

## Catalytic wet peroxide oxidation of *p*-nitrophenol by Fe (III) supported on resin

Rey-May Liou, Shih-Hsiung Chen, Cheng-Hsien Huang, Cheng-Lee Lai, C. Y. Shih, Jing-Song Chang and Mu-Ya Hung

### ABSTRACT

Fe<sup>III</sup> supported on resin (Fe<sup>III</sup>-resin) as an effective catalyst for peroxide oxidation was prepared and applied for the degradation of *p*-nitrophenol (PNP). Catalytic wet peroxide oxidation (CWPO) experiments with hydrogen peroxide as oxidant were performed in a batch reactor with *p*-nitrophenol as the model pollutant. Under given conditions (PNP concentration 500 mg/L, H<sub>2</sub>O<sub>2</sub> 0.1 M, 80°C, resin dosage 0.6% g/mL), *p*-nitrophenol was almost completely removed, corresponding to an 84% of COD removal. It was found that the reaction temperature, oxidant concentration, and initial pH of solution significantly affected both *p*-nitrophenol conversion and COD removal by oxidation. It can be inferred from the experiments that Fe<sup>III</sup> supported on resin was an effective catalyst in the mineralization of *p*-nitrophenol. In an acidic environment of oxidation, the leaching test showed that there was only a slight leaching effect on the activity of catalytic oxidation. It was also confirmed by the aging test of catalysts in the oxidation.

**Key words** | catalytic oxidation, Fe<sup>III</sup>-resin catalysts, hydrogen peroxide, *p*-nitrophenol

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### INTRODUCTION

*p*-nitrophenol and phenolic are widely used as raw materials for the production of insecticides, petrochemicals, and pharmaceuticals (Wu *et al.* 2005; Zhou & Lei 2006; Manera *et al.* 2007). There have been some attempts, but they had failed, to develop an effective process for nitrophenol treatment by dealing with the traditional technologies such as adsorption, sorption, biological degradation, and solvent extraction process (Sabio *et al.* 2006; Shen *et al.* 2006; Ko *et al.* 2007; Qiu *et al.* 2009). The catalytic oxidation of nitrophenols to carbon dioxide and nitrates is the best solution for dealing with nitrophenolic discharge from the effluent of industries (Suarez-Ojeda *et al.* 2005; Rubalcaba *et al.* 2007; Zhao *et al.* 2008). Those advance oxidation processes (AOPs) and wet air oxidation (WAO) could be suitable to generate a low toxic effluent that is acceptable for biological wastewater treatment plant. The WAO process requires high temperature and pressure, which limit the application for toxic effluent treatment and

increase the operating cost. Though the catalyst reduces the critical conditions in WAO process, the stability of catalyst and leaching problem is still a challenge in WAO processes (Zazo *et al.* 2006; Liu & Sun 2007; Xu *et al.* 2007; Ma *et al.* 2009).

The AOPs are the solution to overcome the problems in WAO processes. AOPs are water treatment processes implemented at ambient temperature and pressure, which produce a highly oxidative chemical species as decomposers of pollutants. Ozone and hydrogen peroxide have received much attention for application in water treatment technology due to their high oxidation activity and disinfection potential (Lam & Hu 2007; Matheswaran *et al.* 2007; Yube *et al.* 2007). However, there are few literatures concerning the application of AOPs for wastewater treatment of nitrophenolic materials. Vargas and Nunez reported that photocatalytic oxidation can effectively degrade *p*-nitrophenol by oxidation under optimum pH (Vargas & Nunez 2009).

The purpose of this investigation was to explore a new catalyst and to apply it for nitrophenolic wastewater treatment by the CWPO process. The Fe<sup>III</sup>-resin catalyst was synthesized and characterized in this study, and it was used in wastewater treatment to promote the *p*-nitrophenol decomposition with hydrogen peroxide. Also, the influencing factors in catalytic wet peroxide oxidation were discussed in this study.

