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Adsorption Study of Methylene Blue And Rhodamine B From Aqueous Solution By Hydrated Amorphous Titanium Dioxide

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ABSTRACT

Adsorption removal of cationic dye Methylene blue (MB) and Xanthene dye Rhodamine B (RhB) from an aqueous solution by using hydrous TiO_2 *was investigated at different time intervals. Hydrated titanium dioxide Ha-*TiO_2 *has been prepared by Hydrolysis of Titanium tetra butoxide with 1:1 aqueous ammonia solution. The calcinated powder showed a particle size in the nm region. The obtained product was characterized by XRD, SEM, TGA, DSC, BET and FTIR techniques. The results showed that, the product was in the form of hydrated amorphous titanium dioxide,* $TiO_2 1.06H_2O$ *(Ha-* TiO_2*) and the BET surface area is* $125.67 m^2/g$*. The sample as prepared showed excellent ion-exchanger for the adsorption removal of MB and RhB. Ion exchange studies on 50ml aqueous solution containing dye with 100mg of dispersed exchanger indicates adsorption 76.3% of MB and 39.6% of Rh-B in 90 and 120 minutes respectively.*

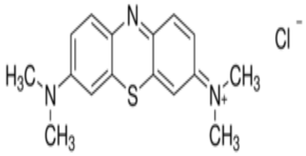
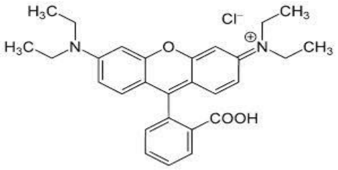
Keywords: Hydrous titanium dioxide; Rhodamine B; Methylene blue; Adsorption; Co precipitation.

INTRODUCTION

The textile industries consume enormous amounts of water during dyeing and finishing operations. Typical medium scale textile factories produce approximately $1000m^3$ of waste water per day. It is estimated that around 30% of the applied dyes remain unfixed and are discharged in the effluent. Dye bearing waste waters is toxic for environment since dyes are stable compounds and may cause carcinogenesis [1]. The presence of coloring material in water system blocks the penetration of sun light and oxygen which are both essential for various aquatic for us of life. Moreover, even small traces of the non-biodegradable and highly toxic dyes can prove harmful to the mankind. Hence, the removal of color synthetic organic dyestuff from waste effluents becomes major concern in environmental protection. Consequently, many treatment processes have been used for dye wastewater treatment including biodegradation [2], coagulation and flocculation [3], reverse osmosis [4], photo catalytic degradation [5], photo-Fenton processes [6], and adsorption [7]. Due to the water-solubility and non-biodegradable nature of dyes, adsorption has been considered as a better approach than these other types of treatment methods. Because the conventional methods for color removal are biological oxidation and chemical precipitation [8-10]. But these processes are not always effective and economic where the solute concentrations are very low. Moreover, most of the synthetic organic dyes undergo very slow biodegradation. Currently the sorption technique is proved to be an effective and attractive process for the treatment of dye containing wastewater [11-13]. Also, this method will become inexpensive, if the sorbent material used is of cheaper cost and does not require any expensive additional pretreatment step.

Among the dyes in commercial use, MB and Rh-B are extensively used for many applications. Although MB is seen in some medical uses in large quantities, it can also be widely used in coloring paper, dyeing cottons, wools, coating for paper stocks, etc. Though MB is not strongly hazardous, it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans [14-15]. Rh-B has moderate wash and light fastness properties on wool. It's also a useful analytical reagent for the detection and determination of metals. However, the use of Rh-B as a food color has been discontinued for a number of years on account of its suspected carcinogenic nature [16]. Titanium dioxide (TiO_2), encompassing all its three crystal forms, has wide applications in various fields. One of the most recent applications is as a photo catalyst [17-18] .Another promising aspect is as an inorganic ion exchange and sorbent due to its high chemical stability and high ion exchange capacity, which may find application in solid phase extraction (SPE). The study centered around the latter aspect usually involving adsorption of Rhodamine B and Methylene blue on the titanium dioxide surface. TiO_2 is used in these studies were in the form of anatase. Ha-TiO_2 powder was mostly present in an amorphous form with some hydrated water molecules. Its surface area was also significantly higher than that of commercially available anatase / rutile or P25 due to its amorphous morphology.

