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A New Ferric Chloride Modified Kaolin Coagulant and Its Application in Treatment of Methylene Blue Wastewater

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In this study, a new coagulant, ferric chloride modified kaolin (Fe-Kaolin) was used to treat the simulated methylene blue wastewater. The coagulant was characterized by powder X-ray diffraction and scanning electron microscopy. The effects of parameters, such as initial pH, coagulant dosage and dye concentration on methylene blue removal were also studied and the procedure was inspected by ultraviolet visible spectroscopy and chemical oxygen demand. The results showed that a maximum color and chemical oxygen demand removal efficiency of 99.64 and 90 %, respectively, for 0.12 g/L methylene blue wastewater were observed. Moreover, the environmental effect of the treated effluent was also studied.

Keywords: Coagulant, Ferric chloride, Kaolin, Methylene blue.

INTRODUCTION

Dyes and pigments are one of the problematic groups of pollutants. They are discharged from various industries such as dyestuff manufacturing, dyeing, printing and textile finishing[1,2]. Today more than 9000 types of dyes have been incorporated in the color index[3,4]. Methylene blue, an organic dye, has been widely used, including coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, medical purpose, *etc*[3]. Although it is not regarded as acutely toxic, but it has various harmful effects. High concentration of methylene blue contacting with eyes would cause corneal and conjunctiva injury to human beings[5]. Thus it has to be removed from wastewater before discharged.

Nowadays, there are many approaches to deal with dye wastewater, such as Fenton oxidation[6], activated carbon adsorption[7], chemical coagulation[8], ultrasonic synergistic degradation[9], membrane separation[10], electrochemical degradation[11], TiO_2 photocatalytic oxidation[12] and so on. Coagulation is widely employed for color removal. There are a number of conventional coagulants based on iron, such as $Fe_2(SO_4)_3$ or $FeCl_3$. When ferric ions are introduced into wastewater, hydrolyzation will be rapidly taken place in an uncontrollable manner, resulting in the formation of various iron species[13]. In recent year, adsorptive flocculation has been recognized as an effective method for organic compounds removal[14] and the interest in wastewater recycling is continuously growing because of ecological and economic consideration[15].

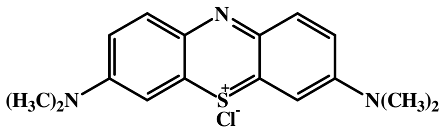
Ferric chloride is a good coagulant, but it is costly when adding it into the wastewater stream directly. Kaolin is a kind of inexpensive, environmentally friendly mineral with an excellent suspended ability in water. So $FeCl_3$ was fixed in the structure of kaolin to enlarge the contact proportion with pollutants, which consequently becomes more effective at a comparatively lower Fe dosage than the conventionally dosage.

The aim of the present work was to prepare a new adsorptive coagulant Fe-kaolin and test the ability in treating methylene blue wastewater. The effect of different parameters, such as initial pH, coagulant dosage and dye concentration on color and chemical oxygen demand removal efficiency were also studied.

EXPERIMENTAL

All chemicals used in the experiment were analytical grade and used without any further purification. Kaolin, provided by Shanghai Reagent Co., China, was composed of $Al_4[Si_4O_{10}](OH)_8$ (surface area: 20 m^2g^{-1} and pore volume: 0.5 cm^3g^{-1}).

Methylene blue, which is a basic dye, used as received and the structure is shown in **Scheme-I**.



Scheme-I: Molecular structure of methylene blue

Analytical methods: The crystallinity of the coagulant was determined by powder X-ray diffraction (XRD) D/Max-3c model (Rigaluc, Japan) using a scanning diffractometer of D/MAX-RA with Ni-filtered Cu K-radiation (λ = 1.5406 Å). Solid morphology and average crystal size were determined by scanning electron microscopy (SEM, Quanta 200, Holland) and a gold film was sputtered onto the sample prior to observation (ISI DS-130). Ultra-absorbance of the samples was monitored using a double beam UV-visible spectrophotometer (UV-7504, China). The chemical oxygen demand was chosen as the parameter by which to evaluate the process of coagulation and was determined according to standard methods.

