



Copper hydroxyphosphate as catalyst for the wet hydrogen peroxide oxidation of azo dyes

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ABSTRACT

Copper hydroxyphosphate was synthesized hydrothermally and characterized by XRD and SEM. The peroxide degradation of azo dye on this material was evaluated by examining initial pH, catalyst loading, H₂O₂ dosage, initial dye concentration and temperature. Although copper hydroxyphosphate is a low surface area material without micropores or mesopores, it shows considerable activity for oxidative degradation of azo dyes under near-neutral pH conditions. A catalyst with such simple and clear structure may be a suitable model material for research on the mechanism of generating hydroxyl radicals and their destruction of organic molecules.

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1. Introduction

Many industries discharge a large quantity of wastewater containing dyes, phenol and its derivatives, pesticides, and other organic pollutants. Because many toxic organic compounds are biorefractory, conventional biological treatment is ineffective for these kinds of wastewater. Some physicochemical technologies, such as adsorption, coagulation, and membrane separation, merely transfer pollutants from one medium to another requiring further treatment [1–3]. Advanced oxidation processes (AOPs), aiming to complete oxidation of organic pollutants to water, carbon dioxide, and other harmless small molecules, are becoming more and more important technologies for wastewater treatment, especially for biorefractory contaminants.

There are basically three main types of AOPs, depending on the type of oxidant (oxygen, ozone, and hydrogen peroxide). Wet air oxidation (WAO) operates typically under oxygen pressure (5–200 bar) (using air about four times higher pressure is necessary) and at elevated temperature (125–320 °C) necessitating high pressure autoclave apparatus. In addition, the reactor should be resistant to corrosion because high concentrations of low molecular weight acids can form as products, and real streams often contain large amounts of ions such as chlorine which may be oxidized under the conditions of wet oxidation, making very corrosive media.

Therefore, the wastewater treatment by WAO processes is very expensive. Moreover, the gas containing NO_x, CO, VOCs and offensive odors discharged from the process must be further treated. Another AOP used is ozonation, but the limited solubility of ozone in water makes this method applicable only to dilute solution. Additionally, the high energy consumption for generating ozone by silent electrical discharges also makes its use expensive [4–7].

Wet hydrogen peroxide catalytic oxidation (WHPCO), which operates under mild conditions (20–80 °C and atmospheric pressure), is considered to be one of the most effective, simple and economical methods for treating biorefractory contaminants [8]. The classical Fenton reagent consisting of a homogeneous solution of Fe²⁺/Fe³⁺ and H₂O₂ has been extensively studied. However, there are two major drawbacks in the classical Fenton processes: the pH of operation should be strictly controlled around pH 3.5; and large amounts of sludge require further treatment [9,10]. In recent years, increasing attention has been paid to research on heterogeneous Fenton systems as alternatives in order to overcome these problems [8].

In general, solid catalysts are porous materials with huge specific surface areas, which provide more catalytic active centers, so a high catalytic activity can be expected. To prepare porous catalysts with large surface areas, various methods can be used especially for immobilizing active species to porous supports through ion-exchange, impregnation, and precipitation [11]. Catalysts like transition metal ions (Fe, Co and Ni) impregnated carbon aerogels [12], Fe and Cu pillared clays [13–15], Fe- and Cu-exchange Y and ZSM-5 zeolites [16–21], and Cu-Silicalite-1 zeolite prepared by

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direct hydrothermal synthesis or by ionic exchange method [22] have been studied for the removal of different contaminants such as phenol and derivatives, dyes, carboxylic acids and MTBE by WHPCO processes.

