

Electrochemical catalytic treatment of wastewater by metal ion supported on cation exchange resin

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Abstract

The electrochemical oxidation of phenol in synthetic wastewater and paper mill wastewater catalyzed by metal ion supported on cation exchange resin in suspended bed electrolytic reactor with graphite electrode has been investigated. The catalyst was characterized by SEM and XPS spectra and the effects of pH, the different metal ion and NaCl on the efficiency of the electrochemical oxidation phenol process were also studied. It was found that the catalyst containing Fe^{3+} had the highest electrochemical catalytic activity for the electrochemical oxidation of phenol. When the initial concentration of phenol was 200 ppm, up to 90% chemical oxygen demand (COD) removal was obtained in 10 min. When the catalyst containing Fe^{3+} was used to the paper mill wastewater, it still showed high efficiency. The COD removal could get to 75% in 60 min. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electrochemical catalytic oxidation; Phenol; Paper mill wastewater; Wastewater treatment; Resin

1. Introduction

Phenols and phenolic compounds have been declared to be hazardous pollutants [1]. Many industrial processes, such as oil refineries, plastic plants, synthetic chemicals, pesticides, coal conversion have been attributed to the phenolic compounds [2]. Likewise, as one of the most important water consumers: 15–60 m³ of fresh water are used to produce 1 t of paper, depending on the type of production proceed involved (Thompson et al., 2001), the paper making processing produce wastewaters containing important amounts of these phenolic compounds [3]. Due to the resistance to common microorganisms, phenolic wastes cannot be treated by biological action. Moreover, they are toxic even in the presence of low concentration. Therefore, the treatment of phenolic pollutants will be of considerable importance in environmental protection [4].

Many technologies and processes have been conventionally attempted for phenolic wastewater, such as extraction [5], biological treatment [6,7], chemical oxidation [8], wet oxidation [9], ozone oxidation [10], photo-catalytic oxidation [11], oxidation in supercritical water [12]. But there are few suitable

processes to deal with this high toxicity effluent [13]. Electrochemical method offers the prospect of relatively simple equipment, environmental friendliness, and the possibility of high-energy efficiency. So, electrochemical oxidation method for removal of phenolic compounds has attracted a great deal of attention [14].

The oxidation of phenolic is principally depended on the hydroxyl radical generated on the surface of the electrodes. Therefore, the processes are called advanced electrochemical oxidation processes (AEOPs) [15]. For the purpose of improving the oxidation efficiency and accelerating the reaction rate, the homogeneous catalyst has applied in the AEOPs processes. But the recovery of the catalyst is very difficult and requires an additional reaction to remove the homogeneous catalyst.

In present work, resin as a heterogeneous catalyst was applied in the electrochemical cell [16]. In contrast to previous studies, the catalyst loading metal ion developed a stable heterogeneous process [17,18], combining the efficiency of homogeneous processes, such as the metal ion oxidization process and Fenton-type process. At the same time, as a heterogeneous catalyst, the cation exchange resin can recover some of the metal ions which maybe as a new pollutant in the process. Except that the resin can absorb some organics to removal pollutants. So resin loading metal ion was choosing to the treatment of the wastewater.

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The principle aim of this investigation was to study the characterization of the catalyst and the possible application of the synthesized metal ion supported on resin system for purifying phenol and paper mill wastewater, as well as to investigate the effect of some factors (pH of the medium, salt existed and different metal ion) on the efficiency of the electrochemical catalytic oxidative degradation of phenol.

2. Materials and methods

2.1. Materials and general measurements

The chemical reagents used were of analytical grade and employed without further purification. The strong acidic cation exchange resin was purchased from tianjin kernel chemical reagents development centre. The paper mill wastewater was from Xi'An Wan Long paper mill.

2.2. Electrochemical cell

The experiments were conducted with undivided cell of 500 mL capacity under constant temperature conditions (25 °C). Two porous graphite electrodes were fixed vertically and parallel to each other in the inner column cylinder. The true surface of graphite electrode (3.2 cm × 6 cm) was 19.2 cm². On the vessel wall of the inner column cylinder there were many small holes. Ten grams of catalyst was packed around the graphite electrode, forming a multi-phase electrochemical oxidation packed bed. The wastewater was put into the outer column cylinder and was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution. The electric power was supplied with regulated dc power supply, WYK302b, Xi'an, China. The current and voltage were adjustable between 0 and 2.5 A and between 0 and 35 V.

