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Advanced purification of methyl orange high concentration

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ABSTRACT

A simple process, vacuum distillation, was utilized for purification of methyl orange (MO) as dye effluent. The dye effluent characteristic of high chemical oxygen demand (COD) value and high chromaticity is difficult to treat for the industrial wastewater treatment. In our work, the effect of some factors on the distillation efficiency (DE), including pressure, concentration and the surfactant based on the optimal conditions was evaluated. The results showed that the COD removal for 99.57% was obtained when the concentration of MO is 2000 mg l^{-1} at the pressure of 0.070 MPa. Moreover, the polyacrylamide (cationic) used in initial concentration of 500 mg l^{-1} show satisfactory removal efficiency in the further test.

Keywords: Methyl orange; Dye effluent; Surfactant; Vacuum distillation; Chemical oxygen demand (COD); Distillation efficiency (DE)

1. Introduction

Dye plays a very important role in our daily life, which is used in many industries widely, such as food, paper, carpets and textiles [1]. While Dye makes our life colorful, it causes severe environmental problem. It is reported that approximately 2% of 1 ton dye discharge every year [2]. Among the organic synthetic dyes, azo dye is the most widely used one. In addition, MO is a representative contamination in azo dye wastewater, which shows poor biodegradability, high COD and high chromaticity [3].

Due to environmental requirements in recent years, several conventional wastewater treatment methods have been used, including physical, chemical and biological methods [4–14]. However, the biological methods are very effective for the disposal of wastewater but they are ineffective if recalcitrant organic compounds present [14]. Meanwhile, the physical and chemical technology displayed inadequately in the purification for wastewater with high pollutants. Recently, wet air oxidation has been used as an effective process to reduce COD of wastewater. However, the high energy requirement and the use of high-pressure reactors with associated equipment make the treatment of large volume of wastewater unviable and uneconomical [15]. Thus, they have individual advantages, but shows powerless on the advanced purification to effluent with high concentration [4]. As a result, an effective approach to purify the dyeing wastewater should be developed.

On the other hand, distillation is considered as an effective separation technology, which was applied to the desalination of seawater and the preparation of ultra-pure water [16–20], so distillation is an appropriate approach to advance purify the MO wastewater with high concentration [20]. However, it is noteworthy that

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dyeing wastewater with high concentration was characteristic of high boiling point (BP) and high COD value in the distillation, which require for high energy cost to purify the effluent [21].

In our work, vacuum distillation process was applied in the advanced purification treatment of MO wastewater, which can reduce the BP under a certain pressure and no additional pollution be produced. Here, some parameters including BP, COD, COD removal, fraction absorbance, DE and recovery efficiency (RE) were investigated under different pressure and concentrations, in order to find the optimum operation conditions. Furthermore, further tests were carried out to analyze behavior of different surfactants under the optimum operation condition, due to the existence of surfactants in the industrial effluent [22].

2. Experimental

2.1. Reagents and instruments

MO of analytical grade was purchased from Tianjin Reagent Co., China; polyacrylamide of chemical grade was obtained from Chengdu Institute of the Joint Chemical Reagent, China; Sodium dodecylsulfonate (SDS), chemical grade, was obtained from Xi'an Reagent Co., China.

The work adopted a usual lab-scale vacuum distillation unit (Yarong Biochemical Instrument Factory in Shanghai, China) with a round-bottomed flask immersed in a heating bath. The vapor was condensed in a water-condenser and collected in a receiving flask. The process was conducted at low pressure by means of a vacuum pump provided with a pressure control device. The wastewater was heated to the BP and the operating vacuum degree was immovable at a certain pressure [20].

COD was evaluated by COD testing (5B-3, Lianhua Technology). UV-visible spectrophotometer (UV-7504PC) was used for the absorbance determination.

2.2. Vacuum distillation experiment

Different concentrations of MO solution were prepared, and the concentration of solution was 120 mg l^{-1}, 180 mg l^{-1}, 240 mg l^{-1}, 500 mg l^{-1}, 1000 mg l^{-1} and 2000 mg l^{-1} respectively.