## MATERIALS AND METHODS

### Materials and characterization

*p*-nitrophenol and chloride iron (99% purity) were purchased from MERCK Co. (Germany). The macro porous weak acidic cation exchange resin (C-160) was purchased from PUROLITE (ion exchange capacity: 3.0 meq/mL/min, United Kingdom). Fe<sup>III</sup>-resin catalysts were prepared from C-160 resin with various molar ratios of chloride iron in aqueous solution. Hydrogen peroxide (OSAKA Co., Japan, 35%) was used as oxidant in solution.

### Catalyst preparation and oxidation

The weak acidic cation exchange resin was pretreated with acetone three to four times and then washed with deionized water to remove the interferential factors. They were soaked in different concentrations of FeCl<sub>3</sub> solution for more than 24 h ( $V_{\text{salt solution}}/V_{\text{resin}} = 10$ ) at ambient temperature. Then, they were filtered through a sieve and washed with deionized water. Resin catalysts were designated CM-1, CM-2, CM-3, CM-4, and CM-5, representing impregnating FeCl<sub>3</sub> concentrations 0.1–0.5 M. The CWPO process was carried out in a 0.6-l batch reactor with a setting temperature.

### Analysis of solution

The *p*-nitrophenol concentration during oxidation was determined by high-performance liquid chromatography (HPLC) (Jasco PU980, Japan Spectroscopic, Tokyo, Japan) with a UV detector. A methanol: water (65:35, v:v) mobile phase was used at a flow rate of 1 ml/min in conjunction with 25 cm × 4.6 mm C-18 column. The HPLC was equipped with an ultraviolet detector at 320 nm. The concentration of iron in solution was measured by

atomic absorption spectrometer (AA) using a GBC 932 plus Spectrophotometer on the solution after hot filtration (at the same temperature of the reaction) of the solution.

