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Application of a montmorillonite clay modified with iron in photo-Fenton process. Comparison with goethite and nZVI

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Abstract Iron pillared clay (Fe-PILC) was prepared from a montmorillonite and was characterized by scanning electron microscopy and X-ray fluorescence. Fe-PILC catalytic activity was evaluated in photo-Fenton processes applied to the degradation of 2-chlorophenol. Different catalyst loads were assayed. The Fe-PILC allowed almost complete degradation of the contaminant. An increase in the contaminant degradation rate was observed, following leaching of iron during catalytic assays, which suggest the existence of a homogeneous photo-Fenton mechanism. The catalytic performance of the Fe-PILC was compared with that for goethite and zero valent iron nanoparticles. Differences were found regarding the achieved degradation levels, the efficiency in oxidant consumption, and the extension of iron leaching.

Keywords Photo-Fenton · Fenton · Fe-PILC · Goethite · Zero valent iron · 2-chlorophenol

Introduction

Advanced Oxidation Technologies (AOTs) are processes based in the use of the highly oxidant property of hydroxyl radicals (HO[•]) and have shown to be successful for cleaning

biologically toxic or nondegradable materials such as aromatics, pesticides, petroleum constituents, and volatile organic compounds in waste water. Hydroxyl radicals (HO[•]) are generated in solution and are responsible for the oxidation of chemical contaminants which are converted to a large extent into stable inorganic compounds such as water, carbon dioxide, and salts, i.e., they undergo mineralization (Legrini et al. 1993, Comminellis et al. 2008, Ameta et al. 2012).

One of the most widely used AOTs is based on the combination of H₂O₂ and UV radiation with Fe (II) or Fe (III), the so-called photo-Fenton process, where iron salts serve as photocatalyst and H₂O₂ as oxidizing agent. It represents an efficient and cheap method for wastewater treatment (Pignatello et al. 2006, Malato et al. 2009, Nogueira et al. 2007) and produces more hydroxyl radicals in comparison with the Fenton system Fe (II)/H₂O₂ or radiolysis UV/H₂O₂.

In order to avoid the disadvantages associated with the use of Fe⁺³ in solution, separation, and recovery for later reuse, iron contained in a solid phase has also been studied as catalyst in photo-Fenton processes (Sum et al. 2005). The possibility of working in a wider pH range has been reported as an additional benefit of such heterogeneous system. Diverse solid iron compounds as oxides or hydroxides have been applied as catalysts. Among them, hematite and goethite, in a wide variety of forms and origins (amorphous or crystalline, natural or synthetic) (Huang and Huang 2009, Ortiz de la Plata et al. 2010a) and zero valent iron, (Morgada et al. 2009, Son et al. 2009, Ortiz de la Plata et al. 2012) can be mentioned. Valued features for solid catalysts are a high specific surface area, insuring the exposure of the catalytic species, and low leaching values of it in order to avoid not only contamination but also and especially catalyst degradation. In this direction, iron species have been supported on different solids (Rodríguez et al. 2010) as silica, alumina, zeolites (Zhang et al. 2011, Gonzalez-Olmos et al. 2012), mesoporous

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materials such as SBA-15 (Martínez et al. 2005) and clays, either synthetic, natural, or modified by different methods (Timofeeva et al. 2005, Cheng et al. 2008, De León et al. 2008, Feng et al. 2009, Deng et al. 2010, Ayodele et al. 2012, Catrinescu et al. 2012).

The chemical environment in which iron is inserted can affect its reactivity and stability. Pecher et al. (2002) reported that the reaction rates and products for the degradation of a given organic pollutant were strongly dependent on the type of mineral-bound Fe (II).

Despite the heterogeneous nature of the reaction system, part of the iron may be solubilized resulting in a possible homogeneous contribution to the catalytic process and/or in the compromise of the catalyst stability (Son et al. 2009, Ortiz de la Plata et al. 2010a). The leaching of iron has been related to the formation of highly soluble iron-reaction intermediate complexes (e.g., oxalate), the required low pH (normally pH 3), high H_2O_2 /reactant ratio, temperature, and radiation intensity (Najjar et al. 2007).

