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## Distillery Wastewater Decontamination by the Fenton Advanced Oxidation Method

Augustine O. Ayeni<sup>1\*</sup>, Opeyemi A. Adeeyo<sup>1</sup>, Temitayo E. Oladimeji<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, College of Engineering, Covenant University, Canaan land Ota, Nigeria

**ABSTRACT:** This study evaluated the effect of Fenton advanced oxidation process on the treatment of an industrial wastewater (distillery). The comparison of the effects of  $Fe^{2+}$  loadings,  $H_2O_2$  dosages (2%(v/v) and 4%(v/v)), reaction temperature and reaction time, established optimum efficiency in terms of BOD and COD reductions. The best operating conditions for the treatment of the distillery wastewater containing 43.85 mg/L BOD concentration and 274.28 mg/L COD concentration in the raw effluent was 2%  $H_2O_2$  dosage at constant loadings of  $Fe^{2+}$  (1.5 g), 80 °C pretreatment temperature, and 1 h reaction time. At this optimized condition, the BOD content reduced to about 35 mg/L (about 21% removal) and COD content reduced to about 53 mg/L (about 81% removal). There was a complete removal of the initial colour present in the wastewater after the treatment process. The process proved the ability to effectively reduce the COD content which when high in industrial wastewaters can lead to serious impacts to the environment.

**Keywords:** Biological oxygen demand, Chemical oxygen demand, Distillery, Fenton reagent, Wastewater,

### I. INTRODUCTION

One of the major threats to water quality is chemical pollution from heavy metals, solvents, dyes, pesticides, etc. Chemicals enter the aquatic medium in several different ways, either dumped directly, such as industrial effluents, or from wastewater treatment plants[1]. The Advanced Oxidation Processes (AOPs) are widely recognized as highly efficient treatments for recalcitrant wastewater. AOPs are considered a highly competitive water treatment technology for the removal of those organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability [1,2]. These processes degrade organic pollutants by forming hydroxyl radicals. AOPs commonly used methods are photo-Fenton or Fenton reagent,  $O_3/H_2O_2$ ,  $O_3/UV$ ,  $H_2O_2/UV$ ,  $TiO_2/UV$ , cavitation (generated either by means of ultrasonic irradiation or using constrictions such as valves, orifice, venture [3]. The Fenton oxidation process is a chemical pretreatment process which involves the use of iron II ( $Fe^{2+}$ ) and hydrogen peroxide ( $H_2O_2$ ). Under acidic conditions, a  $Fe^{2+}/H_2O_2$  mixture produces hydroxide radicals in a very cost-effective manner. The Fenton reaction has a short reaction time among all advanced oxidation processes and it has other important advantages. The Fenton reagent is a cost-effective method, easy to apply, is a homogeneous catalytic oxidation process involving the reaction of hydrogen peroxide with ferrous ions. This reaction generates hydroxyl radicals that have a high oxidation potential [4].



Iron and  $H_2O_2$  are cheap and non-toxic, there is no mass transfer limitations due to its homogenous catalytic nature, there is no energy involved as catalyst and the process is easy to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters, as well as pharmaceutical wastewaters. The treatment option required for remediating wastewaters is a highly complex process. A combination of one or more processes should be considered with reasonable cost. Distillery wastewaters contain a high amount of COD (chemical oxygen demand), BOD (biological oxygen demand), and a dark brown colour, known as melanoidins. High strength wastewater during alcohol production is high in COD and high in BOD. Low strength processed wastewater or diluted wastewater has low concentration of COD, BOD, and colour [5,6]. Melanoidins are formed by Maillard amino carbonyl reaction [7]. The presence of melanoidins lead to serious impacts to the environment due to its colour and COD content. When released to the environment, there is the reduction of photosynthetic activity and dissolved oxygen concentration in aquatic environment.

The aim of this study is to experimentally determine the optimal conditions for Fenton's reagent application, studying the effect of different operational variables such as temperature,  $H_2O_2$  dosages, and  $Fe^{2+}$  concentrations. Therefore, the effect of variation in hydrogen peroxide concentration in relation to  $FeSO_4$  loading, time and temperature to the efficiency of pretreatment method during Fenton oxidation process was evaluated.