In the present paper describes adsorption characteristics of MB and Rh-B from aqueous solution use of hydrated amorphous TiO_2 (Ha- TiO_2).

Dye	**Molecular structure**	**Molecular formula**	**Molecular weight in g mol^{-1}**
MethyleneBlue (MB)	$C_{16}H_{18}N_3SCl$		**319.85**
Rhodamine-B (Rh-B)	$C_{28}H_{31}ClN_2O_3$		**479.02**

MATERIALS AND METHODS

Materials: Titanium tetra butoxide and Iso amyl alcohol were purchased from Sigma Aldrich (AR) and Merck (AR), respectively and were used to prepare hydrous Titanium dioxide. Model dyes MB & Rh-B were purchased from Loba and Himedia were used to prepare stock solutions (1000mg/L in aqueous solution).

Synthesis of adsorbent: Hydrous Titanium (IV) dioxide was prepared by slow addition of 1:1 ammonia solution from burette to the beaker containing mixed solution of Titanium tetra butoxide and iso amyl alcohol in the 1:1 molar ratio with constant stirring after 1 hour stirring the stirred solution was dried at 80^{o}C on magnetic stirrer to evaporation. The dried mass was then calcined at 400 ^{o}C for 4 h. The resultant powder was ground for homogeneity and used for phase identification, stored in bottles for uses. No chemical or physical treatments were used prior to adsorption experiments.

Characterization of adsorbent: Phase purity of the calcined powder was investigated with X-ray diffractometer (PANalytical-X pert PRO) at room temperature, using nickel filtered Cu-Kα,radiation (λ=1.54059A^o),with a scan rate of 2^o min^{-1}. Micro structural and elemental investigation of the sample was performed on the powdered sample using SEM Morphological studies have been carried out using Lica-S440I Field Emission Scanning Electron Microscope (FESEM) by drop casting ethanol dispersed samples on a silicon wafer under high vacuum with an accelerating voltage of 10 kV. A Mettler Toledo TGA/SDTA851^e model thermo balance with star^e software was used for the thermo gravimetric analysis. A Mettler Toledo DSC 823^e model with star^e software was used for the differential scanning calorimetric studies. Fourier transforms infrared spectroscopy (FTIR) using the potassium bromide (KBr) pellet technique and a Bruker FTIR spectrometer. The specific surface area was measured by the BET method using a high speed surface area analyzer (Micro-metrics 2200 model).

Adsorption experiments: Adsorption experiments were carried out in a beaker containing 100 mL of MB solution (5mg L^{-1}) containing 100mg of the exchamger. Then the solution was stirred on KEMI water bath incubator shaker in dark at room temperature, 5 ml aliquots were pipetted at different time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. The filtered solutions were analyzed using a UV-Vis Spectrophotometer (Shimadzu model UV-1601) by monitoring the absorbance changes at a wavelength of maximum absorbance 664 nm. The same procedure has been adopted for Rh-B at a wavelength of maximum absorbance at 554 nm. The amount of adsorbed MB and Rh-B at any time Qe (mg/g) was calculated using following Equation

$$Qe = \frac{(Co - Ce).V}{m}$$

Where, C_0 and C_e are the initial and liquid-phase concentrations at any time t of dye solution (mg L^{-1}) respectively, V is the volume of dye solution (L) and m is the mass (g) of the Hy-TiO_2 used.
The removal efficiency, R (%) (Or) %of adsorption the system was expressed as Equation

$$\%Re = \frac{(co - ce).100}{Co}$$

RESULTS AND DISCUSSION

X-ray diffraction pattern of the resultant powder obtained from the mixture of isoamyl alcohol and titanium tetra butoxide were hydrolyzed by 1:1 ammonia solution, dried and calcinated at 400^{O}C for 4 h as shown in fig 1. All peaks in XRD pattern could be indexed to anatase TiO_2 (JCPDS File no.86-1157).