Smectites, natural or synthetic, are lamellar clays with high capacity for cation exchange and adsorption of polar molecules in the interlamellar space. They have been modified by introducing voluminous organic or inorganic cations that by calcination are transformed in oxidic species generating an adsorption volume in the interlamellar space. These solids are known as pillared interlayered clays (PILCs) and have been used as adsorbents, as catalysts, or as support for catalytic species. Particularly, iron pillared clays (Fe-PILCs) have shown excellent properties in photo-Fenton processes. Herney-Ramirez et al. (2010), in a recent review, present the use of PILCs as catalysts in heterogeneous photo-Fenton oxidation for wastewater treatment. The authors describe different PILC preparation procedures based on the use of iron and other metals like copper, analyze the influence of different experimental conditions such as light wavelength and intensity, initial amount of H_2O_2 , catalyst load, pH and temperature, and address aspects of applied interest such as stability and use under visible light. Different and particularly relevant contaminants have been treated with Fe-PILCs, among them are phenolic compounds and dyes, which are widely used in different industries (e.g., paper and textile).

The aim of this study was to obtain an active catalyst in photo-Fenton processes by iron pillaring of a natural clay, montmorillonite and to compare its catalytic performance with that of other solid materials used as catalysts: goethite and zero valent iron nanoparticles (nZVI). The catalytic activity of the solids was evaluated in the degradation of 2-chlorophenol (2-CP). It was selected because it constitutes an important source of pollution due to its high toxicity and to be widely used in industry (as sanitizer, germicide, precursor in the manufacture of pesticides, and other chlorophenols). Besides, this compound is representative of a group of pollutants reluctant to be degraded by conventional techniques.

Materials and methods

The starting raw material was a clay from Bañado de Medina, Uruguay, being over 80 % of it a montmorillonite. The clay was dried at 110 °C and ground. The fraction of aggregates size less than 250 μm was selected by sieving and used for catalysts preparation.

The clay was exchanged with an aqueous solution of $[\text{Fe}_3(\text{OCOCH}_3)_7\text{OH}\cdot 2\text{H}_2\text{O}] \text{NO}_3$, prepared according to the method described by Yamanaka et al. (1984). A solution of the iron complex was poured on an aqueous suspension (10 % in weight) of the selected aggregates fraction of the clay until a final ratio of 0.5 mmol of the complex per gram of clay was attained. The exchanged clay was recovered by filtration, washed with deionized water, dried at 60°C, and calcined in air atmosphere using a tubular furnace Carbolite CTF-12/65/550. The temperature was increased at 1 °C min^{-1} from room temperature up to 400 °C which was maintained for 2 h to obtain the Fe-PILC.

The chemical composition of the clay and the Fe-PILC was determined by Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF) in the Laboratorio de Tecnogestión of the Ministerio de Industria, Energía y Minería of Uruguay. SEM microphotographs of the solids were obtained with a JEOL JS M-5900LV scanning electron microscope operated at 20 kV.

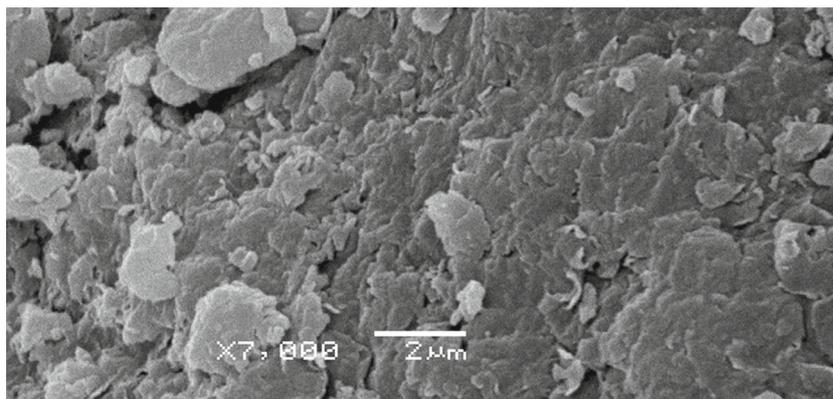
Catalytic tests in Fenton and photo-Fenton conditions were performed in a cylindrical and well-stirred batch reactor with a reaction volume of 2.0 L, optionally irradiated from the bottom with UVA radiation (340 to 410 nm). The reactor was equipped with heat exchangers connected to a thermostatic bath to control temperature. The initial concentration of 2-CP ($C_{2\text{-CP},0}$) was 50 ppm, the initial molar ratio of H_2O_2 to 2-CP (R) was 20, and two different catalyst load (L_{cat}) were employed, 0.2 and 1.0 g L^{-1} . The initial pH of the medium was adjusted to 3 with perchloric acid, and the temperature was maintained at 25 °C.