## II. MATERIALS AND METHODS

The distillery wastewater used was collected in plastic containers from a distillery in Ota, Ogun State, Nigeria. The raw samples were stored at 4 °C until they were ready to be used. All reagents used were of analytical grade.

### Raw and treated wastewater analysis

The total solids (TS) was determined by filtering the distillery wastewater with Whatman filter paper. The difference in weight of the filter paper before and after filtration based on solid retained on the filter paper gave the total solid. The total suspended solid (TSS) was determined by calculating the difference in dry weight (oven drying the filter paper and residue at 105 °C for 2 h) of a filter paper before and after filtration of raw sample. The total dissolved solid (TDS) was estimated by filtering 75 mL of sample in an evaporating dish and was heated at 140 °C in a convection oven until constant weight was achieved. The colour (which is mostly introduced by iron and manganese compounds in the wastewater) was determined (after removing the turbidity and adjusting the pH of the wastewater to 7.6 by the addition of H<sub>2</sub>SO<sub>4</sub> and NaOH) by running a scan for the sample in a UV-visible spectrophotometer which revealed the peak of absorbance at a particular range of wavelength (Fig. 1). Absorbance of the distillery wastewater using a UV-visible spectrophotometer showed the highest peak value at 475 nm with a peak value of 0.024, this wavelength falls within the range of 465-482 nm dedicated as the blue colour, which is melanoidin colour.

### Biological oxygen demand determination

The BOD was determined by an open reflux method. BOD indicates the amount of putrescible organic matter present in water. Therefore, a low BOD is an indicator of good quality water, while a high BOD indicates polluted water. Dissolved oxygen (DO) is consumed by bacteria when large amounts of organic matter from sewage or other discharges are present in the water. DO is the actual amount of oxygen available in dissolved form in the water. When the DO drops below a certain level, the life forms in that water are unable to continue at a normal rate. The decrease in the oxygen supply in the water has a negative effect on the fish and other aquatic life. The raw sample of the effluent was diluted in water and the pH was adjusted to 7.2 by phosphate buffer. Mixture was seeded with microorganism and was further incubated in an incubator controlling temperature within 20±1 °C. The microorganism uses the oxygen dissolved in the water as they degrade the organic matter. The oxygen remaining after five days is determined and the BOD was calculated by comparison with the oxygen in the effluent-free reference sample. The BOD content of the raw sample is as shown in Table 1.

### Chemical oxygen demand determination

The COD analysis was performed by the dichromate closed reflux colorimetric method using a spectrophotometer in accordance with Standard Methods (for a COD range 0–1500 mg O<sub>2</sub>/L. 50 mL of sample was added into a reflux condenser. 1 g of glass beads and 5 mL of H<sub>2</sub>SO<sub>4</sub> were added and cooled. 25 mL of 0.04 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 70 mL of H<sub>2</sub>SO<sub>4</sub> were added in a flask and refluxed for 3 h. Cooling water was circulated round the reflux condenser and the refluxed mixture was cooled and diluted. The excess K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was titrated against standard ferrous ammonium sulphate with ferrous ion used as indicator which showed the color change from blue green to reddish brown. All other analyses were carried out as per the standard methods [8-10]. All of the oxidation experiments were performed in duplicate and the observed standard deviation was always less than 7% of the reported value.

### Pretreatment of wastewater

The pH of the wastewater sample was reduced to 4 from an initial raw material pH of 9.2 (The pH adjustment was carried out with diluted sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide (NaOH) solutions) at a temperature of 27 °C. The concentration of H<sub>2</sub>O<sub>2</sub> was varied for the two experimental runs considered (at 2% (v/v) and 4% (v/v)), the values for all other variables as FeSO<sub>4</sub>, temperature, and time remained constant. 1.5 g of ferrous sulphate was weighed and added to the 500 mL wastewater in 1 L beaker. With the magnetic stirrer, pretreatment was made to occur for the specified time period and temperature. After each pretreatment period, the mixture was allowed to cool to room temperature. Further analysis was subsequently carried out on the treated samples. The results for the treated samples (labeled A and B) are shown in Table 1.

