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Catalytic oxidation of aqueous solutions of organics. An effective method for removal of toxic pollutants from waste waters

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Abstract

Catalytic liquid-phase oxidation of aqueous solutions of organics is presented as a potential, advanced waste water treatment technology. Catalysts are briefly reviewed first, followed by mechanistic speculations and kinetics that have been proposed for liquid-phase oxidation of some model pollutants. Subsequently, oxidation reactors and potential process schemes are discussed.

1. Introduction

A large portion of the waste generated by chemical and related industries is in the form of aqueous streams. In many cases, these aqueous streams contain organic compounds in too small concentrations so that economic recovery is not feasible, yet the concentrations are high enough to pollute the environment, if they are released without treatment. On the other hand, many streams originating in industrial activities contain organic pollutants which are either toxic or poorly biodegradable, so that direct biological treatment is not feasible. In these cases, it is necessary to use less conventional techniques such as chemical oxidation to remove the pollutants. However, these techniques may be prohibitively expensive when used to achieve complete oxidation of all organics present in the waste stream. A possible and less expensive alternative is the partial oxidation of organics to intermediate compounds which are amenable to biological treatment.

In recent years, thermal liquid-phase or wet air oxidation has been demonstrated to be an efficient technology for treating a variety of dilute aqueous streams [1]. However, reaction conditions required to achieve oxidation are severe, typically being in the range of 200–300°C and 70–130 bar. Under such extreme conditions, material selection becomes very critical as corrosion rates are high, and most materials are susceptible to stress corrosion cracking in the presence of chloride ions. Indeed, these considerations adversely affect the economics of such processes. Oxidation of dilute aqueous solutions of organic pollutants using oxygen over a solid catalyst offers an alternative to uncatalyzed wet air oxidation as a means of purifying waste waters. In this process organics are oxidized to carbon dioxide and water in a three-phase reactor at much lower temperatures and pressures than in the uncatalyzed thermal processes.

The aim of this note is, however, to review briefly the results that have been published for catalytic oxidation of organics dissolved in water.

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Particular attention is given to the catalysts that promote the oxidation and to the reaction kinetics. Oxidation reactors and process schemes that may be used for commercial exploitation are also discussed.

2. Oxidation catalysts

The key issue in the effective catalytic oxidation of organics in waste waters is, however, finding a suitable catalyst. The conditions under which small amounts of organics dissolved in a large amount of water are oxidized force a severe demand on the physical and chemical properties of a catalyst. Hot acidic aqueous solutions can promote the solubility of some metal oxides in their higher oxidation states and consequently, deactivate an otherwise favorable catalyst.