Samples of the reaction medium were extracted every 30 min during the tests. The catalyst was separated by filtering the samples through a 0.2- μm pore-size cellulose acetate syringe filter. The 2-CP concentration was determined with a HPLC Waters, equipped with a LC-18 Supelcosil reversed-phase column (Supelco). The eluent was a ternary mixture of water (containing 1 %v/v of acetic acid), methanol, and acetonitrile (60:30:10), and the flow rate was 1.0 mL min^{-1} . Total organic carbon (TOC) was measured with a Shimadzu TOC-5000 Analyzer. H_2O_2 and iron in solution were spectrophotometrically quantified using the iodometric and o-phenanthroline techniques, respectively. For absorbance measurements, a Cary100 Bio spectrophotometer was used.

Results and discussion

The morphology of the clay and the Fe-PILC can be appreciated in the SEM micrographs shown in Fig. 1 and Fig. 2,

Fig. 1 SEM micrograph for the clay



respectively. The well-ordered structure characteristic for the flat particles of the montmorillonite is confirmed by Fig. 1 in which only interparticle pores can be observed. The micrograph in Fig. 2 evidences that the Fe-PILC retains the characteristic lamellar structure of the clay, although the pillaring process has caused the partial swelling of the clay and increased the structural disorder.

The chemical composition for the clay and the Fe-PILC determined by EDXRF is shown in Table 1. The results indicate that the montmorillonite clay used for the preparation of the catalysts is rich in calcium with a low sodium and potassium content. Iron represents only 1.1 % for the host clay and increases to 6.1 % for the Fe-PILC, thus confirming that the iron complex was effectively incorporated during the pillaring process.

The results of the catalytic test for the Fe-PILC performed in photo-Fenton conditions using a catalyst load of 1.0 g L^{-1} are shown in Fig. 3. A slow decrease of 2-CP and H_2O_2 concentration is observed at short reaction times indicating a low rate of 2-CP degradation. The H_2O_2 consumption and the 2-CP degradation are accelerated at approximately 90 min of reaction, thus resulting in an inverse S-shaped curve profile as reported for reactant concentration by Silva et al. (2012) and Guélou et al. (2003) for iron modified clays used in hydrogen peroxide oxidation processes. At 180 min of reaction, the

almost complete removal of 2-CP (98 %) is reached. At this time, only 23 % of the initial TOC was removed indicating that total mineralization of the medium was not achieved. Reaction intermediates such as chlorobenzoquinone, chlorohydroquinone, and oxalic acid have been reported in the 2-CP photo-Fenton degradation (Ortiz de la Plata et al. 2010a, 2010b) and could be responsible for the remaining TOC here observed. Iron concentration in the reaction medium increases slowly in the initial stage of the assay but grows rapidly after 120 min of reaction. Even though 5.4 mg L^{-1} of iron were detected at the end of the test, this represents only the 8.7 % of the iron content of the fresh catalyst. Iron dissolution may be favored by the presence of some reaction intermediates as well other typical parameters for the process (Najjar et al. 2007, Ortiz de la Plata et al. 2010a).

It is interesting to realize that the increase in the rate of 2-CP degradation (and also in the H_2O_2 consumption) is observed when iron content in solution grows, thus suggesting that a homogeneous photo-Fenton mechanism would take place and be responsible, in this case, for the observed curve profile. Ortiz de la Plata et al. (2010c) have proposed an autocatalytic contribution of some of the reaction intermediates in the cycle of iron in solution, which also supports the same curve profile. Other authors have attributed the observed