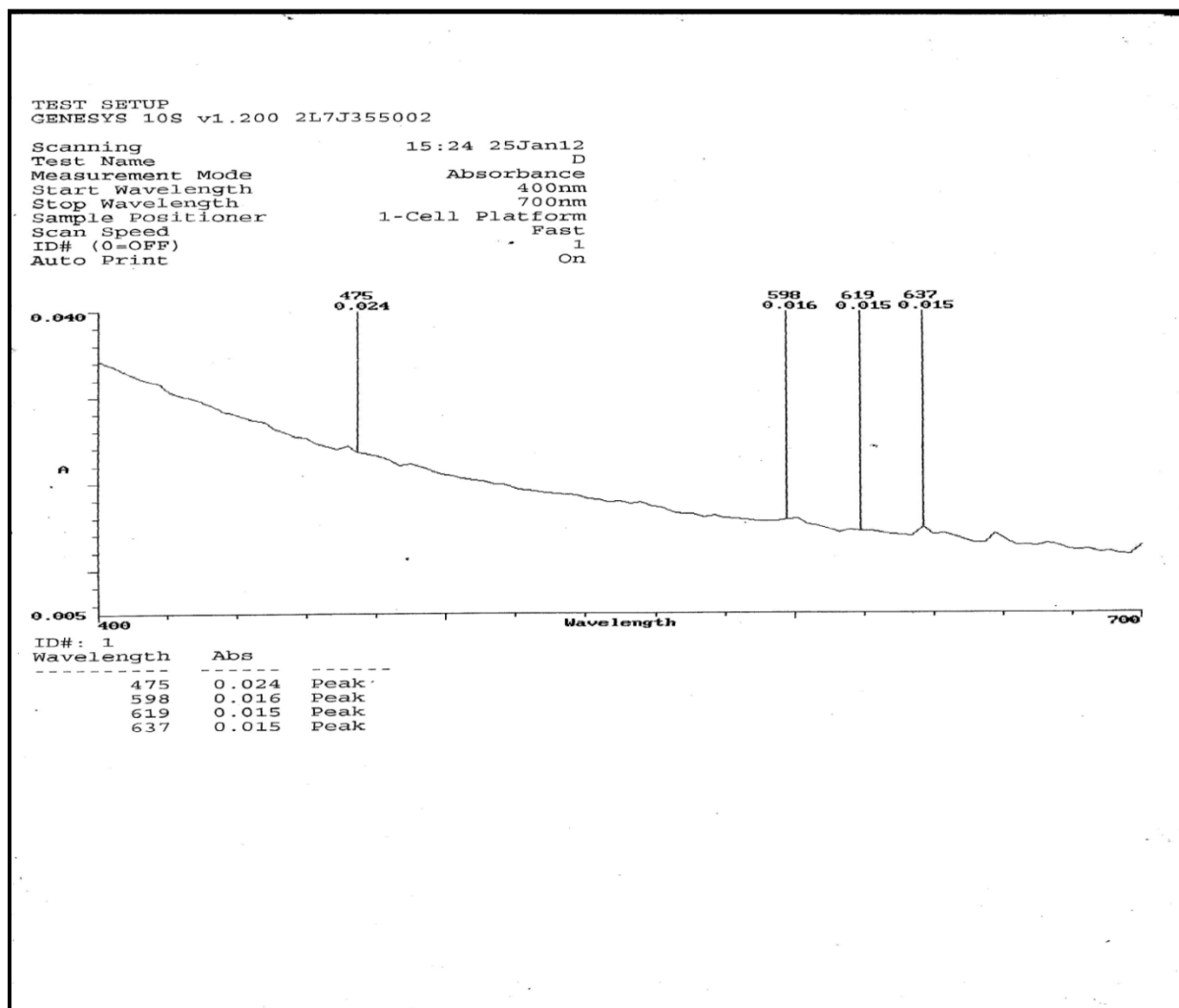


Figure 1: UV-Visible spectrophotometer spectra for the raw distillery wastewater

Table 1. Physico-chemical characterization of the Fenton-oxidation experiments

Parameters	Raw sample	Pretreated sample (A) 1.5 g FeSO <sub>4</sub> , 2% H <sub>2</sub> O <sub>2</sub> , 80 °C, 1 h	Pretreated sample (B) 1.5 g FeSO <sub>4</sub> , 4% H <sub>2</sub> O <sub>2</sub> , 80 °C, 1 h
pH	9.2	-	-
TSS (mg/L)	3.33.	-	-
TDS (mg/L)	2.11	-	-
BOD (mg/L)	43.85	34.82	32.99
COD (mg/L)	274.28	52.53	49.49
TOC (mg/L)	2.13	0.00	0.00
BOD:COD	0.16	0.67	0.67
% BOD removal	-	20.59	24.77
% COD removal	-	80.85	81.96

### III. RESULTS AND DISCUSSIONS

#### Effect of pretreatment on raw wastewater

Chemical oxidation of the wastewater with Fenton's reagent was studied in order to minimize the impact of discharge on natural water courses. Pretreatment of the sample showed that the colour of the sample was completely removed (Fig. 2). This was because no peak value was detected by the UV-visible spectrophotometer, and this was a good characteristic feature for the treated wastewater. The raw wastewater showed the COD (274.28 mg/L) concentration to be higher than the BOD (43.85 mg/L) concentration. Chemical oxygen demand is a vital test for assessing the quality of effluents and waste waters prior to discharge. The COD test predicts the oxygen requirement of the effluent and is used for monitoring and control of discharges, and for assessing treatment plant performance. The impact of an effluent on the receiving water is predicted by its oxygen demand. This is because the removal of oxygen from the natural water reduces its ability to sustain aquatic life. The higher the chemical oxygen demand, the higher the amount of pollution in the test sample. The efficiency of oxidation (and therefore the degree of direct reduction of COD) and the