Some of the earliest studies employed the metals Pt, Pd, and Rh as catalysts for converting organic pollutants dissolved in waste water [2–4]. Rieche and colleagues [5] showed that powdered coal and some types of ash were catalysts for the air-oxidation of phenol in waste water. In 1969 Hamilton and coworkers [6] patented a process for liquid-phase oxidation of dissolved pollutants at 100°C using MnO_2 as a catalyst. Intensified research activities in the seventies directed to the oxidation of organic pollutants dissolved in water have brought new and promising catalytic systems. Thus, Sadana and Katzer [7,8] found γ-alumina supported copper oxide as an efficient catalyst for oxidation of aqueous phenol solutions in the temperature range of 96–246°C. Neither Sadana and Katzer [7] nor the group of Goto [9], which used the same catalyst and model pollutant to study the performance of a laboratory rotating basket reactor, have mentioned leaching of copper from the catalyst. Njiribeako and coworkers [10,11] found that copper in the form of cupric ions contributed about 20% to the total rate as a homogeneous catalyst when copper was supported by γ-alumina, while this figure increased up to 40% when alumina was replaced by silica. Box and Farha [12] designed an oxidation catalyst consisting of copper, manganese, and lanthanum oxide on a zinc aluminate spinel. Its catalytic activity was demonstrated in oxidation of acetic acid solutions [13] with no signs of early deactivation. The activity was found to be about one order of magnitude higher when compared with the iron oxide catalyst [14]. Sadana and Katzer [7] also showed that unsupported cupric oxide was not effective for oxidation of aqueous phenol solutions while copper and manganese oxides supported on alumina were active. Levec and Smith [14] found both palladium (0.1%) on γ-alumina and $CuO \cdot ZnO$ catalysts inactive for oxidation of acetic acid solutions. In contrary, $CuO \cdot ZnO$ was found quite active for oxidation of formic acid solutions [15]. Dissolved organics in waste waters were oxidized at 80 to 112°C and 14 to 61 bar by Chowdhury and Ross [16] using various metals, metallic oxides, and salts: among solid catalysts platinum oxide gave best results. The Japanese patent [17] lists MnO_2 as an active catalyst for oxidation of organic pollutants in waste water at 60°C. Also, mixtures of oxides of Cu, Co, Ni and Fe, and Pt, Pd, Rh, Ru and Ir are reported [18] as effective catalysts at 100°C for waste water purification, presumably by oxidation. At higher temperatures, copper oxide in combination with two of the following oxides CoO, Fe_2O_3, CeO_2, SnO_2, NiO and ZnO are suggested [18]. In the eighties a group of Imamura [19–21] effectively employed different catalytic systems (Ru/Ce, Mn/Ce and Co/Bi) for oxidation of organics frequently found in waste waters. Ito and colleagues [22] oxidized aqueous solutions of oxygen- and nitro-containing organic compounds by means of cobalt oxide. Recently, a catalyst capable of promoting oxidation of organics in aqueous solution below 150°C has been reported [23]. The catalyst consisting of CuO, ZnO and Al_2O_3 promotes oxidation of phenol, chlorophenol, nitrophenol, butyl alcohol, methyl vinyl ketone at 130°C and oxygen partial pressure of 3 bar [24]. The oxides of copper, zinc and cobalt supported by aluminate cement also exhibited high activity in oxidation of phenol aqueous solutions [25]. Relative activities of

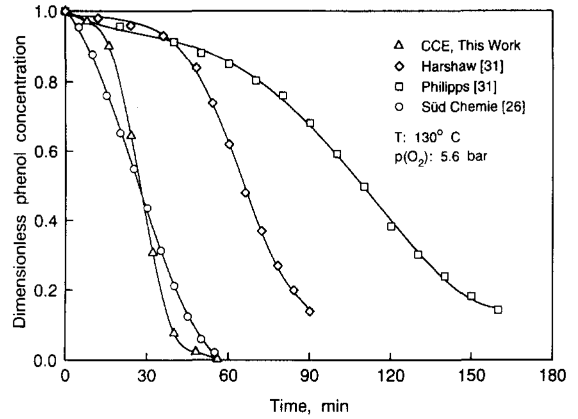

Fig. 1. Relative activities of some experimental and commercial catalysts for oxidation of aqueous phenol solutions in a slurry reactor.

some catalysts for phenol oxidation in slurry reactor are shown in Fig. 1.

When catalytic oxidation undergoes a free radical mechanism, there is no evidence in the literature that pretreatment of the catalyst is necessary. Sadana and Katzer [7] did note that the activity increased from the first to the second run but remained constant thereafter. In contrary, pretreatment was necessary in order to gain constant activity when the catalyst behavior followed an oxidation–reduction sequence [13–15].