Preparation of the coagulant: First, 10.5 g $FeCl_3$ was dissolved in 50 mL distilled water. Then, an aqueous dispersion of kaolin was prepared by adding 100.2 g kaolin to 500 mL distilled water with stirring. The solution obtained from the first step was added dropwise into the dispersion of kaolin with vigorous stirring. This suspension was stirred for 4 h followed by aging at room temperature in air for 30 h and air-dried at 353 K for 4 h. Then, the product was immersed in water in order to eliminate the residual chlorine ion and dried at 353 K for another 4 h. Finally, the dried material was calcined at 773 K for 4 h to immobilize the metal and ground into powder.

Adsorptive coagulation procedures: The adsorptive coagulation experiments were carried out using a jar test apparatus. Stock solution of methylene blue was prepared in distilled water and the pH value was adjusted with NaOH or H_2SO_4. Batch experiments were conducted at various pH (3, 7 and 11), catalytic dose (2.5, 5, 10 and 15 g) and dye concentration (0.12, 0.2, 0.33 and 0.41 g/L). In all schemes, 2 L wastewater was pumped and 5 mL was taken at every 10 min. Then the samples were examined by UV-visible and chemical oxygen demand.

RESULTS AND DISCUSSION

Characterization of the coagulant: As illustrated in Fig. 1, XRD studies indicate that Fe-Kaolin coagulant has a large amorphous structure with small traces of crystalliny. This observation is also supported by the SEM (Fig. 2), it is observed that the particles are mostly irregular in shape and a porous structure with bigger surface was formed.

Evaluation of adsorptive coagulation efficiency

Determination of optimal pH for adsorptive coagulation of methylene blue: The wastewater from textile industries usually has a wide range of pH values. Hence it is necessary to study the influence of solution pH on the methylene blue removal. To investigate these effects, the pH of the dye effluents was adjusted to 3, 7 and 11.

It can be seen in Fig. 3, after reaction for 25 min, the dye removal efficiencies were 79 % (pH = 3), 84 % (pH = 7) and