costs of application of Fenton's reagent depends on the amount of H<sub>2</sub>O<sub>2</sub> used. The partial oxidations in intermediate compounds minimize the consumption of chemicals reagents and often results in substantial reductions of COD and toxicity [11]. Both COD and BOD removal (%) were calculated based on the formula;

$$X \text{ (COD or BOD)} = [(X_i - X_f)/X_i] \times 100 \quad \dots 2$$

Where X<sub>i</sub> = initial values for the COD or BOD in raw wastewater

X<sub>f</sub> = Final values for the COD or BOD after wastewater treatment

Fig. 3 shows the variations in BOD, COD, and TOC of the raw wastewater to the treated material after the Fenton oxidation treatment. The BOD concentration in raw material was not as pronounced as the COD concentration. As a result, the pretreatment caused little or no change in the BOD concentration. Percent BOD removal varied only between 21–25% (Fig. 3). However, the COD concentration decreased to about 6-folds (about 82% removal). As it can be observed, the COD conversion for Fenton experiments, after 1 h of reaction, lay between 80% and 82% depending on the operating conditions. These COD conversions can be attributed to the generally high reactivity of organic compounds with hydroxyl radicals. Results also show that increasing the H<sub>2</sub>O<sub>2</sub> concentration (and proportionally Fe<sup>2+</sup> concentration) has very little effects on both the COD and BOD reductions. It can be noticed that at 2% H<sub>2</sub>O<sub>2</sub> and 4% H<sub>2</sub>O<sub>2</sub> loadings, COD concentration reduced to 52.53 mg/L and 49.49 mg/L respectively from an initial 274.28 mg/L. Equally, BOD values reduced to 34.82 mg/L and 32.99 mg/L respectively from an initial 43.85 mg/L. These variations indicated that loadings beyond 2% H<sub>2</sub>O<sub>2</sub> makes the process not economically viable.