However, an easily overlooked problem is that there is mass transfer resistance in porous materials. According to the mechanism of the heterogeneous Fenton reaction, H_2O_2 first reacting with a solid catalyst generates active hydroxyl radicals, and then hydroxyl radicals degrade organic pollutants to harmless small molecules. Because the active sites are mainly located in the inner surface of porous catalysts, there is considerable diffusion resistance for large organic molecules. In fact, with the exception of the so-called mesoporous zeolite, the pore diameter of most zeolites is less than 1 nm. For example, the pore diameters of ZSM-5 and Y zeolites are about 0.56 and 0.74 nm, respectively [23]. The pore of zeolite is so narrow that it is impossible for the common organic pollutants in the wastewater such as azo dyes and triphenylmethane dyes to diffuse into the channel of the zeolite. Thus, the oxidative degradation of the organic pollutants requires several steps: H_2O_2 diffuses into the inner surface of the catalyst and reacts with active species generating hydroxyl radical, and then hydroxyl radical diffuses out of microporous catalysts and reacts with organic pollutants. It is well known that hydroxyl radicals are extraordinarily reactive species and short-lived [10,24]. They attack the target organic molecules with rate constants usually in the order of 10^6 to $10^9 M^{-1} s^{-1}$. Thus, diffusion limitation often becomes the rate-controlling step. On the other hand, the hydroxyl radicals generated in microporous catalysts may disappear before diffusion out by reacting with each other to produce oxygen molecules [10], or by reacting with some ions such as Cl^- , CO_3^{2-} , and SO_4^{2-} which commonly exist in real industrial wastewater [24]. According to this point of view, a non-porous catalyst with low surface area may not necessarily mean a low catalytic activity.

Copper hydroxyphosphate ($Cu_2(OH)PO_4$), the mineral named libethenite, is a low surface area crystal without micropores or mesopores [25]. Xiao and coworkers first discovered its excellent catalytic properties for the oxidation of olefins and alcohols by molecular oxygen under air pressure [26], and hydroxylation of phenol, benzene, naphthol, and 2,3,6-trimethylphenol by hydrogen peroxide [27–29]. Electron spin resonance (ESR) investigation suggested that $Cu_2(OH)PO_4$ decomposed hydrogen peroxide to generate a high concentration of hydroxyl radicals, which could be responsible for the high catalytic activity [27,28]. This implies that such a catalyst may be effectively used to degrade wastewater containing organic pollutants through the Fenton mechanism.

Recently, Xu and Xue reported the hydrothermal synthesis of $Cu_2(OH)PO_4$ with complex morphologies [30]. Cho et al. reported the synthesis of $Cu_2(OH)PO_4$ with various 3D hierarchical superstructures by using a wet-chemical method. They demonstrated firstly the useful photocatalytic activity of these complex structures in the degradation of methylene blue dye under visible light irradiation [31]. In this paper, we investigated the wet hydrogen peroxide catalytic oxidation of an azo dye (Direct Brown 2) using $Cu_2(OH)PO_4$. Effects of variables such as initial pH, catalyst loading, H_2O_2 dosage, initial dye concentration, and temperature were studied.

2. Materials and methods

2.1. Materials

Direct Brown 2 (C.I. 22311), which purchased from Tianjin Shengda Chemical Plant (Tianjin, China), was of commercial grade and directly used without further purification. The molecular structure is shown in Fig. 1. Diammonium hydrogen phos-

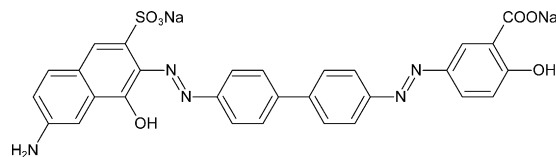


Fig. 1. The molecular structure of Direct Brown 2.

phate ($(NH_4)_2HPO_4$) was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$) was purchased from Beijing Hongxing Chemical Plant (Beijing, China). Tetraethyl orthosilicate (TEOS) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Hydrogen peroxide (30%, v/v) was purchased from Luoyang Haohua Chemical Reagent Co., Ltd. (Luoyang, China). NaOH and H_2SO_4 were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All these chemical reagents were of analytical grade. Deionized water was used throughout the study.