Fig. 2 SEM micrograph for the Fe-PILC

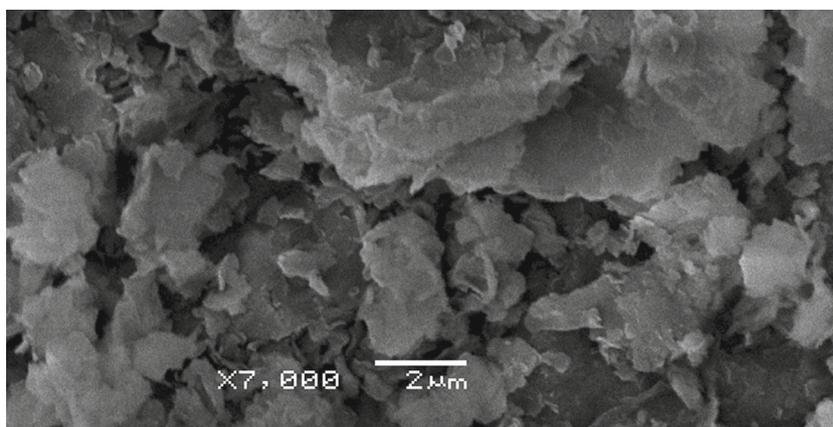


Table 1 Chemical composition of the clay and the Fe-PILC determined by EDXRF

Element	Content	
	Clay	Fe-PILC
Na	<100 ppm ^a	<100 ppm ^a
Mg	<2 %	<2 %
Al	7.9±0.8 %	4.5±0.5 %
Si	31±3 %	25±2 %
K	0.14±0.05 %	0.11±0.05 %
Ca	1.38±0.05 %	0.96±0.10 %
Ti	542±35 ppm	844±80 ppm
Mn	1,610±100 ppm	1,832±150 ppm
Fe	1.1±0.5 %	6.1±0.5 %
Cu	6.1±0.5 ppm	8.6±0.5 ppm
Zn	117±5 ppm	122±10 ppm
Rb	7±1 ppm	7.1±1.0 ppm
Sr	257±8 ppm	172±15 ppm
Pb	30±3 ppm	33±3 ppm

^a 100 ppm is the limit of detection for Na

initial induction period to the time needed for the activation of the surface iron species in cases in which iron concentration in solution was found to be negligible during the experiments, and the homogeneous contribution to the process was discarded (Luo et al. 2009, Silva et al. 2012).

Figure 4 shows the results of the catalytic test performed in photo-Fenton conditions using a 0.2 g L⁻¹ of the Fe-PILC. The behavior was similar to that observed for a catalyst load of 1.0 g L⁻¹ (Fig. 3). Almost negligible diminutions (below 2 %) of the 2-CP and H₂O₂ concentrations were detected in the first 90 min of the test, while iron in solution was less than

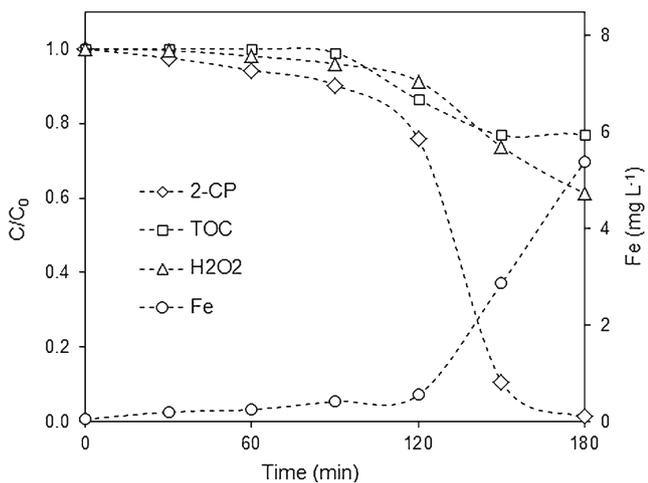


Fig. 3 Results for the photo-Fenton test: dimensionless concentrations of 2-CP, H₂O₂, and TOC and iron concentration in solution (mg L⁻¹) in presence of UV radiation. $L_{cat}=1.0 \text{ g L}^{-1}$, $C_{2-CP_0}=50 \text{ ppm}$, $R=20$, $\text{pH}=3$, and $T=25 \text{ }^\circ\text{C}$