An 80 ml of MO (120–2000 mg l^{-1}) solution was added into the round-bottomed flask, then the vacuum pump was adjusted at a certain vacuum degree (0.067, 0.070, 0.075, 0.080 and 0.085 MPa) respectively. During the continuous vacuum distillation experiment, the fraction was collected when solution was heated to a desired temperature (BP). 0.0625 mg l^{-1} SDS and polyacrylamide were selected as the surfactants were investigated [21].

Meanwhile, BP (°C), COD and COD removal of the fraction, absorbance, DE and RE were also investigated.

The COD removal efficiency at any distillation time t, Re_{COD} is calculated as follows:

$$Re_{COD} = \left(1 - \frac{COD_t}{COD_0}\right) \times 100\% \quad (1)$$

where COD_0 is the initial COD value of raw wastewater and COD_t is the concentration of COD of fraction at any time t.

DE and RE are calculated as follows:

$$DE = \frac{V_b}{t} \quad (2)$$

$$RE = \frac{V_b}{V_a} \times 100\% \quad (3)$$

where V_a (ml) is the volume of raw wastewater and V_b is the volume of fraction, t (min) stands for the time of distillation.

3. Results and discussion

3.1. The effect of initial concentration

3.1.1. The effect of initial concentration on BP

The experiments were performed with different concentrations (120, 180, 240, 500, 1000 and 2000 mg l^{-1}) under different vacuum degree (0.067, 0.070, 0.075, 0.080 and 0.085 MPa), respectively. Fig. 1 showed the BP trend of the effluents. It can be observed clearly that the BP values of the effluents increased when the concentrations ranged from 120 to 1000 mg l^{-1}, and then dropped

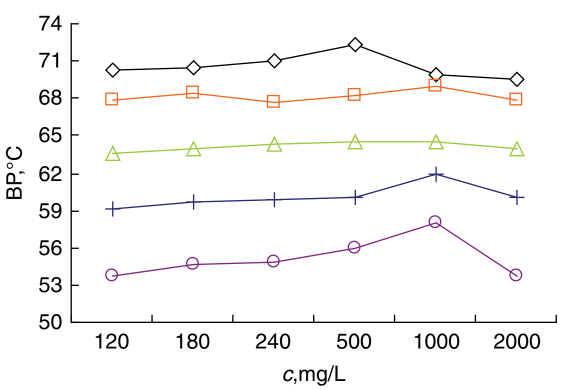

Fig. 1. The effect of initial concentration on BP under different vacuum degree. -◇-: 0.067 Mpa; -□-: 0.070 Mpa; -Δ-:0.075 MPa; -+-: 0.080 Mpa; -O-: 0.085 MPa.

as the concentration reached to 1000 mg l^{-1}. During the continuous vacuum distillation experiment, when the returning velocity of molecule reached to the velocity of escaping, the temperature of the solution is BP. The energy of evaporation rise with the force between the molecules increases. The ascent of BP may be ascribed to the alteration of the dye molecules force as the increasing of the solution concentration. While the repulsive force is greater than the attractive force, the BP should be declined [23].

3.1.2. The effect of initial concentration on absorbance

Fig. 2 displays the absorbance variation trend of the effluents at different concentrations. It can be seen that the effluents absorbance increased slightly when the concentration was lesser than 500 mg l^{-1}, and the color removal of the effluents were higher than 95% after treatment. Thus, it can come to the conclusion that the vacuum distillation process is an effective approach for the treatment of MO wastewater. The low absorbance may result from the short distillation time and the BP difference between water and MO molecular (>30°C). However, the absorbance of the effluents >500 mg l^{-1} increased sharply at the vacuum degree of 0.067 MPa and 0.085 MPa, it may rest upon the longer distillation time and the higher temperature of bath what can result in the entry of the organic substance into the gas phase.

3.1.3. The effect of initial concentration on COD and COD removal

In order to evaluate the quality of effluents after treatment, the variation trend of the COD and COD removal of the effluents are shown in Fig. 3. It was obvious that all COD values after treatment can meet the Wastewater Discharge Regulations, and the COD removal reached to 99.57% and the lowest value was 92.76%, indicating that vacuum distillation process for MO dye wastewater is an efficient method. More importantly, the experiment proved vacuum distillation method is applicable to high concentration of dye wastewater treatment.