2.3. Preparation of the catalyst

Prior to use, the cation exchange resin was washed by distilled water several times, then immersed into the same concentration (0.2 mol/L) of ferric chloride solution, cobalt chloride solution or copper chloride solution for 3 h, respectively, and then dried at 70 °C for 4 h.

2.4. Characterization of the catalyst

The micrograph of the catalyst without metal iron and the catalyst loading on metal iron before and after reaction were taken by using scanning electron microscopy (SEM, Hitachi H-700 instrument) and a gold film was sputtered onto the sample prior to observation.

X-ray photoelectron spectroscopy of the catalyst loading metal iron before and after phenol electrochemical oxidation process were recorded by using an X-ray photoelectron spectrometer equipped with a Mg K α (1253.6 eV) source.

The initial pH of the solution was measured using an Orion 290 pH meter. The chemical oxygen demand (COD) was measured according to standard method [19,20].

2.5. Water purification process

The concentration of phenol in wastewater used in the experiments was 200 ppm, NaCl (2000 ppm) was used as electrolyte, and NaOH or HCl in proper amounts was used to get the suitable pH value. The temperature of the electrochemical reaction was maintained at 25 °C. The voltage applied was 10 V.

3. Results and discussions

3.1. Characterization of the catalyst

3.1.1. SEM analysis

The SEM images in Fig. 1 visually showed the morphological differences of the surface of the cation exchange resin (a); resin-Fe³⁺ before phenol oxidation process (b); resin-Fe³⁺ after phenol oxidation process (c). It can be found that image (b) showed many cracks existed on the surface of the resin, which was attributed to the ferric ion exchanged onto the resin. After the electrochemical oxidation reaction, the resin had transformed. The larger cracks appeared on the surface of the resin; some resin split and something like chain formed from the resin, which might due to that the resin loading on metal ion acted with the substances existed in the electrochemical process and produced some stable substance, leading to the deformation of the structure of resin.

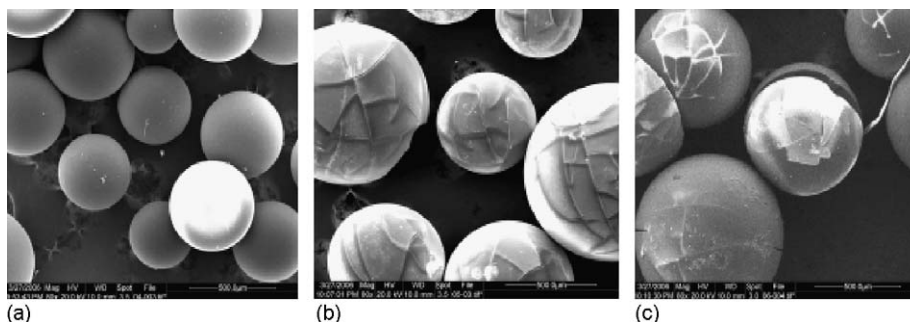


Fig. 1. Solid morphology by SEM.