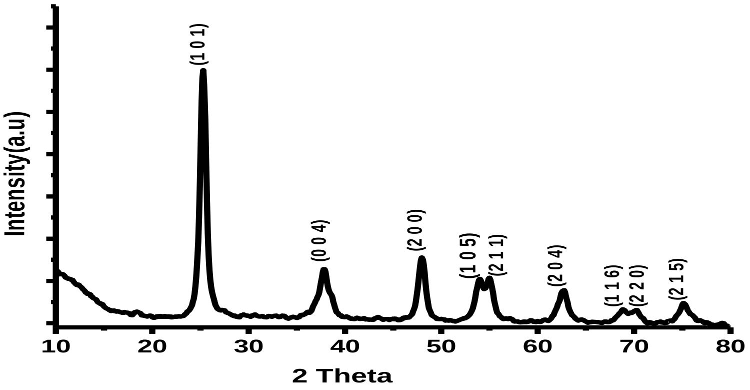


Fig.1 XRD pattern of Hydrous TiO_2

Micro structural investigation of the sample was performed on the powdered sample using FESEM showed in fig 2(a) reveals no characteristic morphology and the observed particle size is in the nm range. Purity of the Ha-TiO_2 was checked by EDS by using silicon probe showed in fig 2(b), from which only the Ti and oxygen peaks are observed indicating no contamination by other species.

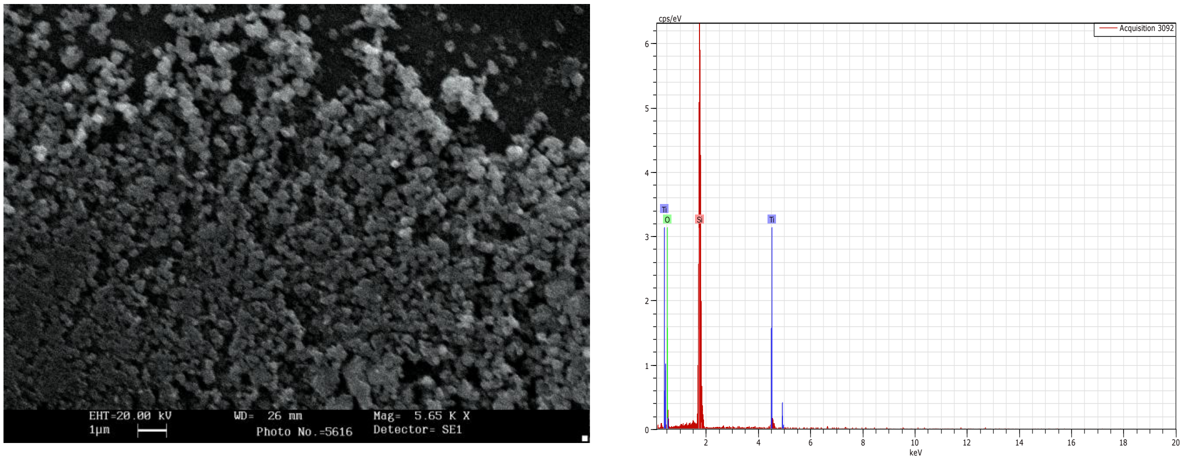


Fig. 2(a) SEM image and **(b)** Elemental dispersive spectra of calcined powder

The TGA curve of Ha-TiO_2 (Fig. 3a) shows less than 150°C of weight loss corresponds to the moisture quantity present. It is almost 10% of the respective ion exchange material. There is a gradual decrease in the weight in the range 50-350 ° C. Weight loss below 120° C corresponds to the loss of water molecules present in the ion exchange material. Above 120° C temperature the rate of decrease was slow and reached the completion at around 320 °C. The overall weight loss was 24.42% in the range 50-850°C. The majority of the weight loss was observed in the range of 30-320°C and that weight loss was around 22.42%.this corresponds to the liberation of mixed H_2O and NH_3 (OH and NH_4 as identified by FT-IR).

From the DSC data(fig 3(b)), the sample has possesses exothermic in nature at the temperature range 170-300°C. This data was exactly coincided with TG data. With this DSC data, as the sample could not only liberated the gases NH_3 and H_2O but also heat energy so that it is in the range 170-300°C. The DSC pattern of TiO_2 sample showed an endothermic peak at around 100°C. This could be because of the liberation or decomposition of water molecule from the sample itself from M. Kanna. et. al, exothermic peak for TiO_2

was observed at 426 °C. But the author has studied based on the DSC studies that the exothermic peak was observed but at around 457.12°C. Both the data's are closely said the nature of the exothermic material and the probable gases emitted at these temperature ranges from 426°C to 457°C. [19].