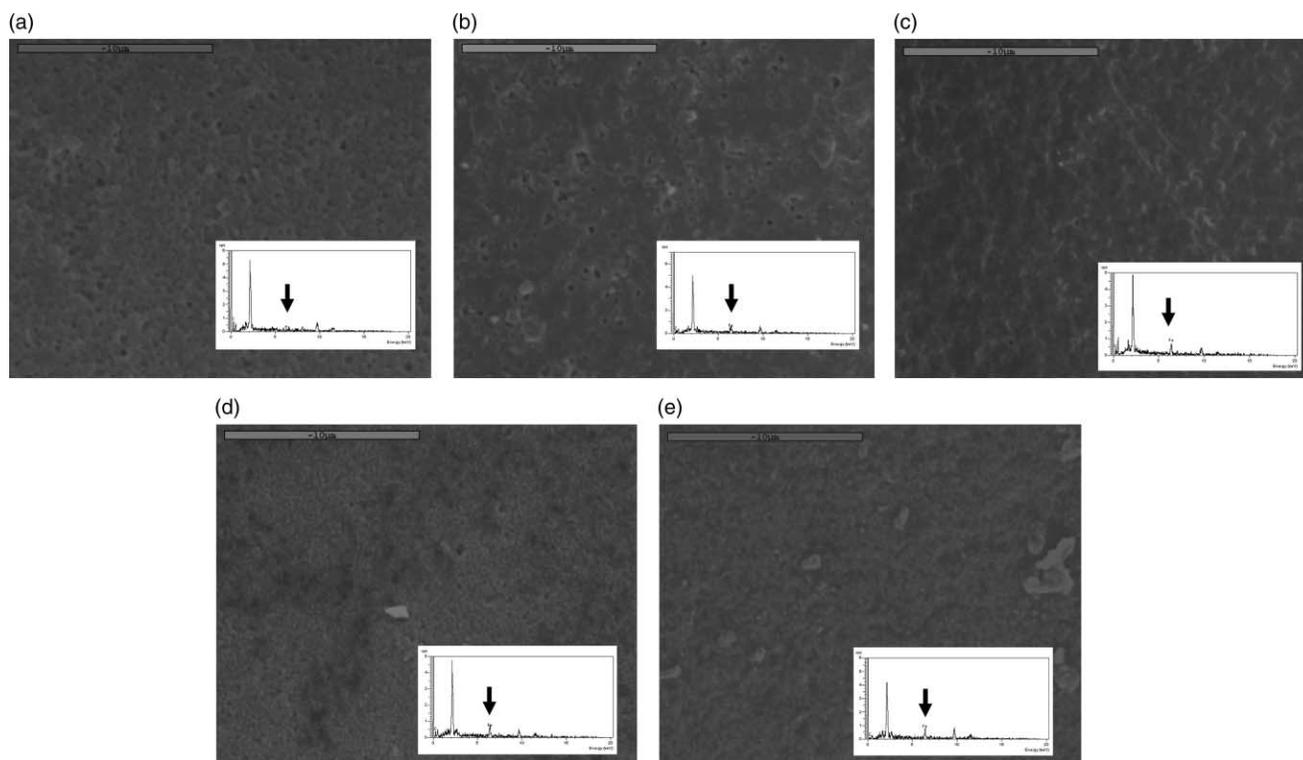
## RESULTS AND DISCUSSION

### Characterization of Fe(III)-supported catalyst

The effect of impregnation iron concentration on the surface morphology of Fe<sup>III</sup>-resin catalysts is shown in Figure 1. It can be seen that the porous surface generally disappeared with increasing impregnating iron concentration. As shown in Figure 1, the iron peak in the EDS spectra became stronger with increasing iron loading in the resin. It is implied that the increase in impregnation iron concentration increased the iron composition on the surface of the resin. A highly active heterogeneous catalyst should be highly dispersed with an active phase on the surface of the catalyst. It was expected that the active phase was proportional to the active metal loading on the surface of the catalyst. Quantitative iron loading measurements were made with EDS analysis. Figure 2 shows the effect of impregnated iron concentration on the iron composition on the surface of resins. It can be seen that the Fe composition on the surface was not proportional to the loading concentration. The iron composition increased with increasing iron concentration up to 0.1 M and then slightly leveled off up to 0.5 M ferric iron impregnation in preparation. This result indicates that the amount of iron loading could be limited by the ion exchange capacity of resin. When the resin was saturated at high concentration of iron solution, the iron composition was never increased with further increase in impregnating concentration. The active metal dominated the oxidation activity of the resin catalyst, which was proportional to the iron loading in the resin. Similar results can also be found in the polymer chelating catalyst that anchors transition metal and presents a good activity in CWPO process (Gupta & Sutar 2007; Liotta *et al.* 2009). Therefore, it is worthwhile to clarify the catalytic oxidation activity of Fe<sup>III</sup>-resin in CWPO system.

### Effect of Fe loading on activity of catalyst

The oxidation of *p*-nitrophenol by Fe<sup>III</sup>-resin catalyst was carried out in a stirred batch reactor with 0.1 M (mole/L)



**Figure 1** | SEM photographs and EDS spectra of Fe-resin catalysts with various iron loading (a) CM-1, (b) CM-2, (c) CM-3, (d) CM-4 and (e) CM-5.