2.2. Preparation and characterization of $Cu_2(OH)PO_4$

Copper hydroxyphosphate was synthesized hydrothermally from diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$). A solution of diammonium hydrogen phosphate (8.66 g $(NH_4)_2HPO_4$ in 40 mL water) was dropped slowly into the solution of copper chloride (5.59 g $CuCl_2 \cdot 2H_2O$ in 15 mL water) under vigorous stirring. The resulting mixture was added 30 μL tetraethyl orthosilicate (TEOS) and it was further stirred for 1 h, and then transferred into a Teflon-lined stainless steel autoclave. The crystallization was carried out at 150 °C for 48 h without stirring. The autoclave was then quenched to room temperature. The solid product was filtered, washed with water, and dried at 80 °C overnight. About 3.5 g dark green crystal powder was obtained. The powder XRD data were obtained in a Y-2000 automated X-ray diffractometer system (Dandong Aolong Radiative Instrument Co., Ltd., China) using $Cu K\alpha$ radiation scanning at a scan rate of 5/min. Scanning electron microscopy (SEM) analyses were carried out in a JSM-5600LV (Jeol, Japan).

2.3. Batch experiments of dye decolorization

The catalytic degradation of dye was carried out in a 150 mL cylindrical jacketed glass reactor with magnetic stirring. The reaction temperature was controlled by circulating constant temperature water. In a typical run, a given amount of $Cu_2(OH)PO_4$ was added into 100 mL Direct Brown 2 solution which has been adjusted to the desired pH by adding diluted NaOH or H_2SO_4 . When the temperature was constant, the reaction was initiated by adding a known dosage of H_2O_2 (30%, v/v) to the solution. At given time intervals 5 mL solution was taken out and centrifuged to remove residual catalyst. The solution concentration of dye was measured using a SP-756PC UV–vis spectrophotometer (Shanghai Spectrum Instrument Co., Ltd., China) at 470 nm. The degradation efficiency of dye was calculated by the equation:

$$\text{Degradation efficiency} = \frac{A_0 - A_t}{A_0} \times 100\%$$

where A_0 is the initial absorbance and A_t is the absorbance at time t .

To study the effect of variables on degradation reaction, the experiments were repeated under different initial pH values (3–7), catalyst loading (0–100 mg), H_2O_2 dosage (0.1–1.2 mL), initial dye concentration (10–80 mg/L) and temperature (20–60 °C).

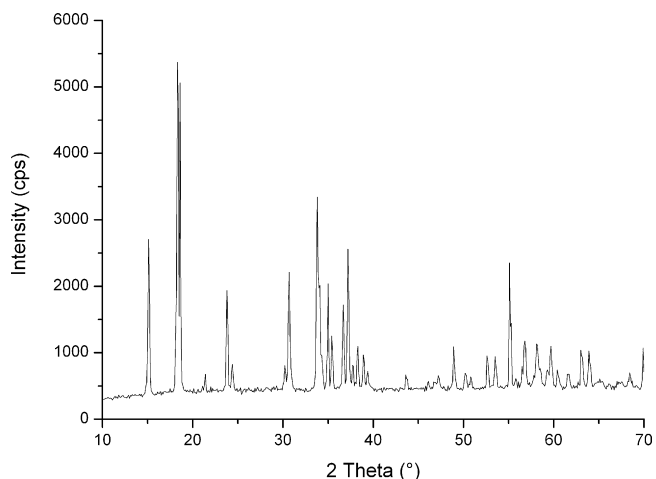


Fig. 2. XRD pattern of copper hydroxyphosphate.

3. Results and discussions

3.1. Characterization of $\text{Cu}_2(\text{OH})\text{PO}_4$

XRD pattern of the as-prepared $\text{Cu}_2(\text{OH})\text{PO}_4$ is shown in Fig. 2. Although the relative peak intensities of XRD pattern were different from the earlier literature [30,31], the peak position is closely consistent with the reported data (JCPDS card File No. 360404). All peaks can be indexed as the pure phase of $\text{Cu}_2(\text{OH})\text{PO}_4$. No diffraction peaks for other phases or materials are observed in the XRD pattern, indicating a high purity of the final products. The crystal morphology of $\text{Cu}_2(\text{OH})\text{PO}_4$ varies with the synthesis conditions [30]. In this study the product synthesized is elongated octahedral, as shown in Fig. 3.

3.2. Effect of initial pH

The solution pH significantly influences the degradation of organic compounds. It is common knowledge that the classical Fenton process exhibited the optimum performance in only a narrow range of pH 2–4. When solid catalysts containing iron as active species are used, higher pH can be adopted [14,18]. In some cases, the catalytic activity of iron species is extremely low when the pH is greater than 5 [16].