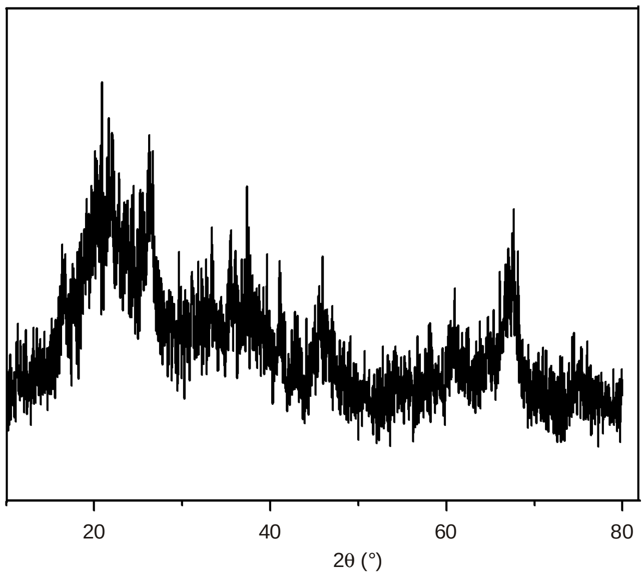


Fig.1. XRD pattern of Fe-Kaolin coagulant

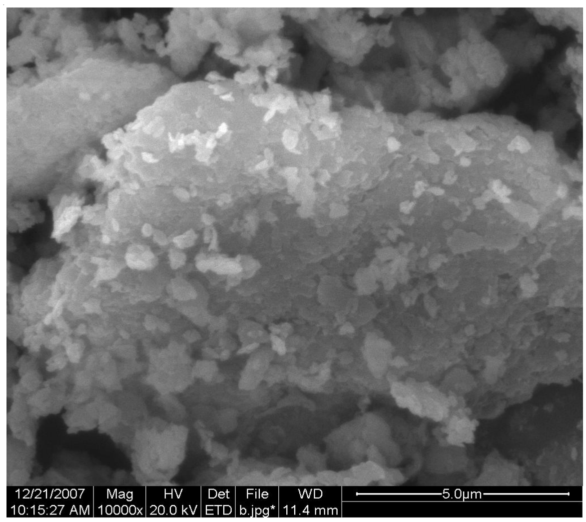


Fig. 2. SEM image of Fe-Kaolin coagulant

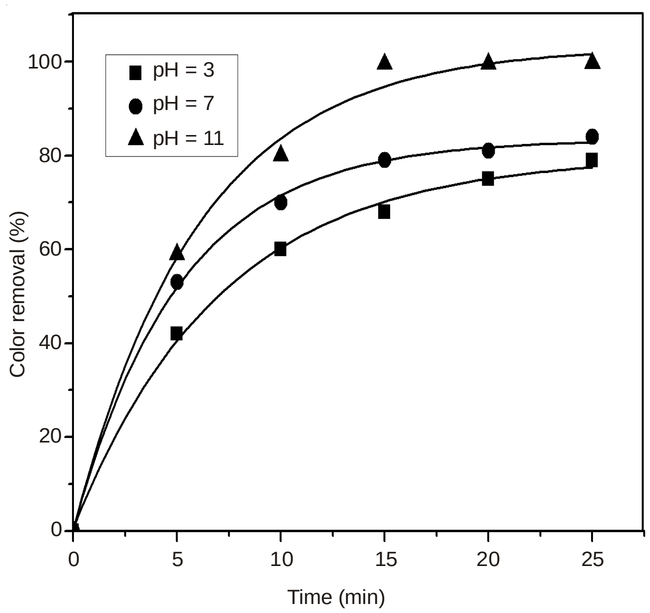


Fig. 3. Effect of initial pH value on the color removal efficiency (dye concentration, 0.12 g/L; coagulant dosage, 10 g)

99.7 % (pH = 11), respectively. Clearly, the dye removal efficiency increased with the pH increasing, which maybe due to that the Fe-Kaolin coagulant has higher activity in the alkaline condition. Besides, the chemical oxygen demand removal was another important parameter which should be investigated. It shows in Fig. 4, a higher chemical oxygen demand removal (94 %) at pH = 11 was obtained as compared with that of pH = 3 (52 %) and pH = 7 (70 %) and the increasing trend of chemical oxygen demand removal in consistent with the dye removal. Hence, it can come to the conclusion that pH = 11 is the best pH condition for the removal of methylene blue.

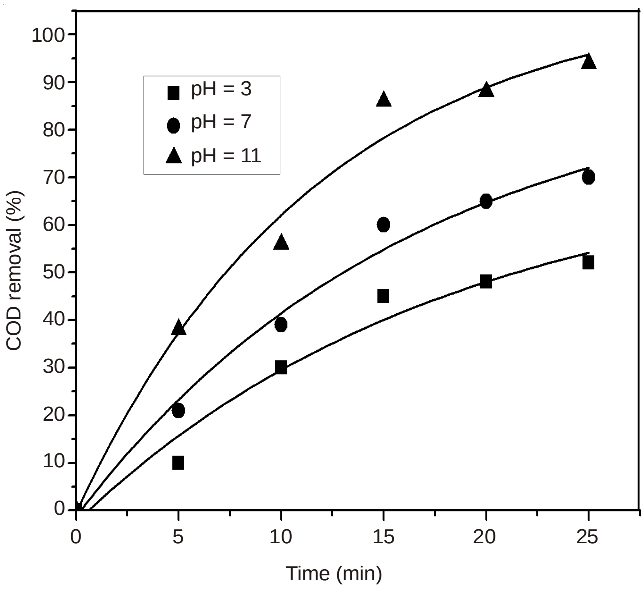


Fig. 4. Effect of initial pH value on the chemical oxygen demand removal efficiency (dye concentration, 0.12 g/L; coagulant dosage, 10 g)

Determination of optimal coagulant dosage for adsorptive coagulation of methylene blue: To optimize the coagulant dosage for the removal of dye and chemical oxygen demand from its aqueous solutions, coagulate reaction was carried out with different coagulant dosage (m = 2.5, 5, 10 and 15 g) at pH = 11 and the results are shown in Figs. 5 and 6. It can be observed that an increasing in coagulate efficiency has been obtained with the increasing of the coagulant dosage. The removal of dye (Fig. 5) increased from 68 % (m = 2.5 g) to 99.6 % (m = 15 g) and chemical oxygen demand removal (Fig. 6) increased from 49 % (m = 2.5 g) to 91 % (m = 15 g), respectively. Furthermore, when the coagulant dosage increased from 10 to 15 g, the dye removal and chemical oxygen demand removal are almost the same, thus, a coagulant dosage with m = 10 g can be assumed to be an optimum value under the treatment conditions. It can be interpreted as follows: with the increasing of the coagulant dosage, more coagulant particles available for the methylene blue molecules and consequently higher coagulate efficiency takes place. When the coagulant dosage is 10 g, all methylene blue molecules in the system almost have been removed. Hence, the additional coagulant is useless when the amount of coagulant beyond a certain limit.