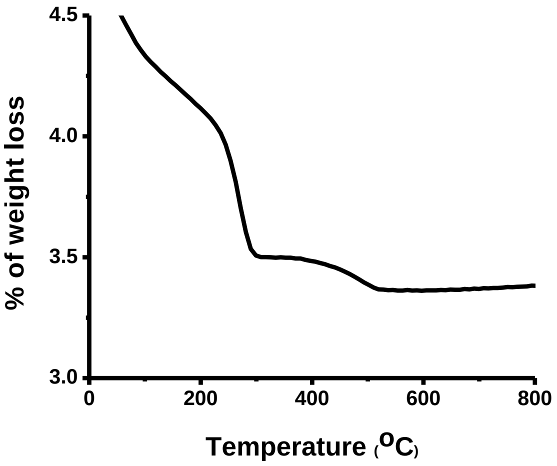
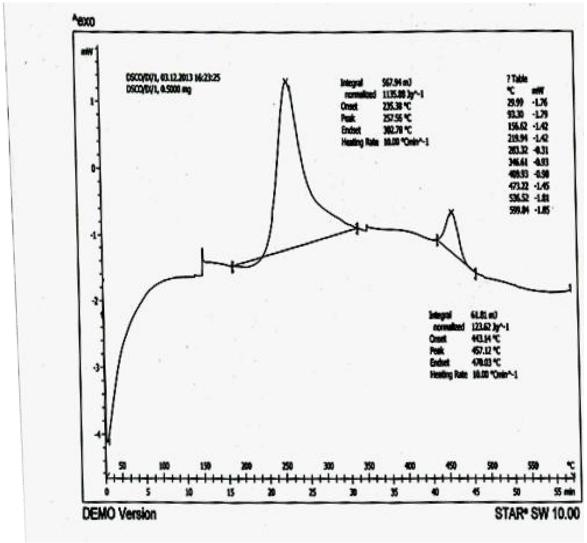


Fig. 3(a) TGA curve of Ha-TiO_2



3(b) DSC spectra of Ha-TiO_2

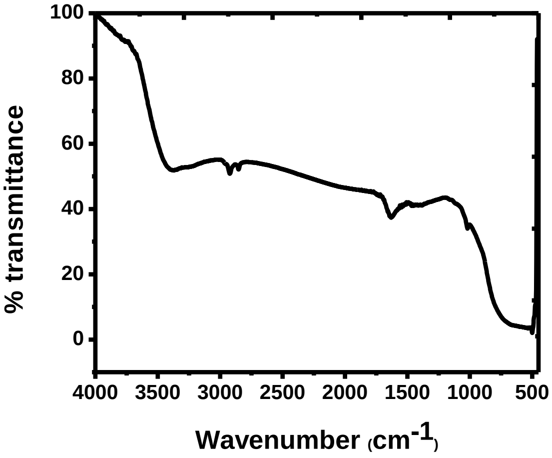


Fig. 4 Fourier transfer infra red spectra of calcined powder

The FTIR spectrum of Ha-TiO_2 (Fig 4) showed a large broad band at 3100-3600 cm^{-1} and rather narrow band at 1630 cm^{-1}. The broad band in the range of 3100-3600 cm^{-1} could be assigned to both δ_{OH} and δ_{NH} (stretching modes) while at 1630 cm^{-1} is due to δ_{OH} (bending mode) of hydroxyl (OH). The absorption at 442 cm^{-1} can be assigned to the δ_{Ti-o} (stretching modes) of Ti-O band. The BET surface area of Ha-TiO_2 was 125.67m^2 g-1. Samples of commercially available anatase/rutile and degusa-P25 were also measured and their surface areas were significantly lower than as prepared hydrous titanium dioxide (Ha-TiO_2) [20]

Effect of contact time: Fig 5 depicts the effect of the amount of Dyes (MB/RhB) adsorbed on the hydrous TiO_2 exchanger. The amount of MB adsorbed was rapid for first 30 min and there after it proceeded at slower rate and finally reached saturation. Where as in the case of RhB, rapid adsorption was observed up to 40 min, after that it proceeded at slower rate.76.3% of (5mg L^{-1}) MB, and 39.6% of (5mg L^{-1}) RhB was adsorbed after 90 and 120 minutes respectively.