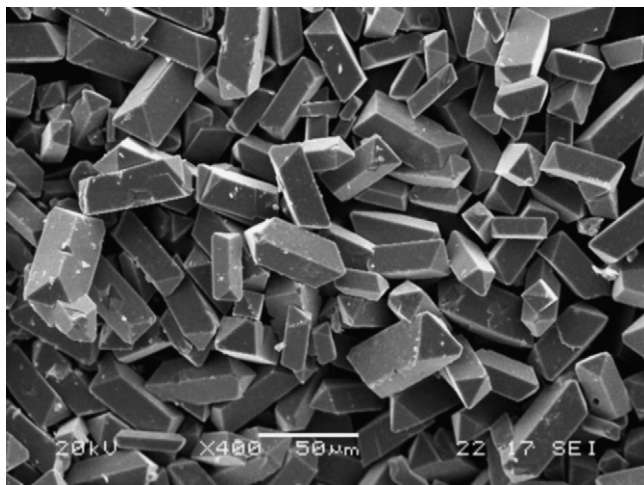


Fig. 3. SEM image of copper hydroxyphosphate.

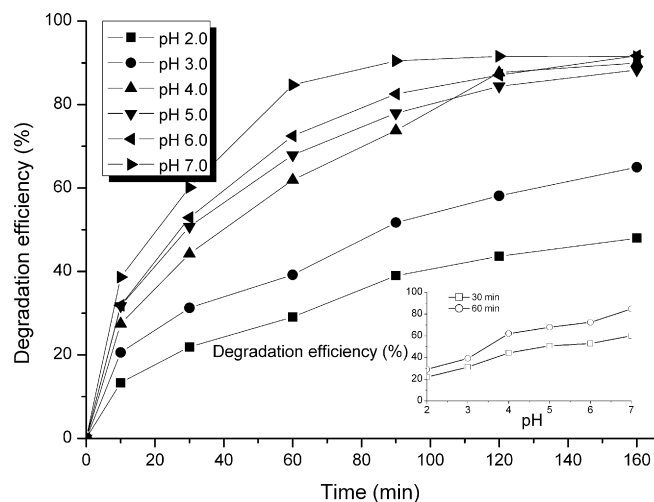


Fig. 4. Effect of initial pH on the catalytic degradation of Direct Brown 2 (dye 20 mg/L, H_2O_2 0.8 mL, catalyst loading 100 mg, $T = 50^\circ\text{C}$). Inset: relationship of pH and dye degradation at 30 and 60 min, respectively.

In this study the effects of pH were examined by adjusting the initial pH of dye solution in the range 2–7. The results indicate that the catalytic activity of $\text{Cu}_2(\text{OH})\text{PO}_4$ increases with the increase of initial pH (Fig. 4). Similar conclusions have been reported when using copper as active species to degrade organic contaminant, through either heterogeneous [17] or homogeneous processes [32,33]. In this study, the degradation efficiency after 160 min was 48.0, 65.0, 90.0, 88.3, 91.7 and 91.5% at pH values of 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0, respectively. The optimal pH range for the degradation is 4–7. A near-neutral pH condition is preferable because operation under near-neutral conditions can easily apply to most wastewater. On the other hand, acidic conditions significantly enhance the leaching of active component [22].

3.3. Effect of catalyst loading

To investigate the effect of $\text{Cu}_2(\text{OH})\text{PO}_4$ addition on dye degradation, five different catalyst loadings (0, 3, 25, 50 and 100 mg) were tested. As can be seen from Fig. 5, without catalyst the degradation efficiency was very low with only 1.8% after 130 min. Addition of only 3 mg catalyst in 100 mL dye solution the degradation efficiency after 160 min reached at 47.0%, indicating the catalyst was highly