Determination of optimal dye concentration for adsorptive coagulation of methylene blue: The effect of dye concentration on the color removal and chemical oxygen demand

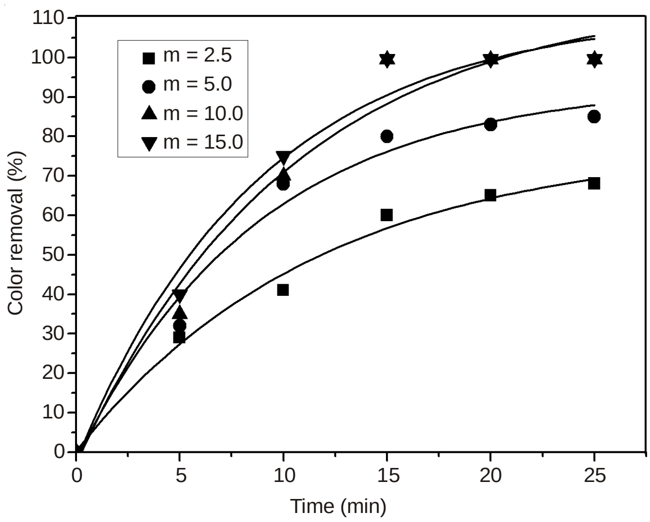


Fig. 5. Effect of Fe-kaolin coagulant dose on the color removal efficiency (dye concentration, 0.12 g/L; pH, 11)

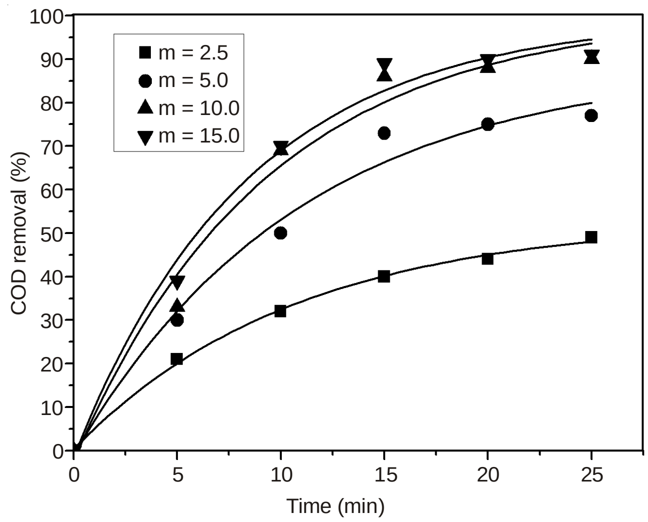


Fig. 6. Effect of Fe-kaolin coagulant dosage on the chemical oxygen demand removal efficiency (dye concentration, 0.12 g/L; pH, 11)

removal were also tested, experiments were conducted by varying the methylene blue concentration from 0.12 to 0.2, 0.33 and 0.41 g/L at pH = 11 and constant coagulant dosage (10 g). From Figs. 7 and 8, it can be seen that, a maximum removal of dye (99.64 %) and chemical oxygen demand (90 %) for 0.12 g/L methylene blue wastewater are observed with coagulant dosage 10 g in 2 L wastewater at pH = 11. This can be explained by the ratio of coagulant dosage with methylene blue molecules. With the constant coagulant dosage, when increasing the dye concentration, the dye and chemical oxygen demand removal was decreased. In other words, when the amount of coagulant is constant, the number of active sites is constant. By increasing the amount of methylene blue, the removal percent should be decreased due to the limitation of the active sites.