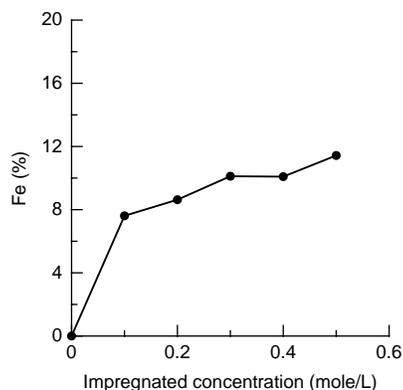
$\text{H}_2\text{O}_2$  and 3 g  $\text{Fe}^{\text{III}}$ -resin catalyst at  $80^\circ\text{C}$  and atmospheric pressure. The profiles of residual *p*-nitrophenol concentration and COD with various Fe loading in the catalyst are shown in Figure 3(a, b), respectively. It can be seen that all catalysts showed promising catalytic activity during the catalytic peroxide oxidation of *p*-nitrophenol with high mineralization efficiency. It can be seen that complete degradation of *p*-nitrophenol did not distinctively show the dependence between the iron content of the catalyst and the oxidation activity in the reaction. On the other hand, it can be seen that the conversion efficiency of *p*-nitrophenol was higher than the removal of COD during the period of oxidation. It was possible due to the incomplete oxidation of intermediates limiting the COD removal and leading to poor oxidation. Incomplete oxidation of phenolic material has been widely reported in previous literatures in the case of the CWPO processes (Quiroz *et al.* 2005; Bo *et al.* 2006).

As shown in Figure 3(b), it is indicated that COD rapidly decreased in the first 40 minutes and then leveled off on 180 minutes of oxidation. The 80% COD removal could be obtained in the oxidation. It was proposed that the

heterogeneous catalytic oxidation could follow the free radicals reactions generated by the oxidant (Tian *et al.* 2007; Bo *et al.* 2008). The free radical of hydrogen oxides played a main role in decomposing the pollutant in the CWPO process. Therefore, it can be proposed that the intermediates were formed during the oxidation and then the intermediates were further degraded rapidly to low molecules in the reactor. It is concluded that the iron supported on the resin presented a good activity in the catalytic peroxide oxidation and the effective conversion of *p*-nitrophenol could be obtained in 40 minutes.

#### Effect of initial pH on activity of catalyst

The activity of catalyst in Fenton or Fenton-like reaction shows a strong dependence on the initial pH of the solution during the oxidation (Catrinescu *et al.* 2003; Lu *et al.* 2009). They reported that high acidity in oxidation,  $\text{pH} = 2\text{--}4$ , was beneficial to generate free radical and process the chain reaction to degrade the organic material. Figure 4(a) shows the relationship between initial pH and residual

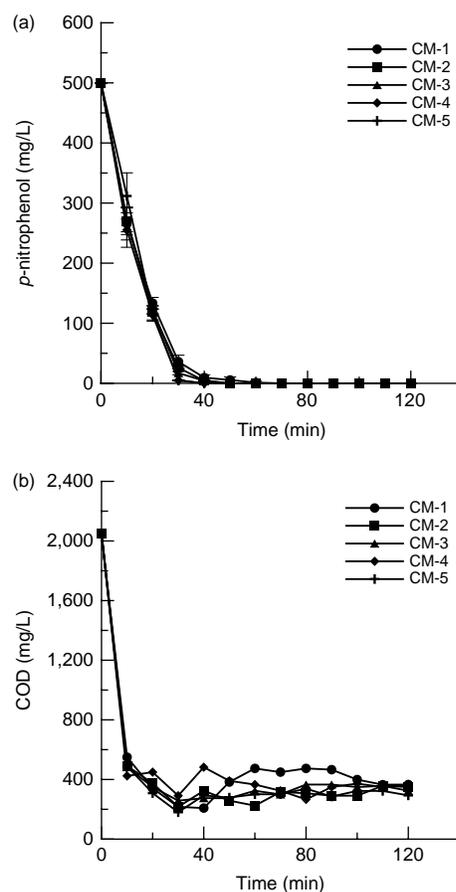


**Figure 2** | Effect of impregnated iron concentration on the iron composition on the surface of resins (based on EDS analysis).