3. Oxidation mechanism and kinetics

In comparison with numerous studies for pure organic liquids, relative few mechanistic concepts have been published for the catalytic oxidation of organic compounds in aqueous solutions. Sadana and Katzer [7,8] found that catalytic oxidation of phenol in aqueous solution with copper oxide occurred by a free radical mechanism, in agreement with results for pure component oxidations. It was reported that the reaction involved a free radical initiation on the catalyst surface, homogeneous propagation, and either homogeneous or heterogeneous termination processes. Radical initiation could occur by dissociative adsorption of phenol or by hydroperoxide decomposition on the catalyst surface. Pintar and Levec [26] reported additionally the formation of polymers, in agreement with the observations of Ohta and coworkers [9] but opposed to Sadana and Katzer [7]. A simplified reaction scheme for phenol oxidation in slurry reactor is shown in Fig. 2. The polymers were formed by two reactions taking place in the liquid phase: (1) stepwise addition polymerization of the C-2 aldehyde (glyoxale) to phenol, and (2) polymerization of the C-2 aldehyde [26]. This homogeneous polymerization markedly reduces the extent of total oxidation, with only 50 to 60% of initial carbon content being converted via the heterogeneous reaction route to carbon dioxide. The above investigations have been performed in a slurry reactor, with the exception of the experiments performed by the group of Goto [9] which used a rotating basket reactor. In a liquid-full operated fixed bed reactor (with predissolved oxygen in the liquid feed of phenol) it was discovered [27] that the homogeneous reactions were suppressed due to the high catalyst to liquid ratio. However, Pintar and Levec [27] have shown that catalytic oxidation of aqueous phenol solution in this case underwent a combined redox and heterogeneous free radical mechanism. The role of catalyst was ascribed to be in the activation of both reactants, phenol and oxygen. Each of these steps requires different active sites at the catalyst surface. Phenol is believed to adsorb exclusively on the metal ion sites at their higher oxidation states and is via a surface redox cycle and hydroxyl hydrogen abstraction transformed to phenoxy radicals. This homolytic, one electron transfer initiation process in which free radicals appear has been proposed by many authors [8,28,29]. The same mechanism has been proposed for catalytic oxidation of aqueous solutions of *p*-nitrophenol and *p*-chlorophenol [30]. Hydrogen abstraction was also postulated as a radical formation step in catalytic oxidation of alcohols and amines [22].

The activity of catalyst in oxidation of formic acid solution was explained by an oxidation–reduction mechanism [15]. Evidence for this was the reduction of the catalyst at dissolved oxygen concentrations approaching zero and reoxidation when the oxygen concentration in the formic acid

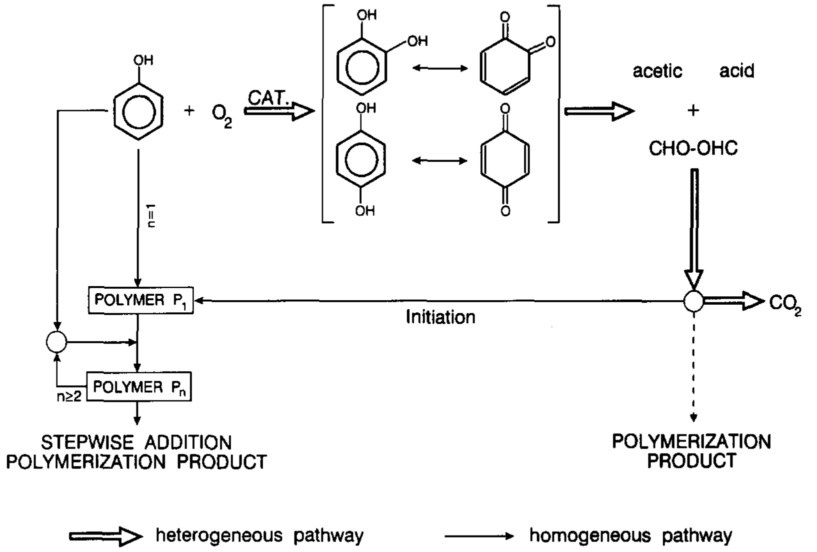

Fig. 2. Simplified reaction pathway of phenol oxidation in a slurry reactor.

solution was increased. The data for acetic acid oxidation also showed that catalytic activity was associated with an oxidized state [14]. The proposed mechanism was that the acid reacts with an oxidized site with subsequent formation of carbon dioxide and water via multiple steps, and, finally, adsorption of oxygen on the reduced site to convert it to the oxidized state.

Data on the kinetics of catalyzed oxidation of model organic pollutants dissolved in water are meager. Most of the reports on the oxidation are of a general nature with little quantitative rate data. Experimental rate data have been presented for model pollutants such as acetic acid [14], formic acid [15], phenol [7–9,26,27], and chloro- and nitrophenol [30]. Formic acid oxidation was found to be of the first order with respect to both oxygen partial pressure and formic acid concentration. The rate data on acetic acid showed an overall dependency of one-half order with respect to oxygen, and a $C_{acid}/(1+K\cdot C_{acid})$ functional variation with acetic acid concentration [14]. From the kinetic point of view, reported results on phenol oxidation disagree. Sadana and Katzer [7,8] have found out that catalytic oxidation of phenol underwent an induction period with transition to a much higher steady-state activity regime. They found the reaction to be of first order with respect to phenol in both regimes, but the oxygen dependence decreases from first order to one-half order in shifting from the induction period to the steady-state activity regime. On the other hand, Ohta and coworkers [9] have found different kinetic behavior with the same catalyst: an order of 0.44 and 0.55, for phenol and oxygen, respectively. In a thorough kinetic investigation of Pintar and Levec [26], the rate of phenol disappearance in a slurry reactor has been expressed as a sum of heterogeneous and homogeneous (polymerization) contribution, thus