Effect of Exchanger Dosage: The effect of hydrous TiO_2 adsorbent dosage on the removal of MB and RhB in illustrated in Fig 6. The percentage removal of MB/RhB increased with increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption active sites resulting from the increase dosage of the adsorbent.

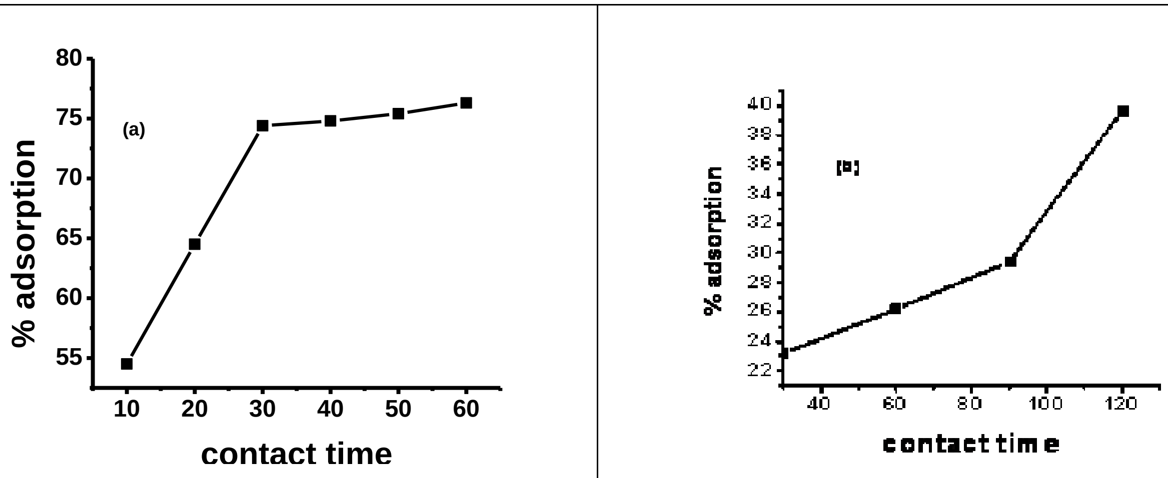


Fig. 5 Effect of contact time on the adsorption of MB (a) and Rh-B (b) on Ha-TiO_2

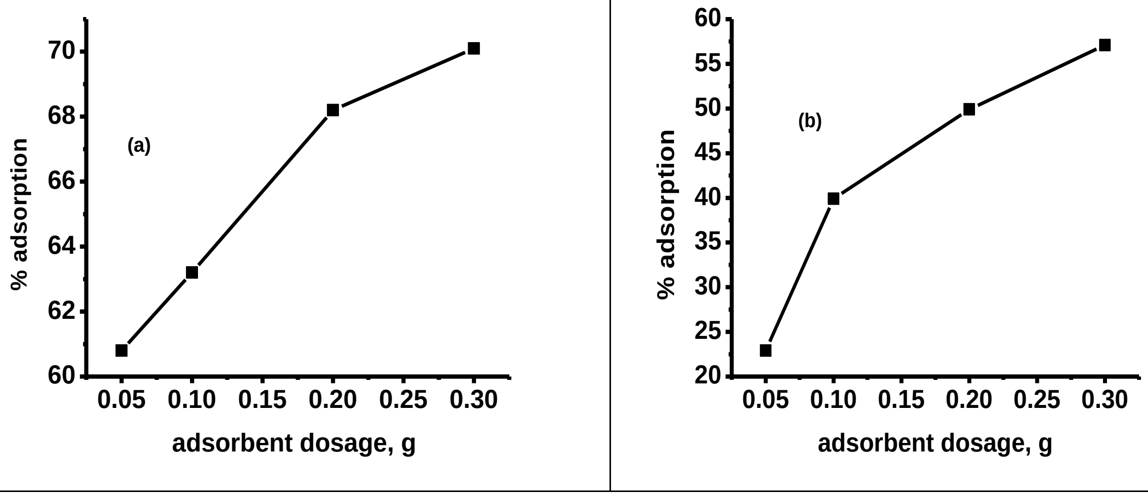


Fig. 6 Effect of adsorbent dosage on the adsorption of MB (a) and Rh-B (b) on Ha-TiO_2