UV-visible absorption spectra: UV-visible absorption spectra at different time (Fig. 9) were obtained to study the destruction of methylene blue molecules at pH = 11 with coagulant dosage 10 g and dye concentration 0.12 g/L. Two peaks in the visible region at about 612 and 665 nm due to heteropolyaromatic linkage were observed in the initial

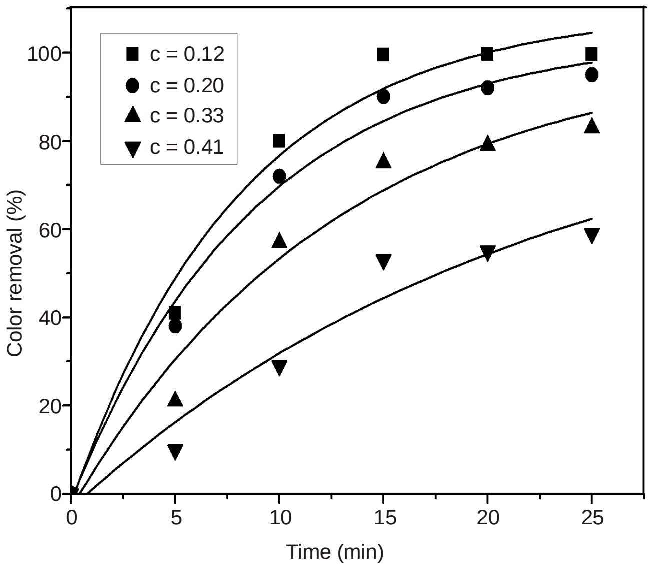


Fig. 7. Effect of dye concentration on the color removal efficiency (coagulant dosage, 10 g; pH, 11)

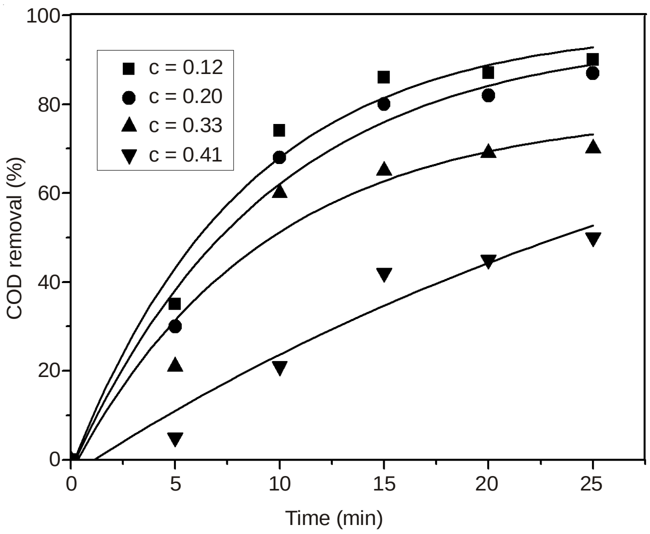


Fig. 8. Effect of dye concentration on the chemical oxygen demand removal efficiency (coagulant dosage, 10 g; pH, 11)

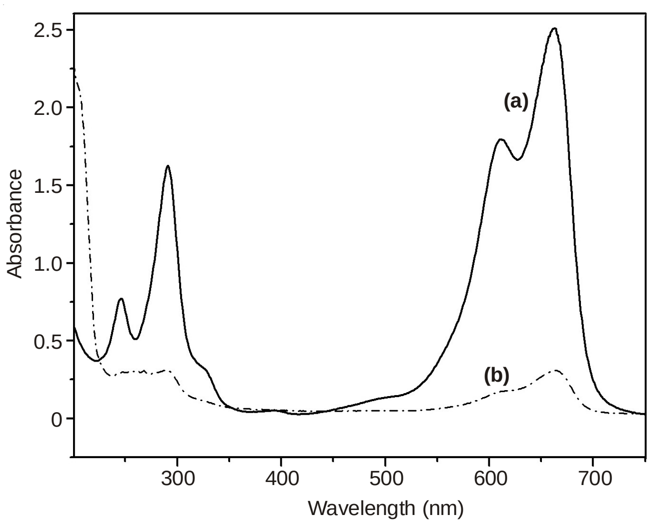


Fig. 9. Spectral change of absorption: (a) initial methylene blue solution, (b) after treated 15 min (dye concentration, 0.12 g/L; coagulant dosage, 10 g; pH, 11)

methylene blue wastewater. The absorbance at 291 and 246 nm were considered as evidence of aromatic groups in the methylene blue molecules. With the time prolong, these four peaks almost disappeared in 15 min, indicating the the destruction of heteropolyaromatic linkage and aromatic groups structure was happened. In other words, the degradation of methylene blue has been carried out at the first 15 min treatment, which was consistent with results of the chemical oxygen demand and removal of dye.