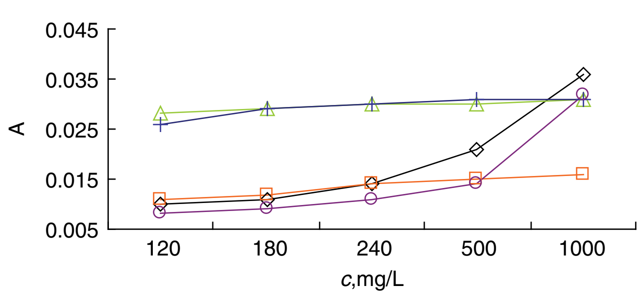

Fig. 2. The effect of initial concentration on absorbance at different vacuum degree. -◇-: 0.067 Mpa; -□-: 0.070 Mpa; -Δ-:0.075 MPa; -+-: 0.080 Mpa; -○-:0.085 MPa.

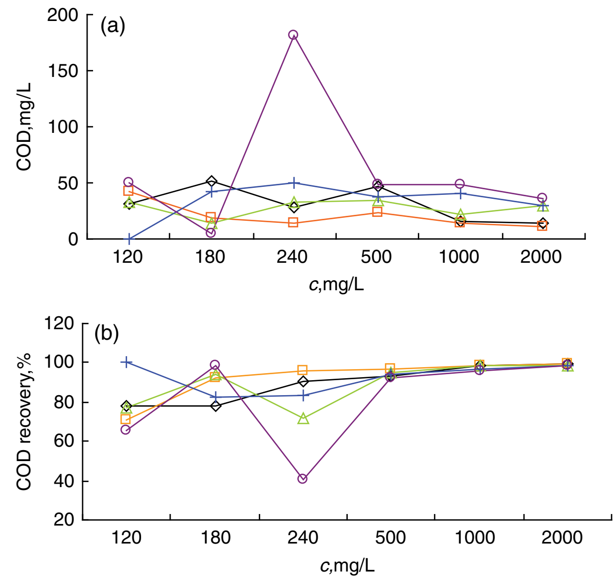

Fig. 3. (a) COD, (b) COD removal for the different concentration at different vacuum degree. -◇-: 0.067 Mpa; -□-: 0.070 Mpa; -Δ-:0.075 MPa; -+-: 0.080 Mpa; -○-:0.085 MPa.

Table 1 shows the optimal conditions and the treated results for the different dye concentrations.

3.1.4. The effect of initial concentration on DE and RE

According to the fraction volume and time, the DE and RE were calculated and shown in Fig. 4. It can be seen that the DE of effluents less than 0.5 ml min^{-1} was observed and changed slowly. RE of high concentrations generally increased with the concentration increased. 31% of RE for 500 mg l^{-1} and 71% for 2000 mg l^{-1} were obtained at the vacuum degree of 0.067 MPa.

In theory, distillation time depends on the DE, the DE and RE trends should be unity. However, the results deviated from theoretical. The possible reason maybe due to the instable operation vacuum induced the instability of the fraction temperature.

Table 1
The optimal conditions for methyl orange with different concentration

c (mg l^{-1})	*p* (MPa)	COD (mg l^{-1})	COD removal (%)
120	0.080	0	100
180	0.085	4.198	98.23
240	0.070	13.38	95.60
500	0.070	23.66	96.46
1000	0.070	13.54	98.93
2000	0.070	10.64	99.57