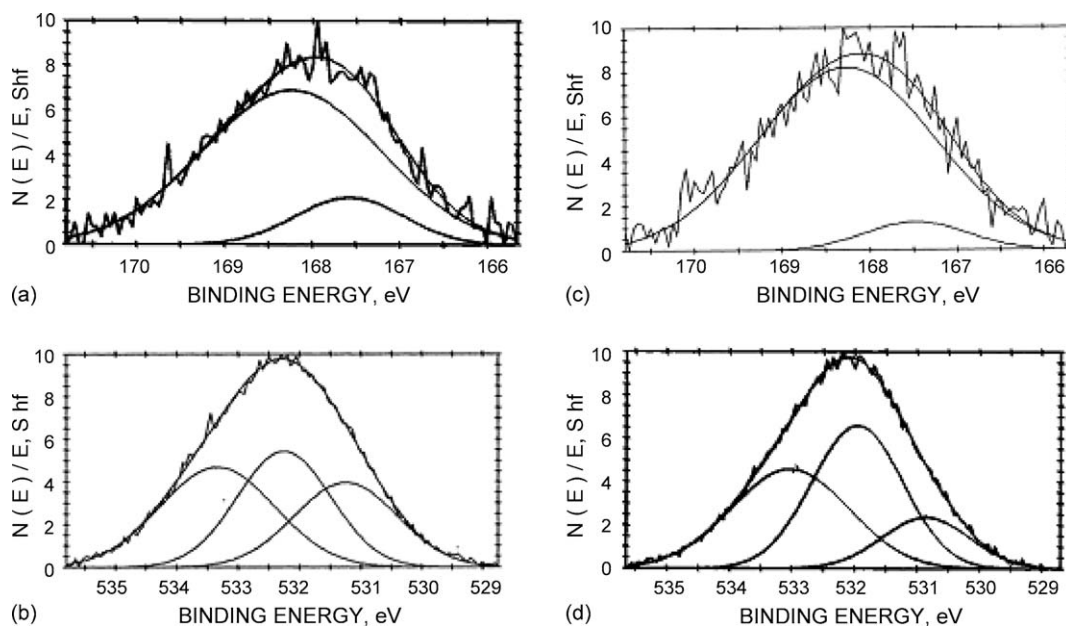


Fig. 2. XPS spectra of S 2p (a, b) and O1s (c, d).

3.1.2. XPS analysis

The catalyst containing Fe^{3+} was characterized by XPS spectra. Fig. 2 showed the spectra of catalyst before and after the water treatment process. The spectra (a) and (b) showed the XPS signals of S 2p before and after phenol oxidation. Before the electrochemical oxidation process, two peaks were observed in the spectra. The band at 168.2 eV was attributed to the polymer- SO_3H . The binding energies at about 167.5 eV maybe corresponded to the polymer- SO_3Fe . The area of band at 168.2 eV was about five times to that of the band at 167.5 eV, which indicated that about 15% Fe^{3+} iron was exchanged onto the cation-exchanged resin. After the oxidation process, the peak at 167.5 eV became decreased, which was in agreement with that the Fe^{3+} which combined indirectly with S had taken part in the oxidation process.

The spectra (c) and (d) showed the XPS signals of O 1s before and after phenol oxidation, respectively. In spectra (c), it was observed that three chemical environmental oxygen atoms were existed in the system and the ratio of the three O 1s peaks were 1:1:1, which might be attributed to different SO bond (533.1 and 532.0 eV) and the O-Fe bond (530.9 eV). After the phenol oxidation (showed in spectra (d)), the peak of O-Fe decreased, which confirmed that the Fe^{3+} was consumed as an oxidant in the electrochemical process. At the same time, the peak at 530.9 eV was shifted to higher binding energies, which probably due to that the more stable substance was produced in the oxidation process.

3.2. The application of the catalyst to the electrochemical degradation phenol

3.2.1. Effect of Fe ion on COD removal

Fig. 3 showed the effect of Fe^{3+} loading on the cation exchange resin on the COD removal in pH 7. As can be seen the

COD removal over 90% was obtained when used resin- Fe^{3+} catalyst, and less than 4% COD removal was obtained when used catalyst without Fe^{3+} , which indicated that the Fe^{3+} ion played an important role in the electrochemical oxidation of phenol. When the resin was used only, the COD could get to 480 mg/L in the first 10 min, and could not decrease in the last 30 min, which maybe due to the resin combined with some organics and produced stable substance which hampered the electrochemical reaction proceeded. While the catalyst with Fe^{3+} was used, the COD could get to 220 mg/L in the first 10 min and it decreased continually in latter 30 min, its higher efficiency on the COD removal might be attributed to the two reasons: one was the reduction of Fe^{3+} to Fe^{2+} , which underwent the normal Fenton reaction; the other was that the Fe^{3+} may oxidized directly the intermediates of phenol decomposition, i.e. hydroxylated phe-