Environmental estimate: The environmental effect of the discharged pollutants from the pulp and paper industry, such as water, air and land have been widely studied[16,17], but concerning the effect of secondary treated dyeing water on irrigation is less. In order to estimate the treated methylene blue effluent whether can be used to irrigate, the amount of chlorophyll a and b were determined by a spectrophotometer at wavelengths of 665 and 649 nm and the experiment was conducted in laboratory. The plants were planted 2 cm apart and the irrigation was supplied once a day at 8:15 am. Leaves were collected per 2 h a day from 8:15 am to 6:15 pm. According to the Lambert Beer law, the concerned formulas are expressed as follows:

$$c_a(\text{mg/L}) = 13.7A_{665} - 5.76A_{649} \quad (1)$$

$$c_b(\text{mg/L}) = 25.8A_{649} - 7.6A_{665} \quad (2)$$

$$M_a(\text{mg/L FW}) = c_a \times 25/1000 \times 0.2 \quad (3)$$

$$M_b(\text{mg/L FW}) = c_b \times 25/1000 \times 0.2 \quad (4)$$

$$M_{total}(\text{mg/L FW}) = M_a + M_b \quad (5)$$

c_a, c_b are the concentration of a, b. A_{665}, A_{649} are the absorbance of a, b at wavelength of 665 and 649 nm and M_a, M_b, M_{total} are the content of chlorophyll a, b and total. It can be seen from Fig. 10, when the treated wastewater was irrigated into the soil, the chlorophyll content can reach maximum at 12:15 p.m. and then gradually decreased, indicating that the overall chlorophyll content was accorded with the photosynthesis. It showed that the treated wastewater has no bad effect on the content of chlorophyll and the treated wastewater could totally be recommended to irrigation in lawn.

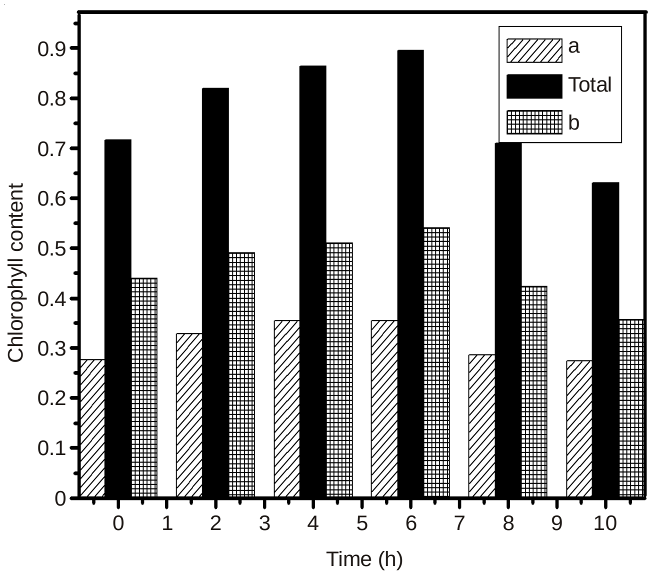


Fig. 10. Changes of chlorophyll content after irrigation by the treated methylene blue effluent

Conclusion

In this study, a new adsorptive coagulant, which was prepared by ferric chloride with kaolin, was used to treat the dye methylene blue wastewater. It is evident from the above studies that the Fe-Kaolin coagulant can be successfully employed for the removal of methylene blue. This is a simple and economical method for methylene blue wastewater treatment and can be recommended for methylene blue treatment in industry. A maximum removal of color and chemical oxygen demand for 0.12 g/L methylene blue wastewater are 99.64 % and 90 %, respectively, with coagulant dosage 10 g at pH = 11. The advantage of this coagulant compared with the commercial $FeCl_3$ salts coagulant is that a comparatively lower $FeCl_3$ dosage was fixed up in the structure of kaolin, but the contact proportion with pollutant is very large.

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