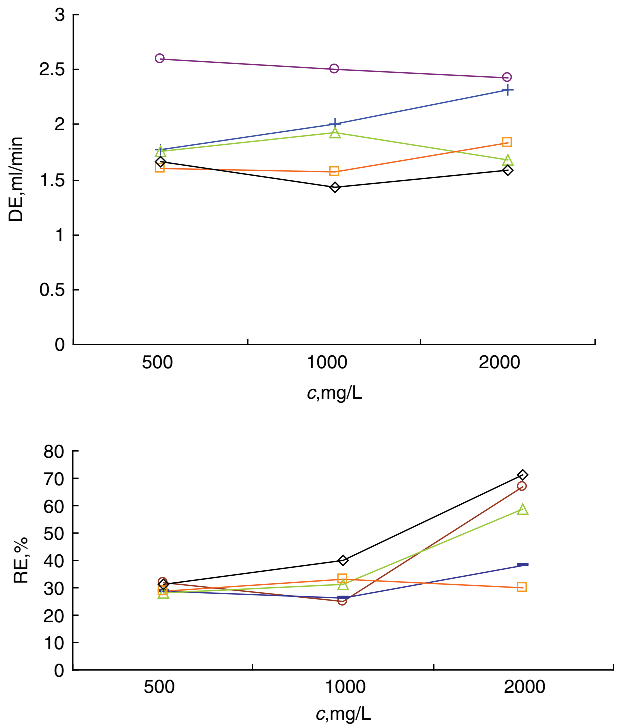

Fig. 4. (a) DE, (b) RE for MO wastewater at high concentration. -◇-: 0.067 Mpa; -□-: 0.070 Mpa; -Δ-: 0.075 MPa; ---: 0.080 Mpa; -O-: 0.085 MPa.

3.2. The effect of vacuum degree

3.2.1. The effect of vacuum degree on BP

The MO wastewater with different concentrations under the vacuum degree of 0.067, 0.070, 0.075, 0.080, and 0.085 MPa, respectively, was studied. Table 2 has given the correlative operating details. It showed that the BP rose with the pressure increased. The temperature at which the vapor pressure of the liquid equal to atmospheric pressure is the BP of the solution, and the BP decreased when the atmospheric pressure decreased [24]. Under the industrial wastewater discharge temperature (60–70°C), the vacuum degree of 0.07 to 0.08 MPa should be the optimal.

Table 2
The BP of the solutions at different pressure

c (mg l^{-1})	*p* (MPa)				
	0.085	0.080	0.075	0.070	0.067
120	53.8	59.2	63.6	67.8	70.2
180	54.6	59.7	63.9	68.5	70.4
240	54.8	59.8	64.4	67.7	71
500	56	60	64.6	68.2	72.4
1000	58	61.9	64.5	69	70
2000	53.8	60	63.9	67.7	69.5

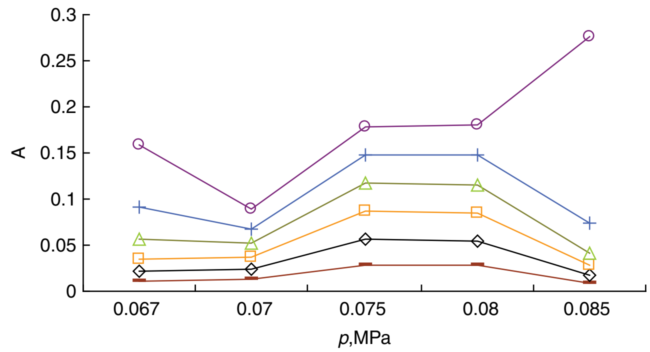

Fig. 5. The variation trend of absorbance at different pressure. -—-:120 mg l^{-1}; -◇-: 180 mg l^{-1}; -□-: 240 mg l^{-1};-Δ-:500 mg l^{-1}; -+-:1000 mg l^{-1}; -O-:2000 mg l^{-1}.

3.2.2. The effect of vacuum degree on absorbance

Fig. 5 displays the absorbance variation trend of different concentration (120–2000 mg l^{-1}) at different vacuum degree (0.067–0.085 MPa). It can be seen from Fig. 5 that the variation of absorbance is regular. The absorbance increased with the vacuum degree increased from 0.067 to 0.080 MPa, then it decreased when the vacuum degree varied from 0.080 to 0.085 MPa. In general, absorbance changed very slowly. The absorbance was sharply increased when the concentration reached to 2000 mg l^{-1}, it maybe originate in the longer distillation time which can lead to the organic substance's entry to the gas phase.

3.2.3. The effect of vacuum degree on COD and COD removal

The variation of COD and COD removal of the effluents at different vacuum degree shows in Fig. 6. It can be found that the COD values after treatment were satisfied. The COD of effluent for 120 mg l^{-1} MO treated at 0.080 MPa is 0 mg l^{-1}. Moreover, the COD removal values were all higher than 92% when the concentration of the solution changed from 500 to 2000 mg l^{-1}. These results suggested that the vacuum distillation method is suitable for high concentration of dye wastewater treatment.