$$(-r_{PhOH}) = k_{het}\cdot C_{PhOH}\cdot C_{O_2}^{1/4} + k_{hom}\cdot C_{PhOH}\cdot \Sigma C(P_n), \qquad (1)$$

where k_{het} is the apparent rate constant for the heterogeneous oxidation steps, and k_{hom} is the lump polymerization rate constant including initiation (phenol plus glyoxale) and propagation steps. It is interesting to note that the rate data for oxidation of p-chlorophenol showed dependency of the one-half order with respect to oxygen [31]. However, integrated form of Eq. (1) is confronted with the experimental data in Fig. 3. On the other hand, the phenol oxidation rates obtained in a liquid-full operated fixed bed reactor were well interpreted by means of the Langmuir–Hinshelwood

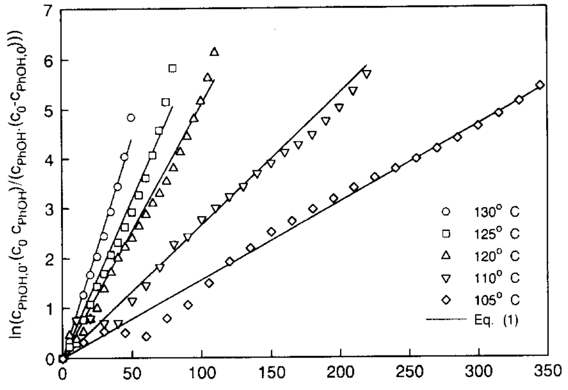

Fig. 3. Test for heterogeneous–homogeneous reaction of integrated form of Eq. (1).

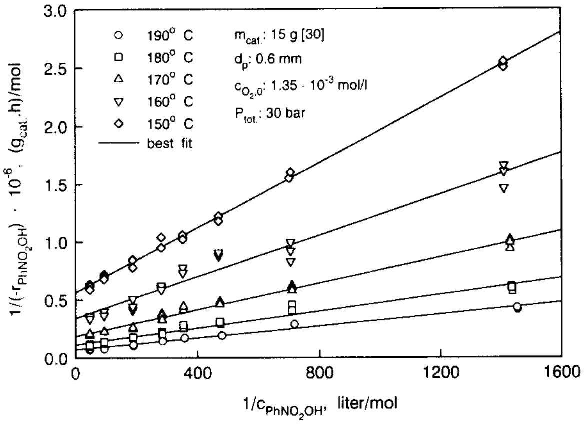

Fig. 4. Comparison of experimental liquid-full fixed bed reactor data and linearized Eq. (2): catalytic oxidation of *p*-nitrophenol.

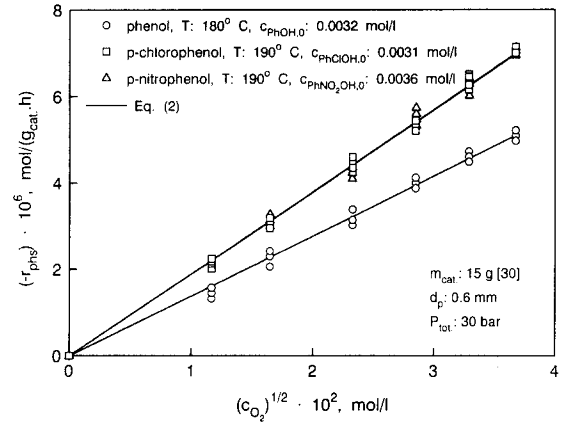

Fig. 5. Test of oxygen functional dependency of Eq. (2).