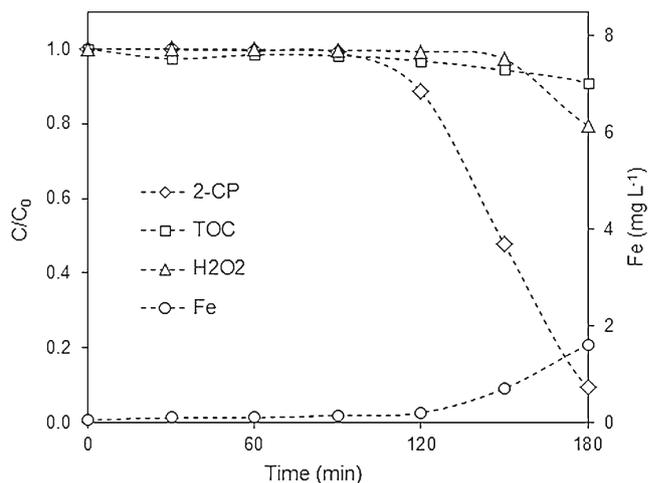


Fig. 4 Results for the photo-Fenton test: dimensionless concentrations of 2-CP, H₂O₂, and TOC and iron concentration in solution (mg L⁻¹) in presence of UV radiation. $L_{cat}=0.2 \text{ g L}^{-1}$, $C_{2-CP_0}=50 \text{ ppm}$, $R=20$, $\text{pH}=3$, and $T=25 \text{ }^\circ\text{C}$

0.15 mg L⁻¹. In the second stage, a more rapid decrease of 2-CP and H₂O₂ concentration took place with a 2-CP and a TOC removal at 180 min of 90 and 10 %, respectively. As in the assay performed with a higher catalyst load (Fig. 3), the increase in the degradation rate of 2-CP degradation is accompanied by a more rapid increase of iron in solution which reaches 1.6 mg L⁻¹ at 180 min.

Comparing the amount of iron leached in experiments using different catalyst loadings, it is observed that the increase of the latter does not lead to a proportional amount of the first. Iron leaching seems to be a highly complex process depending on a series of factors among which the amount and type of reaction intermediates are mentioned (Najjar et al. 2007). This approach would be supported by the observation reported by several authors that the iron concentration in solution reaches a

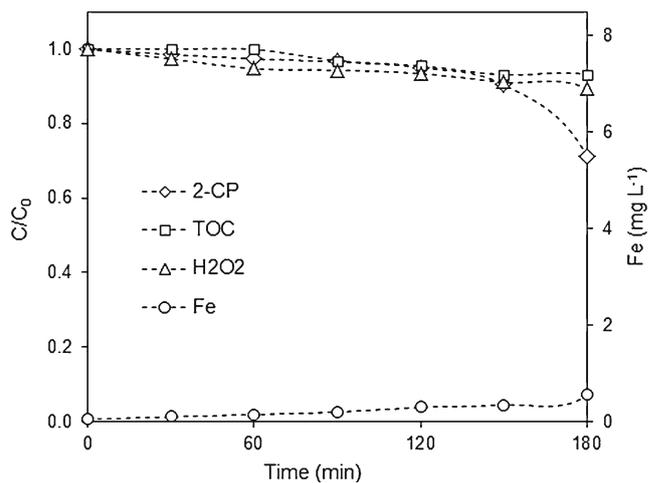


Fig. 5 Results for the Fenton test: dimensionless concentrations of 2-CP, H₂O₂, and TOC and iron concentration in solution (mg L⁻¹) in absence of UV radiation. $L_{cat}=1.0 \text{ g L}^{-1}$, $C_{2-CP_0}=50 \text{ ppm}$, $R=20$, $\text{pH}=3$, and $T=25 \text{ }^\circ\text{C}$

Table 2 Catalytic performance in the degradation of 2-CP for the solids: Fe-PILC, nZVI, and goethite in photo-Fenton conditions

Solid	L_{cat} (g L ⁻¹)	Fe (mg) ^a	R	$X_{2\text{-CP}}$	$X_{\text{H}_2\text{O}_2}$	X_{TOC}
Fe-PILC	0.2	24	20	90	20	9
Fe-PILC	1.0	122	20	98	39	23
nZVI	0.02	36	13	88	18	9
Goethite	0.5	628	30	41	45	20

Conversion values at 3 h for Fe-PILC, and nZVI and at 6 h for goethite

^aTotal iron incorporated to the reactor calculated from the iron content of the solid and the mass of solid used in each assay

maximum and then decreases in advanced stages of the mineralization process. This fact has been ascribed to the destruction of organic intermediates that maintained iron in solution and to the fixation of iron ions onto the solid catalyst (Sum et al. 2005, Feng et al. 2009, Chen and Zhu 2011).