3.2.4. The effect of vacuum degree on DE

According to the volume of fraction and distillation time, the RE and DE have been calculated. This study focused on the high-concentration dye wastewater treatment, so Fig. 7 presented the DE of the high concentration of MO only. With the increasing of pressure, the DE decreased, and the maximum was 2.60 ml min^{-1} (500 mg l^{-1}, 0.085 MPa). The reason for the variation may be as follow: When vacuum degree increases, the pressure decreased and the BP will decrease, the speed of molecules escaping from the surface increase and the DE will increase [25].

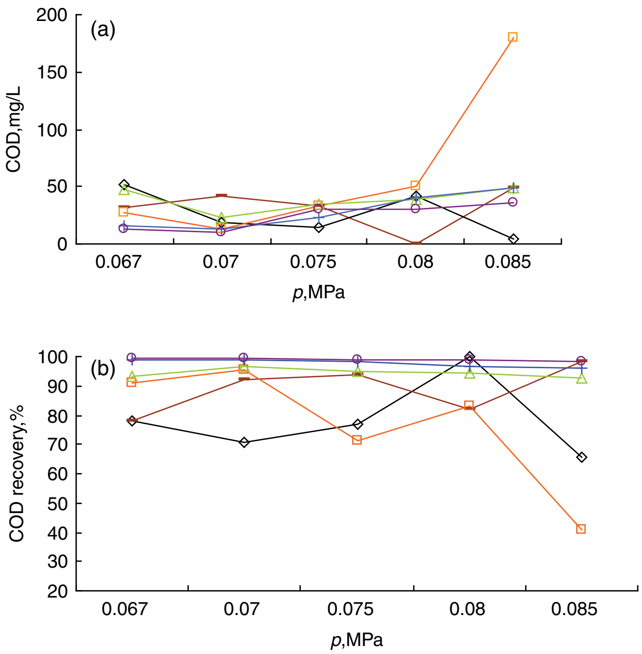

Fig. 6. (a) COD, (b) COD removal of the effluents at different vacuum degree. -◇-: 120 mg l^{-1}: -—-: 180 mg l^{-1}; 1 -□-: 240 mg l^{-1}; -Δ-:500 mg l^{-1}; -+-:1000 mg l^{-1}; -O-:2000 mg l^{-1}.

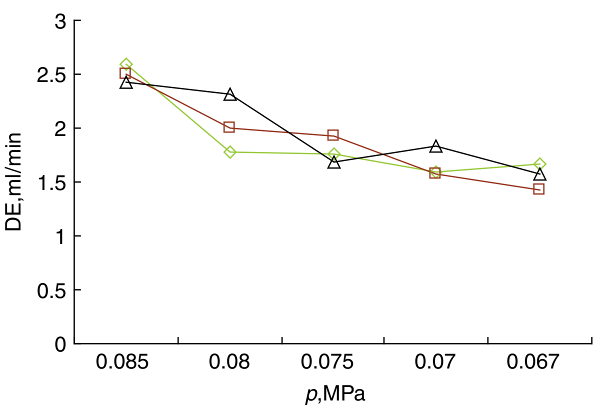

Fig. 7. Distillation efficiency for high concentration of MO. -◇-:500 mg l^{-1}; -□-:1000 mg l^{-1};-Δ-: 2000 mg l^{-1}.

Table 3 expressed the optimization operated pressure decided by COD, COD removal efficiency, absorption fraction, RE and DE for higher concentrations (500–2000 mg l^{-1}).

Table 3
Optimization operated pressure for high concentration

c (mg l^{-1})	500	1000	2000
p (MPa)	0.085	0.075	0.085

3.3. The effect of surfactant

Industry effluents usually contain surfactants, so it is necessary to study the effect of surfactant on purification efficiency. According to the optimized result, the effect of surfactant under a certain optimal conditions (concentration: 500 mg l^{-1} and 2000 mg l^{-1}; vacuum: 0.085 MPa; surfactant: SDS and Polyacrylamide) was investigated.