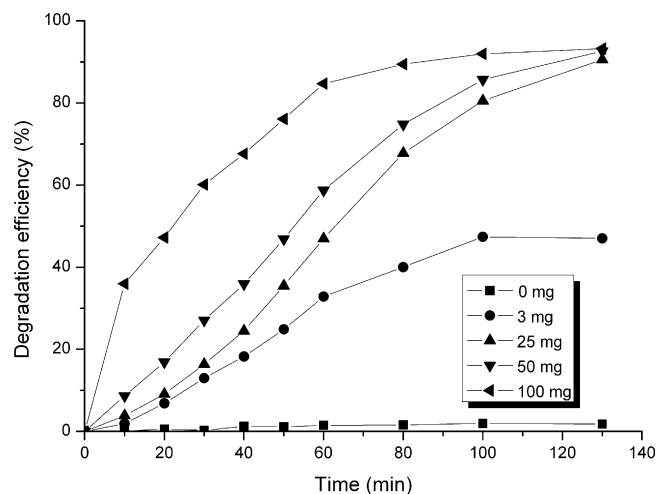


Fig. 5. Effect of catalyst loading on the catalytic degradation of Direct Brown 2 (pH 7.0, dye 20 mg/L, H_2O_2 0.8 mL, $T = 50^\circ\text{C}$).

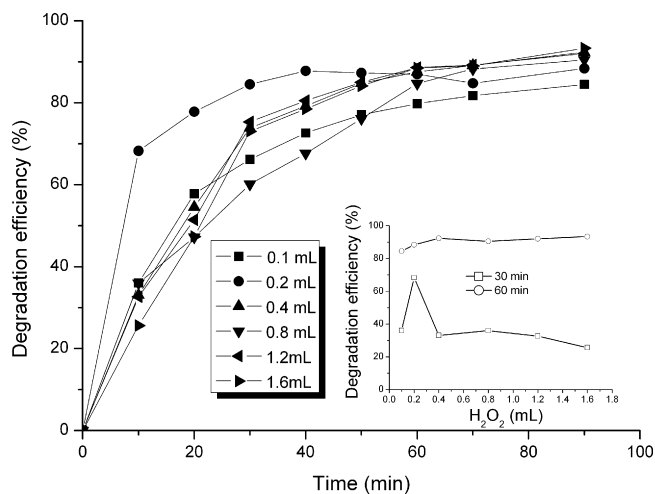


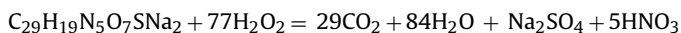
Fig. 6. Effect of H_2O_2 dosage on the catalytic degradation of Direct Brown 2 (pH 7.0, dye 20 mg/L, catalyst loading 100 mg, $T = 50^\circ\text{C}$). Inset: relationship of H_2O_2 dosage and dye degradation at 30 and 60 min, respectively.

active. The degradation efficiency after 160 min reached 90.6, 92.6 and 93.2% when catalyst loading was 25, 50 and 100 mg, respectively.

3.4. Effect of H_2O_2 dosage

The effect of H_2O_2 dosage on degradation of dye is shown in Fig. 6. Because the H_2O_2 concentration is directly related to the number of hydroxyl radicals generated in the Fenton reaction, H_2O_2 dosage significantly influences the initial reaction rate. The degradation efficiency after 10 min was 36.1 and 68.2% when the H_2O_2 dosage is 0.1 and 0.2 mL, respectively. More than 0.2 mL H_2O_2 results in a decrease in initial reaction rate. This means that there is an optimal concentration of H_2O_2 to degrade organic contaminants. Addition of excess of H_2O_2 results in a decrease in reaction rate. This phenomenon can be explained by the scavenging effect of excess H_2O_2 , which decreases the number of hydroxyl radicals in the solution [17].

The overall stoichiometry for the complete degradation of Direct Brown 2 by H_2O_2 can be written as



According to this equation, 77 mol of H_2O_2 are theoretically needed to completely degrade 1 mol of Direct Brown 2. In the present study, when 0.2 mL H_2O_2 was added into 100 mL Direct Brown 2 solution with the concentration of 20 mg/L, the H_2O_2 /dye molar ratio is about 554. This value is 7.2 times larger than the theoretical value. A similar result was observed by Bobu and coworkers [34].

3.5. Effect of initial dye concentration

The effect of initial dye concentrations on the degradation was investigated between 10 and 80 mg/L dye solutions as shown in Fig. 7. The degradation rate was decreased by increasing initial concentrations. The increase in dye concentration increases the adsorption of dye molecules on catalyst surface, limiting the generation of hydroxyl radicals, and so the degradation rate decreases [16]. Hence, oxidation process requires more catalyst loading and longer reaction times for higher dye concentrations.