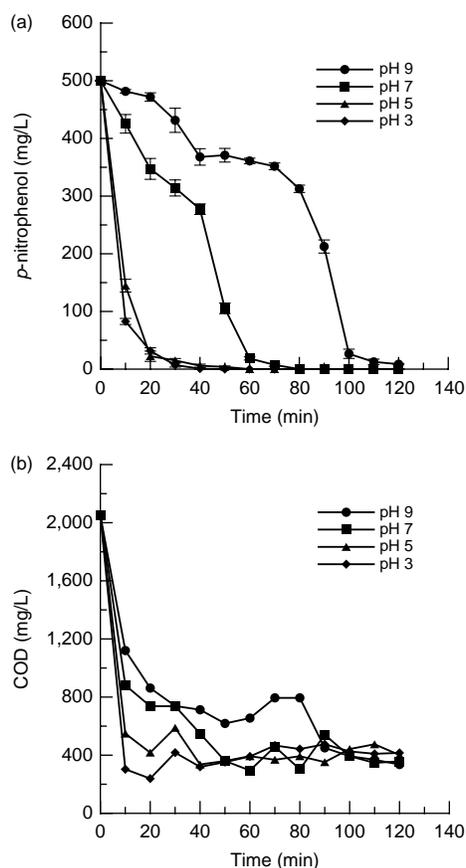
*p*-nitrophenol concentration with time profile in oxidation. The residual *p*-nitrophenol concentration complete conversion in 40 minutes at pH 3 and 5 (acidic solution) can be seen. On the other hand, the *p*-nitrophenol slowly declined the residual concentration of *p*-nitrophenol, but the complete conversion could also be achieved at a basic pH (pH = 9). The complete *p*-nitrophenol conversion was achieved in 80 minutes at pH = 7 and the complete conversion was also achieved in 120 minutes at pH = 9. It is interesting to note the low free radical generation rate of Fenton or Fenton-like reaction at a pH value higher than 4, and it is difficult to initiate the chain reaction for pollutant degradation at basic condition. In this study, it can be found that the lower initial degradation rate of *p*-nitrophenol rate could be found at basic environment. But the degradation rate of *p*-nitrophenol accelerated with increasing acidity in the solution, and then the intermediates further degraded at acidic condition in the oxidation. The degradation rates of *p*-nitrophenol were accelerated with increasing acidity in solution, and the final pH of solution was in the range of pH 2.8–3.3. Though the pH dependence showed strong influence on the degradation of *p*-nitrophenol, the oxidation could be effectively initiated in the catalytic oxidation and it was accelerated by the active species formed at acidic condition and finally, a complete conversion of *p*-nitrophenol was achieved. The catalytic oxidation of phenolic compounds with basic solution is by Co-TDTAPc-ACF/H<sub>2</sub>O<sub>2</sub> system and Cu-exchanged Y zeolite AOP system (Fathima *et al.* 2008; Lu *et al.* 2009). Though the real initiation mechanism of this catalytic

oxidation is still not clear. However, it is believed that ion-exchange structure of this catalyst system promotes the generation of free radical or the oxidation of *p*-nitrophenol in the solution even at basic solution.

On the other hand, Figure 4(b) shows the relationship between residual COD and initial pH value during the oxidation. The COD value showed the same rapid decrease at pH 3 and pH 5, which was similar to the trends of *p*-nitrophenol conversion. It is interesting to note that both *p*-nitrophenol conversion and COD removal were worse at high initial pH values than lower pH conditions in the oxidation. It was proposed that basic condition induces a low generation of active species (such as HO· and organic hydroperoxy radical) in the solution (Sotelo *et al.* 2004). Subsequent reactions were limited due to the low concentration of active species, and then poor



**Figure 3** | Effect of Fe loading on the activity of catalytic oxidation (a) *p*-nitrophenol conversion (%) (b) Residual COD (mg/L), condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, resin 3 g/l, 85°C.



**Figure 4** | Effect of initial pH on *p*-nitrophenol conversion and COD in oxidation with CM-5 resin (a) *p*-nitrophenol conversion (%) (b) Residual COD (mg/L), condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, resin 3 g/l, 85°C.

conversion and COD removal rate were obtained in the CWPO process.