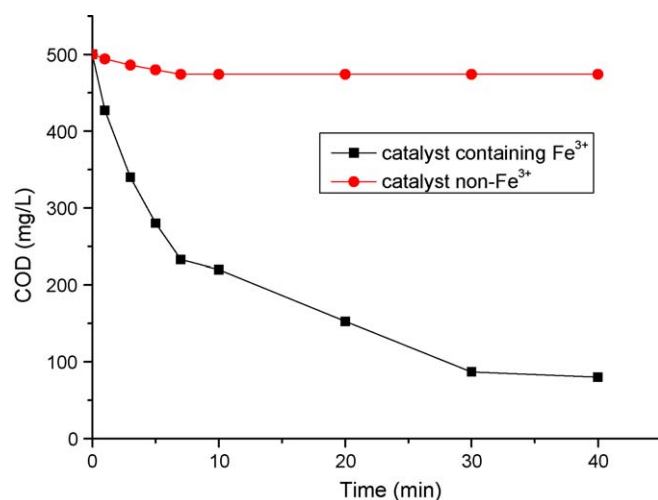
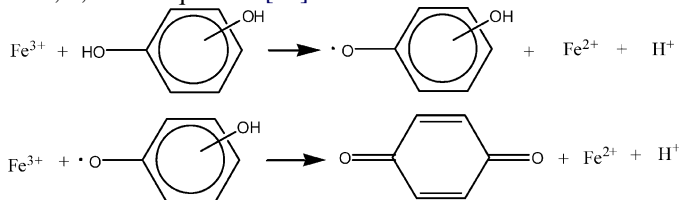


Fig. 3. The effect of Fe ion on COD removal in pH 7.

nols, 1,4-benzoquinone [21]:

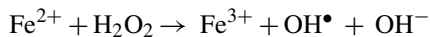


This speculation was consistent with the result that only 35% COD removal was achieved at the same reaction conditions but in the absence of the electrolysis, which was indicated that the Fenton's-like reaction was existed in the electrochemical system combined with Fe^{3+} -resin.

3.2.2. Effect of initial pH on COD removal

Fig. 4 showed the effects of initial pH of the solution on the efficiency of COD removal and it could be seen that the initial pH strongly affected the phenol removal efficiency.

A significant COD removal could be obtained at a relatively lower pH value within 20 min, while a less COD removal was observed at neutral or basic solution, which might attribute to the following reasons: first, an effective iron cycle can be taken place at low pH values. Almost constant Fe^{3+} concentration and traces of Fe^{2+} which will be readily transformed, mainly according to the reaction:



because Fe^{3+} ion and $\cdot\text{OH}$ all displayed as oxidant in the phenol oxidation process; second was that the oxidation ability of $\cdot\text{OH}$ was fairly stronger at acidic conditions. And in acidic solution free radical can easily be formed and organic material was easily to be oxidized [21]. Consequently, the oxidation proceeded rapidly and thoroughly at acidic conditions.

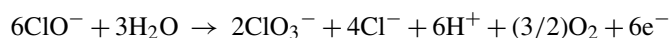
However, it is interesting to observe that COD removal again increases at slightly alkaline conditions (pH 8), which can be explained that more hydroxyl in the system were gathered at anode and competed with anode materials to react to produce oxygen, which was able to establish an effective red-ox sys-

tem with H_2O_2 [22], so the oxidation proceeded slowly in basic condition and need longer time than that of the acidic medium.

The speciation of Fe^{3+} , in interaction with the catalyst surface, at different pH value was not elucidated, but it was certainly different from that in solution [23]. With increasing the pH, the precipitation of the insoluble ferric hydroxides taken place and the decomposition of H_2O_2 became preponderant. So the phenol oxidation requires acidification of the initial solution [24].

3.2.3. The effect of NaCl existed on the COD removal

Fig. 5 showed the effect of NaCl on the COD removal in pH 7 in the presence of the resin- Fe^{3+} . A considerable increasing in COD removal at shorter times was observed when chloride ions were presented and the COD removal can be reached up to 90% in 5 min, while only lower than 50% removal efficiency was observed for the system in the absence of NaCl, which maybe due to that the electrochemical process was improved by the hypochlorite formed near the surface through oxidation of chloride [21]:



3.2.4. The effect of different metal ion on the COD removal

Fig. 6 showed the influence of different metal ion loading on the cation exchange resin on the electrochemical oxidation of phenol in pH 7. The COD removal over 90% was obtained when the cation exchange resin containing Fe^{3+} was used, only about 50% COD removal was obtained while the cation exchange resin containing Co^{2+} was used in 70 min. At the same time the Cu^{2+} could not yield to the perfect COD removal as the Co^{2+} or Fe^{3+} . From these results it could be concluded that the cation exchange resin containing Fe^{3+} was the most suitable one in the process of electrochemical degradation of phenol. It can be attributed to the Fenton reaction taken place in the process. The ferrous iron deoxidized from ferric iron initiated and catalyzed up the decomposition of H_2O_2 produced from the electrode surface,