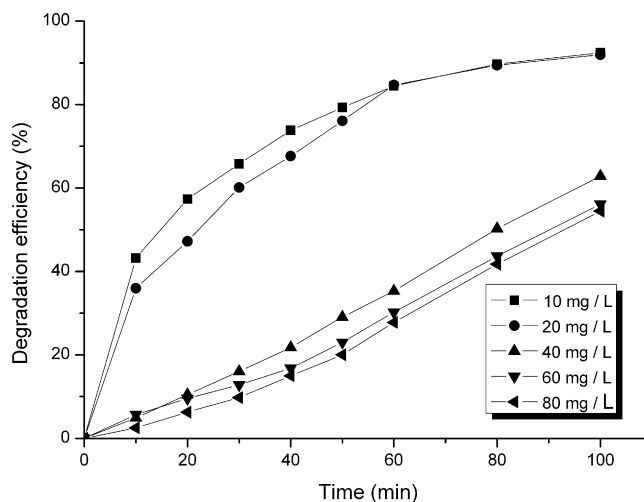


Fig. 7. Effect of initial dye concentration on the catalytic degradation of Direct Brown 2 (pH 7.0, H_2O_2 0.8 mL, catalyst loading 100 mg, $T = 50^\circ\text{C}$).

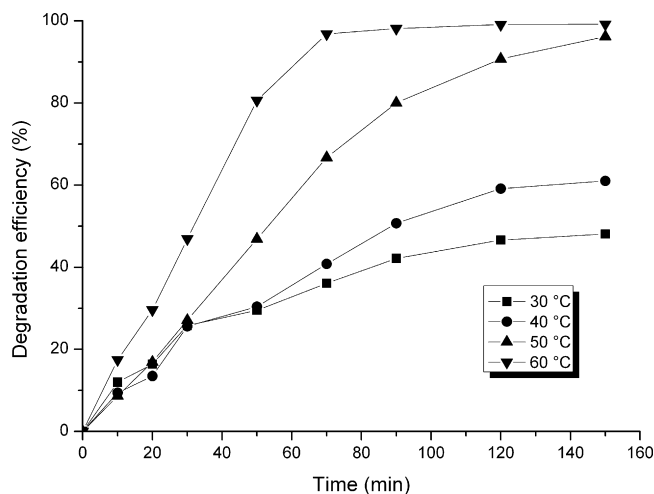


Fig. 8. Effect of temperature on the catalytic degradation of Direct Brown 2 (pH 7.0, dye 20 mg/L, H_2O_2 0.8 mL, and catalyst loading 50 mg).

3.6. Effect of temperature

The effect of temperature on the degradation reaction was investigated at 30, 40, 50, and 60 °C, respectively. The results are given in Fig. 8. As expected, rising temperature significantly enhanced the catalytic activity of degradation. At 60 °C the degradation efficiency reached 98.1% after 90 min and 99.2% after 150 min; at 50 °C it reached 80.0 and 99.6% after 90 and 150 min, respectively. The reactivity was low when temperature is lower than 40 °C. The degradation efficiency after 150 min was 48.1 and 61.0% at 30 and 40 °C, respectively. To achieve complete decolorization of the added dye, a temperature higher than 50 °C is a necessary.

4. Conclusions

The peroxide degradation of an azo dye on copper hydroxyphosphate was evaluated by examining initial pH, catalyst loading, H_2O_2 dosage, initial dye concentration and temperature. Although $\text{Cu}_2(\text{OH})\text{PO}_4$ is non-porous structure material with low surface area, as a catalyst it shows considerable activity for oxidative degradation of azo dyes by hydrogen peroxide under near-neutral pH condition. If nano-sized $\text{Cu}_2(\text{OH})\text{PO}_4$ crystals can be synthesized,

it may be expected to obtain higher catalytic activity for treating wastewater. Moreover, a catalyst with such simple and clear structure may be a suitable model material for research on the mechanism of generating hydroxyl radicals and their destruction of organic molecules.

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