formulation [27]. It has been found out that the disappearance rate of phenol as well as *p*-chlorophenol and *p*-nitrophenol [30] in a liquid-full operated fixed bed reactor is well expressed in the following form

$$(-=r_{\text{poll.}}) = \frac{k_{\text{sr,app.}}\cdot K_{\text{poll.}}\cdot K_{O2}^{1/2}\cdot C_{\text{poll.}}\cdot C_{O2}^{1/2}}{1+K_{\text{poll.}}\cdot C_{\text{poll.}}}, \qquad (2)$$

where subscript 'poll.' stands for either one of the model pollutants. Linearized form of Eq. (2) is compared with the experimental data for *p*-nitrophenol in Fig. 4. In Fig. 5 the rate dependency on oxygen concentration is tested for all three pollutants. These results clearly indicate (Fig. 2) that the heterogeneously catalyzed reaction route is favorized in liquid-full operated fixed bed reactors. Comparison of the results obtained in slurry and fixed bed reactors suggests that the distribution of intermediate products, and consequently the oxidation rate, depends on the reactor system used. Therefore, rate expressions developed from the data of slurry system cannot be used for the design purposes if compounds tend to polymerize.

A very plausible reaction scheme was proposed by Ito and coworkers [22] for catalytic oxidation of oxygen- and nitrogen-containing compounds. They assumed first order with respect to each reactants (intermediates) and zero order with respect to oxygen partial pressure (large excess of oxygen) and found fairly good agreement between predicted and measured carbon dioxide appearance. In catalytic oxidation of strong waste waters it has been found that the reaction obeyed first order with respect to the pollutant concentration [16]. It has been concluded in almost all kinetic investigations that the oxidation rate depends on the catalyst loading (in slurry systems), initial organic compound concentration and pH value of solutions, thus providing enough evidences of free radicals involvement in the oxidation reactions [7,9,16,20,26].

Large disagreement is reported on the apparent (overall) activation energy values. No attempts have been made to correlate or even summarize the diverse results. For example, the activation energy values for the oxidation of phenol with supported copper oxide have been reported to be 85.7 [9], 84 [26], 176 [7], and 127 kJ/mol [27], respectively. Comparing the results of Ohta and coworkers [9] and Sadana and Katzer [7], which were obtained with the same catalyst, one can conclude that the lower value proceeded due to the polymerization reactions involved. However, apparent activation energies appear to be for the most part in the range of 70 to 170 kJ/mol.

4. Oxidation reactors

For reactions necessitating a solid catalyst and which involve both relative volatile (oxygen) and nonvolatile reactant (pollutant in waste water), three-phase reactors are required. Equipment used to achieve intimate contacting of the three phases has been predominantly in the form of slurry reactors or fixed bed reactors in which the two fluid phases flow through a stationary bed of catalyst either concurrently upwards (bubble column fixed bed) or downwards (trickle bed). Trickle bed reactors avoid the disadvantage of separating small catalyst particles from the fluid product streams associated with slurry reactors, and also avoid the limitation of flow rates encountered with upflow through fixed beds. As discussed above, in a reactor with high liquid to catalyst ratio (such as slurry and bubble column fixed bed reactors), waste waters containing pollutants that tend to polymerize (aromatic compounds) should not be treated.

It seems that Katzer with coworkers [32] were the first who evaluated the catalytic liquid-phase oxidation as a potential waste water treatment technology and offered a process scheme. They have demonstrated that catalytic oxidation may not be economically attractive for low concentrations of organics because of the energy requirement to heat up waste water stream. High organic concentrations in waste waters provide enough heat so that the process is thermally self-sufficient; in these cases the process becomes economically feasible. Farha and coworkers [33] elaborated experimentally in great detail the possibility of using catalytic oxidation in advanced waste treatment facilities. Their process design and economic evaluations have indicated that the process is economically sound. They also found out that organics removal in the two reactor systems, bubble column fixed bed and trickle bed, are comparable despite somewhat different mass transfer conditions.

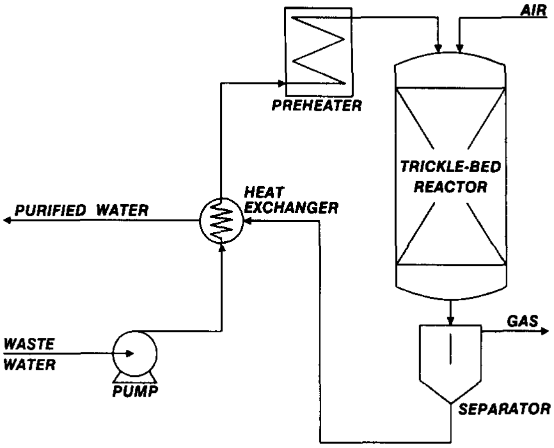

Fig. 6. Schematic drawing of simple process for a catalytic liquid-phase oxidation.