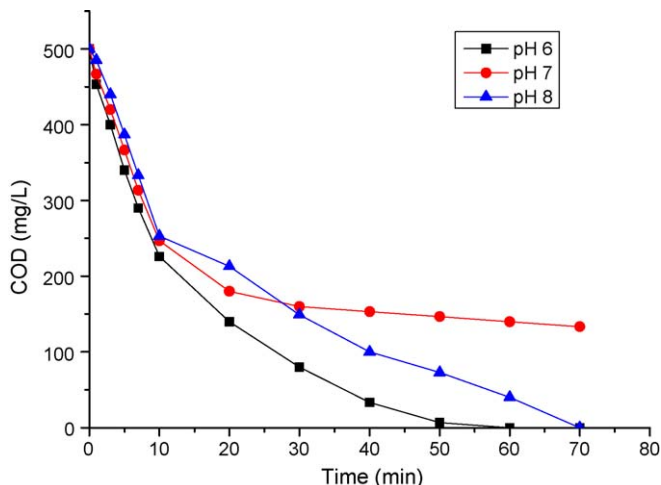


Fig. 4. The effect of pH on the COD removal.

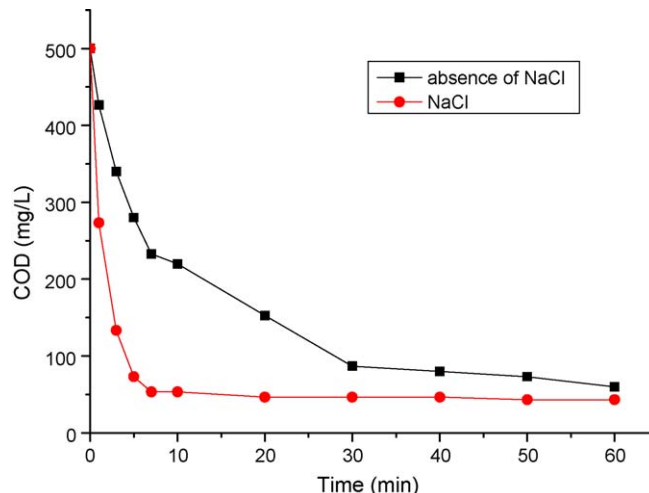


Fig. 5. The effect of NaCl on the COD removal in pH 7 with the resin- Fe^{3+} .

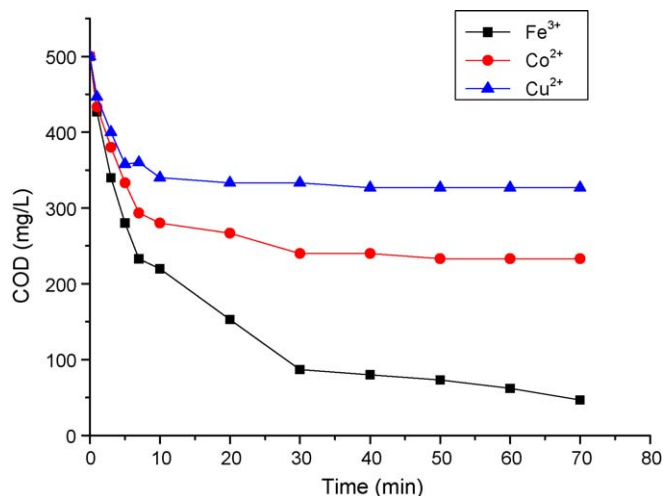
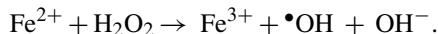


Fig. 6. The effect of different metal on the COD removal in pH 7.

resulting in the generation of hydroxyl radicals according to the reaction (Kitis et al., Yoon et al., Lu et al.):



The generation of the radicals involved in the process of the phenol oxidation in an aqueous solution. So the resin loading Fe^{3+} showed the highest electrochemical catalytic activity for the electrochemical oxidation of phenol.