3.3.1. The effect of surfactant on BP

It can be found from Fig. 8 that the existence of surfactant can reduce the value of BP, which maybe ascribed to the increasing interaction between the surfactant molecular and the dye. In addition, the presence of surfactant reduced the surface tension of the liquid, so the BP will be lower. Moreover, the BP of 500 mg l^{-1} was higher than that of 2000 mg l^{-1} in the blank experiment, while the BP of 2000 mg l^{-1} decreased slower than that of 500 mg l^{-1} in the presence of surfactant, maybe due to the higher strength interaction of the surfactant molecular and the dye molecular for 2000 mg l^{-1} than that of 500 mg l^{-1}, so the surface tension is lower in 2000 mg l^{-1} and the BP of 2000 mg l^{-1} changes slower [25]. It can also be found that SDS (anionic surfactant) played a more important role in reducing the BP. Micellar properties and chain length may make contribution to this phenomenon.

3.3.2. The effect of surfactant on absorbance

Fig. 9 displays the effect of surfactant on the absorbance. It can be seen that the surfactant can reduce the absorbance, and polyacrylamide (cationic surfactant) act as a more positive effect for improving the water quality. Increasing of the solubilization may be the reason for the improvement of water quality and different HLB values may lead to the different degree of improvement [26].

3.3.3. The effect of surfactant on COD and COD removal

The variation of COD and COD removal were shown in Fig. 10 in the presence of the surfactant. The surfactant can play an active role in improvement of water quality, moreover, SDS and polyacrylamide had the same effect

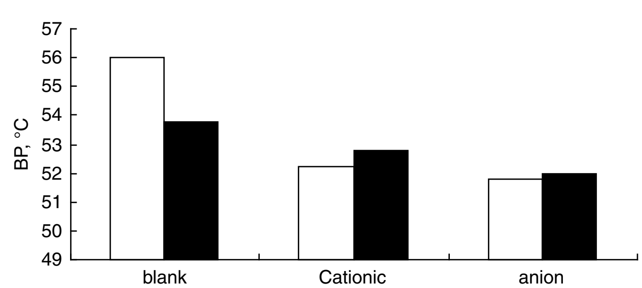

Fig. 8. The effect of surfactant on BP. -□-: 500 mg l^{-1}; -■-: 2000 mg l^{-1}.

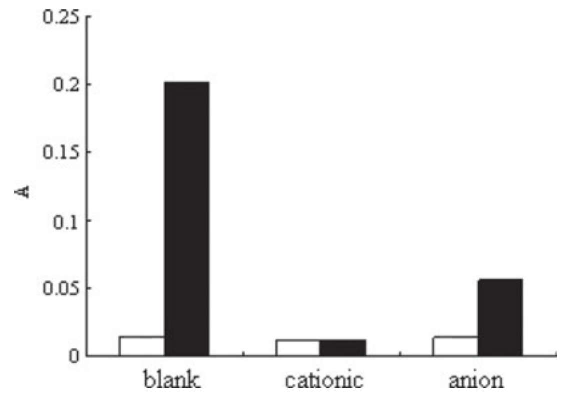

Fig. 9. The effect of the surfactant on the absorbance. -□-: 500 mg l^{-1}; -■-: 2000 mg l^{-1}.

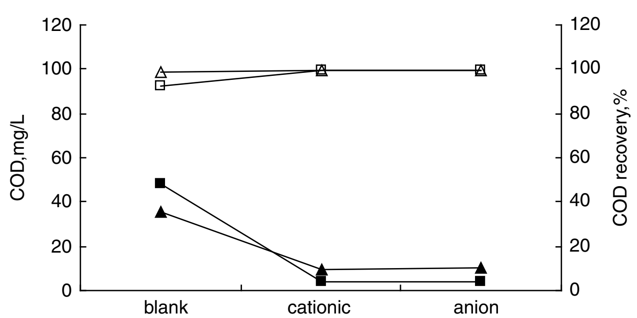

Fig. 10. The variation of COD and COD removal. -■-,-□-: 500 mg l^{-1}; -▲-, -Δ-: 2000 mg l^{-1}.

on COD. In addition, the water quality of 500 mg l^{-1} was significantly improved, indicating that surfactant had a promotive effect on the improvement of water quality.

4. Conclusions

Based on the above discussion, the purification of MO wastewater by vacuum distillation was proved to be feasible, the wastewater after treatment was pellucid with low COD value. The absorbance of the effluent is nearly the same as that of the tap water, indicating the quality of effluent is fine remarkably. It may also be concluded that the quality of treated effluents can meet the requirements of effluent discharged, this method maybe be applied in the dyeing wastewater treatment.

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