A simplified process scheme for the catalytic liquid-phase oxidation of organics in waste waters is depicted in Fig. 6. Prefiltered waste water is pumped to operating pressure, and brought to the reactor operating temperature by a feed/effluent heat exchanger. Together with the preheated waste water, a compressed air stream — at stoichiometric excess — is also fed to the top of the trickle bed reactor. Since energy cost precludes vaporization, the reactor must operate at pressures above the vapor pressure of water. The treated reactor effluent may be suitable for surface discharge. In the case when a waste stream contains relatively low concentrations of organic contaminants, a step in which organics are preconcentrated may be required. The process which uses an activated carbon adsorption–preconcentration step is shown schematically in Fig. 7 [34]. Once the carbon bed is saturated with organics, it is regenerated by routing hot water at temperatures up to 180°C and elevated pressure through the adsorber. This procedure desorbs most of the organics, and subse-

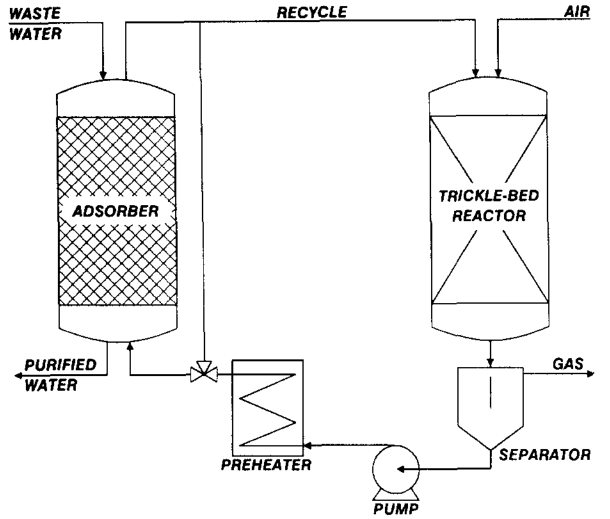

Fig. 7. Schematic drawing of process for a catalytic liquid-phase oxidation with an adsorber for preconcentration.

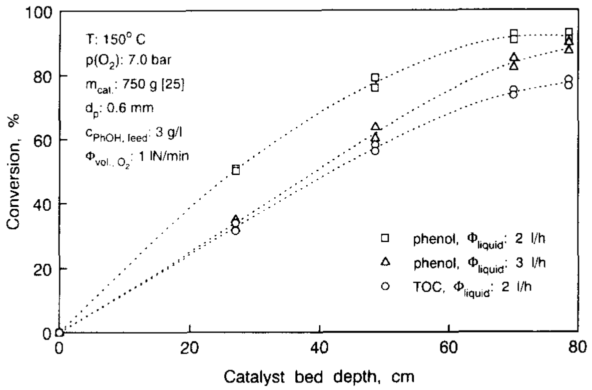

Fig. 8. Typical conversion profiles along the catalyst bed in a trickle bed reactor.

quently ensures their destruction by oxidation over the bed of catalyst in a trickle-bed reactor. Conversion profiles in a trickle-bed reactor during the catalytic oxidation of phenol aqueous solution are shown in Fig. 8. The difference appearing between phenol and T(otal) O(rganic) C(arbon) concentrations is typical for the deactivation of catalyst due to polymers adsorbed on the catalyst surface.

5. Conclusions

The key issue of the effective catalytic oxidation of organics in waste water is the catalyst. Oxidation most probably undergoes a complex redox and/or heterogeneous nonbranched-chain free radical mechanism. In order to develop effective catalyst and process, more kinetic and mechanistic studies with different systems in aqueous solutions are needed.

For optimal effect, a catalytic liquid-phase oxidation process should be installed at the source of waste water production in an industrial plant. Dependent on the class and the amount of organic compounds dissolved in waste water, the process can be designed either to reduce their concentration or ultimately destroy them. In the former case, intermediate products that are formed during the oxidation must be biodegradable.

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