1), 0.0015 min^{-1}. From the Langmuir linear plot, maximum monolayer adsorption capacity was determined as 49.04 mg g^{-1} which was superior or equal to the results of some recent studies. Adsorption process followed an ion-exchange mechanism and was depended on temperature. The increasing temperature supported the adsorption process and reduced Gibbs free energy down to − 15.99 kJ mol^{-1} at 323 K, a sign of spontaneity. The proposed material is a good candidate for economical treatment of waste waters without leaving any adsorbent residue, eliminating heavy and costly filtration steps.

Compliance with ethical standards

Conflict of interest The authors declare that there is no confict of interest regarding the publication of this article.

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