3.2.5. The UV spectra of the electrochemical oxidation process in pH 7 with resin- Fe^{3+}

The electronic spectra of the reaction system in distilled water were investigated. Fig. 7 showed the reaction catalyzed by the cation exchange resin containing Fe^{3+} in pH 7 at different time.

It can be seen that the absorption at 211 nm was disappeared and the absorption at 270 nm was weakened in the first 10 min, maybe due to that the substituted group on the benzene ring had changed and the benzene ring still existed in the system, but benzene ring maybe disturbed might due to the intermediates such as hydroquinone, benzoquinone were formed in the process

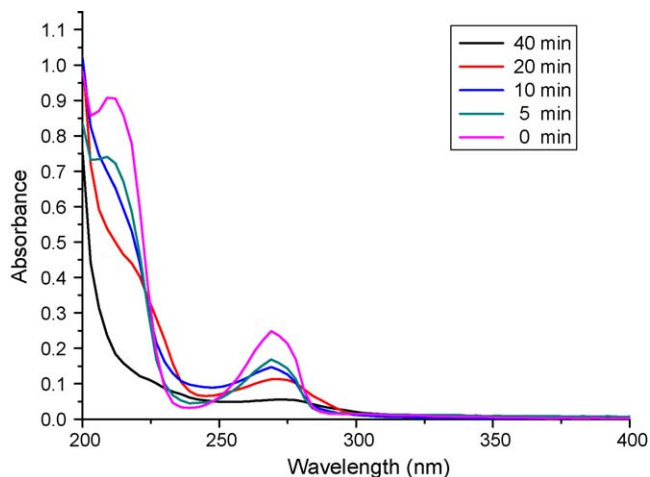


Fig. 7. The effect of time on the reaction system catalyzed by the resin- Fe^{3+} in pH 7.

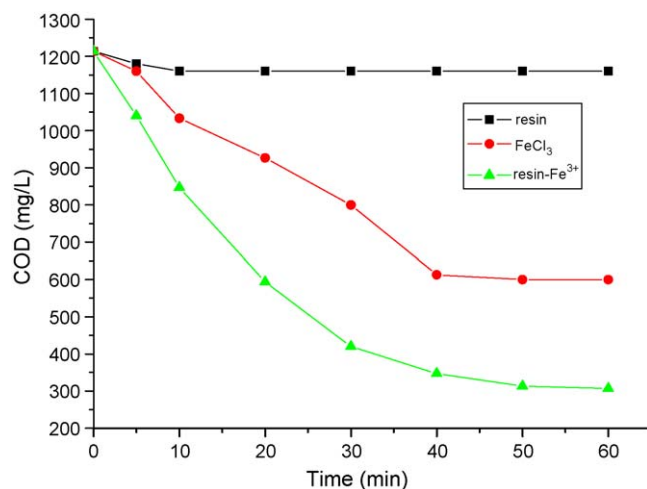


Fig. 8. The effect of different catalyst on the reaction system.

of the oxidation [25]. Forty minutes later, the absorptions at 211 and 270 nm were all disappeared, which indicated that the benzene ring was broken and the phenol in water was almost completely oxidized.

3.3. The application of the catalyst to the treatment of paper mill wastewater

Fig. 8 showed the different catalyst on the COD removal of paper mill wastewater in pH 7. The COD removal could get to 75% when the resin- Fe^{3+} was used and the COD removal get to 50% while only ferric ion present in the electrochemical system, at the same time only 5% COD removal was achieved when only the resin was used, which maybe due to that the Fenton's-like reaction might exist in the resin- Fe^{3+} catalyst system, companied by the absorbability of the resin, so that the ion-exchange resin supported Fe^{3+} catalysts showed the highest activity to oxidize phenol in the electrochemical oxidation process. The activity of ferric ion is higher than that of only the resin used, maybe due to that the attribution of Fenton's-like reaction was more important than that of the absorbability role, which might also taken place when the ferric ion was used, while only absorbability attributed to the activity of the resin system.

4. Conclusion

Based on the above discussions, it can be concluded that the cation exchange resin containing Fe^{3+} acted as a good catalyst not only in the process of electrochemical oxidation degradation of phenol but also in the treatment of paper mill wastewater.

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