Figure 5 shows the results obtained in a test performed with a catalyst load of 1.0 g L⁻¹ under the same conditions but in absence of radiation, i.e., Fenton conditions. The 2-CP conversion reached at the end of the test was of 29 % accompanied by a low consumption of H₂O₂ and a TOC removal of only 7 % of the initial value, which indicates a low mineralization of the reaction medium. These results evidence the important role of UVA radiation in the reaction mechanism leading to the degradation of 2-CP and reaction intermediates. The iron leaching in these conditions was scarce being the iron concentration at the end of the test less than 0.6 mg L⁻¹ which represents less than 1 % of the iron initially contained in the catalyst.

For the sake of comparison, Table 2 summarizes the results for the catalytic performance of the Fe-PILC and those reported for nZVI (Ortiz de la Plata et al. 2012) and goethite (Ortiz de la Plata et al. 2010b) in the degradation of 2-CP evaluated in the same photo-reactor and under similar photo-Fenton conditions.

It is interesting to realize that Fe-PILC allows high conversions of 2-CP with a marked improvement from 90 to 98 % associated to a higher catalyst load, which implies higher iron content in the reaction medium. This increment appears as moderate compared to the 2.5-fold increase in the TOC removal with about a twofold consumption of H₂O₂. Namely, a higher iron content increases the reaction rate provoking not only the increase (moderately) of 2-CP degradation but also (and perhaps mainly) the mineralization of the reaction intermediates which reflects in the much higher values of TOC removal and H₂O₂ consumption.

The catalytic performance of the Fe-PILC in 2-CP degradation is comparable to that of the nZVI when quite similar iron contents (24 and 36 mg, respectively, when 0.2 g L⁻¹ of Fe-PILC is used) are present in the reactant medium. Furthermore, the same TOC removal and similar H₂O₂

conversion are observed for these catalysts even when a lower value of R was used for the nZVI. So, a more efficient use of the oxidant was achieved with the nZVI since a lower consumption of H₂O₂ was required to attain the same mineralization level.

Both catalysts, Fe-PILC and nZVI, have shown a higher catalytic activity than goethite in 2-CP degradation in photo-Fenton conditions, even when for goethite a double reaction time and much higher iron content and R value were used. It should be noted that as goethite is a bulk iron mineral with a greater particle size (75 to 150 μm), the amount of iron atoms that are surface-exposed and thus available for catalysis is lower.

Iron leaching during the assays must also be considered. Indeed the homogeneous mechanisms, Fenton and photo-Fenton, could contribute to the global process leading to 2-CP degradation depending on the amount of iron in solution. This could be the case for the Fe-PILC here studied for which iron concentration in solution reached values of 1.6 and 5.4 mg L⁻¹ at 180 min of reaction. On the contrary, for nZVI and goethite, iron concentration in solution at the end of the assays was below 0.1 mg L⁻¹. Even when iron leaching could affect the catalytic activity of the solid, for Fe-PILC, it represented no more than an 8.7 % of the catalytic species of the catalyst.

Conclusions

A clay, montmorillonite, was modified with iron giving rise to a solid containing a 6.1 % (w/w) of Fe. The resulting Fe-PILC was active in the degradation of 2-CP in photo-Fenton conditions. Practically, the total degradation of 2-CP was achieved, although the mineralization level was significantly lower. Iron leaching was detected and it could be related to the observed increase in the 2-CP degradation rate probably accounted for a homogeneous photo-Fenton mechanism. A diminution of the catalyst loading led to lower iron concentration in solution but also to a slightly decrease in 2-CP degradation and mineralization of the reactant medium.

The catalytic performance of the Fe-PILC in 2-CP degradation is comparable to that of the nZVI when quite similar iron contents are present in the reactant medium. Both catalysts, Fe-PILC and nZVI, have shown a higher catalytic activity than goethite in 2-CP degradation in photo-Fenton conditions.

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