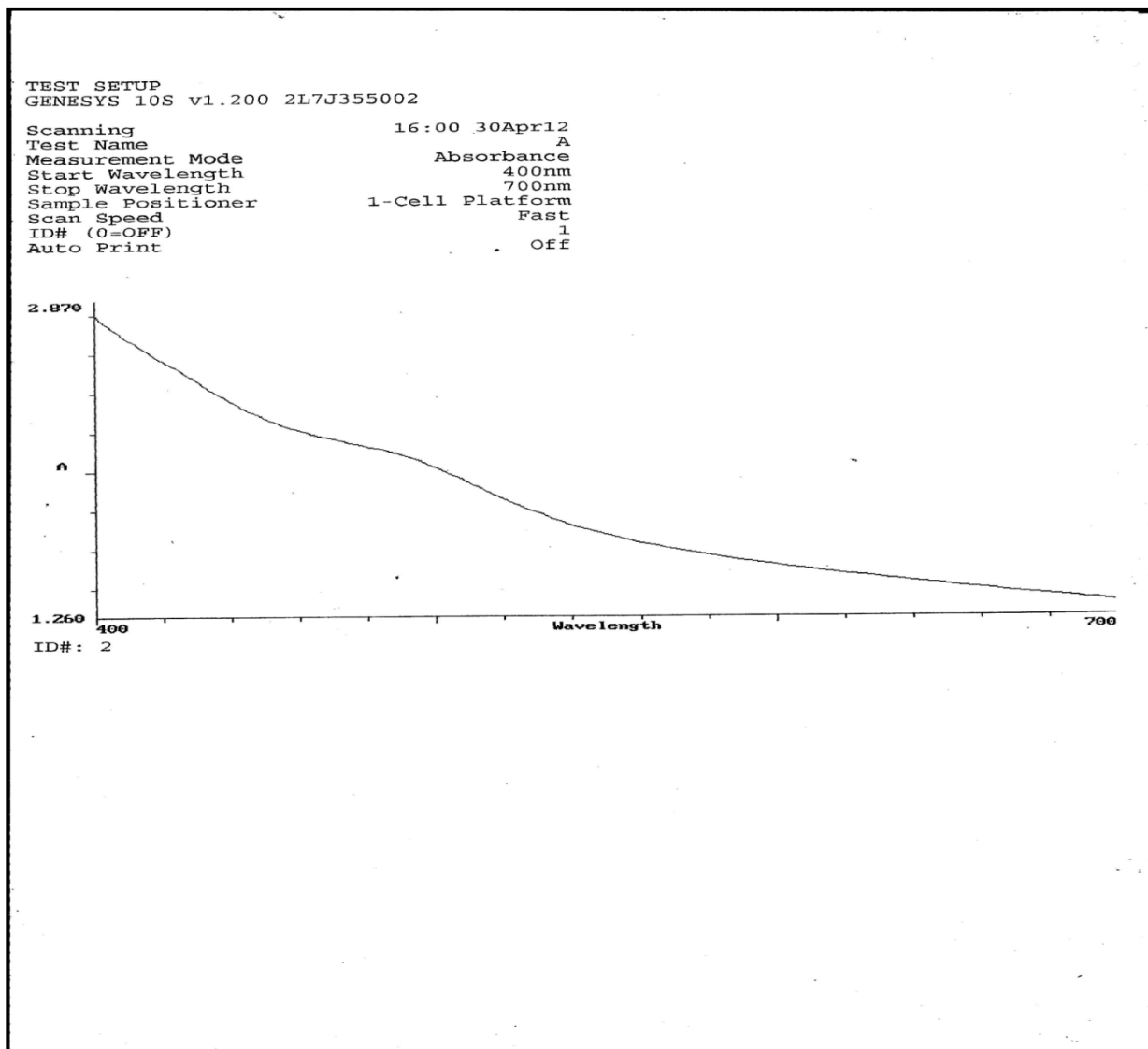
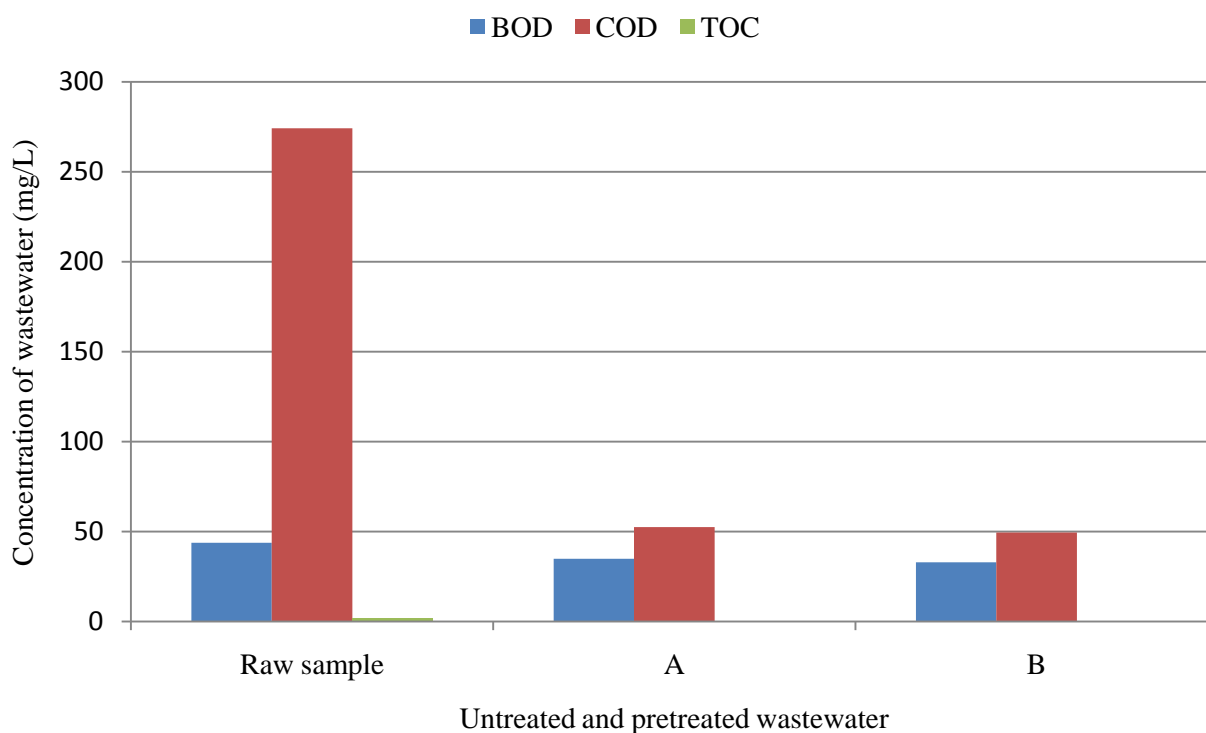


Figure 2: UV-Visible spectrophotometer spectra for the treated distillery wastewater



**Figure 3. Characteristic evaluation of BOD, COD, and TOC in treated and untreated distillery wastewater**

#### IV. CONCLUSIONS

This study showed that advanced oxidation method such as Fenton's reagent can be effectively utilized for enhancing the biodegradability of industrial wastewater such as for a distillery along with reduced toxicity, lower COD and color removal. The best operating conditions for the treatment of the distillery wastewater containing 43.85 mg/L BOD concentration and 274.28 mg/L COD concentration in the raw material was 2% H<sub>2</sub>O<sub>2</sub> dosage at constant loadings of Fe<sup>2+</sup> (1.5 g), 80 °C pretreatment temperature, and 1 h reaction time. At this optimized condition, the BOD content reduced to about 35 mg/L (about 21% removal) and COD content reduced to about 53 mg/L (about 81% removal). The initial colour present in raw effluent was also completely removed. The process proved the ability to effectively reduce the COD content which when high in industrial wastewaters can lead to serious impacts to the environment when discharged. Consequently, there is the reduction of photosynthetic activity and dissolved oxygen concentration in aquatic environment if such waste is not adequately treated.

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