Effect of pH: Fig 7. Shows the effect of pH on the adsorption of MB and RhB. The experiments were conducted at 5mg. L^{-1} initial dye concentration, 0.1g sorbent and 25^oC+1^oC as shown in fig 7. The equilibrium adsorption capacity was minimum at pH =7, and maximum adsorption observed at pH =8.for both MB and RhB. The lower adsorption of MB and RhB at acidic pH is due to the presence of excess H^+ ions competing with the cation groups on the dye adsorption sites. At higher pH, the Ha-TiO_2 possible negatively charged and enhances the positively charged dye cations through electrostatic forces of attraction. A similar result was reported for the adsorption of Rh-B onto TW [21].

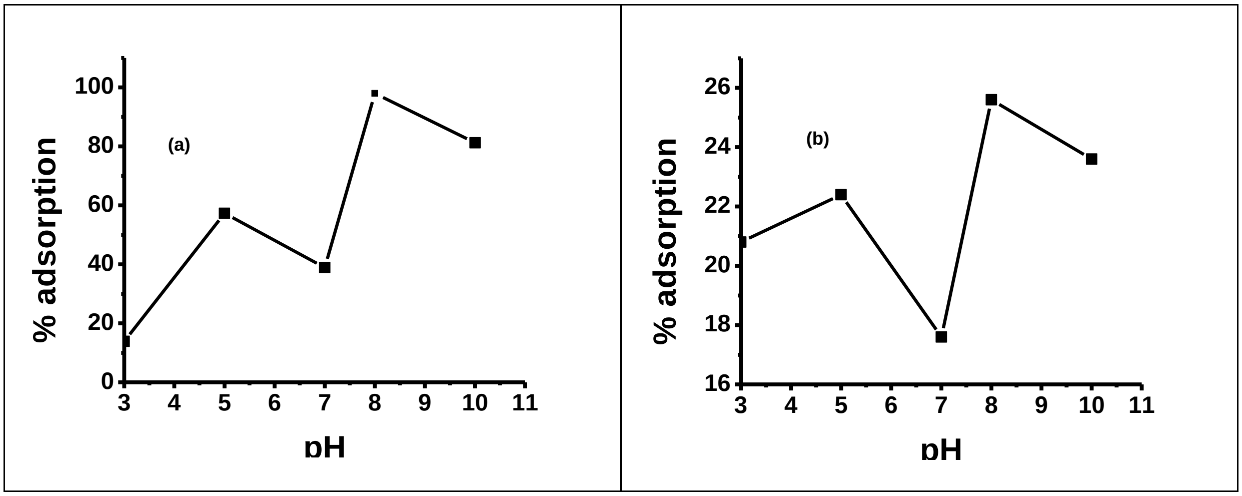


Fig. 7 Effect of pH on the adsorption of MB (a) and Rh-B (b) on Ha-TiO_2

APPLICATIONS

These results suggest that the use of these adsorbents is the simple and cost effective method and shows excellent adsorption removal properties on dyes for industrial applications.

CONCLUSIONS

Adsorption removal of cationic dye Methylene blue (MB) and Xanthene dye Rhodamine B (RhB) from an aqueous solution by using hydrous TiO_2 was investigated at different time intervals were studied. The Ha-TiO_2 powder was characterized using XRD, SEM, and BET surface area. The results showed that, the product was in the form of hydrated amorphous titanium dioxide with anatase phase, and the BET surface area of Ha-TiO_2 is 125.67m^2 g^{-1}. The sample as prepared showed excellent ion-exchanger for the adsorption removal of MB & RhB. Ion exchange studies on 50ml aqueous solution containing dye with 100mg of dispersed exchanger indicates adsorption 76.3% of MB and 39.6% of Rh-B in 90 and 120 minutes respectively. These results suggested that the simple and cost effective method and shows excellent adsorption removal properties on dyes for industrial applications.

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