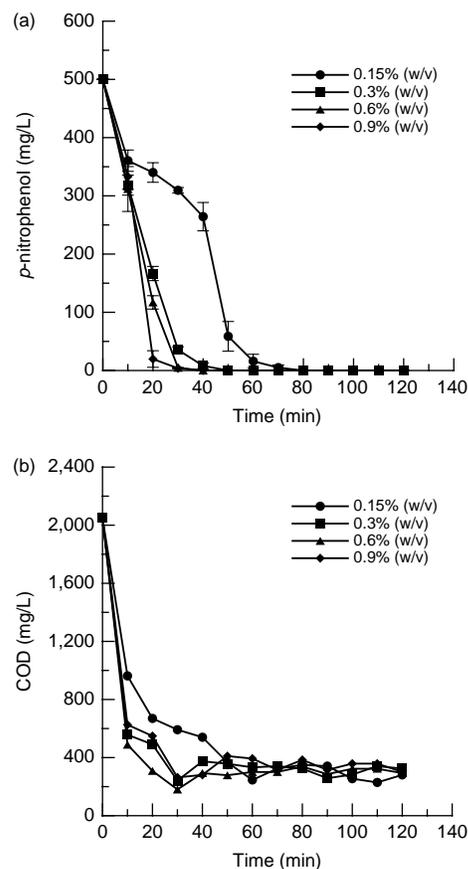
### Influence of catalyst dosage

The influence of catalyst dosage on the *p*-nitrophenol oxidation by Fe (III)-resin catalyst (CM-5) is presented in Figure 5(a). The *p*-nitrophenol conversion rate increased with increasing Fe<sup>III</sup>-resin catalyst dosage in the solution. The effect of catalyst dosage on the COD removal during oxidation is shown in Figure 5(b). It is indicated that the decrease of COD strongly depended on the catalyst dosage in the oxidation. This decrease in COD supported the enhancement of catalyst in the oxidation rate of organic material. As shown in Figure 5(a), *p*-nitrophenol completely decomposed after 60 minutes of oxidation with a dosage of

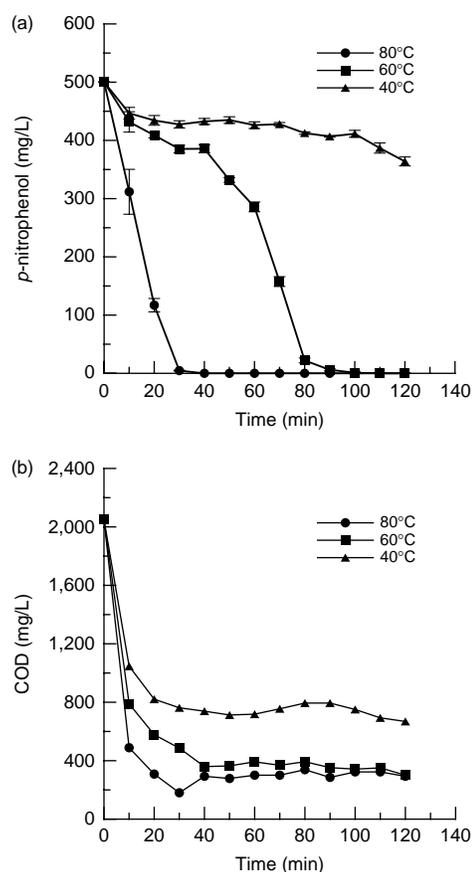
0.15% catalyst dosage in the reactor. When the catalyst loading was higher than 0.15%, it was found that less time was needed to achieve complete conversion in the reactor. It is evidenced that the oxidation rate of *p*-nitrophenol increased with increasing catalyst loading in the reactor and increased the degradation rate of the PNP and COD removal in the reactor.

### Influence of reaction temperature

As shown in Figure 6(a), *p*-nitrophenol oxidation was carried out with Fe<sup>III</sup>-resin at temperatures of 40–80°C. It can be seen that the residual *p*-nitrophenol concentration rapidly decreased at 60 and 80°C but changed a little at 40°C. The effect of reaction temperature on the COD removal is shown in Figure 6(b). The COD removal showed a slight decrease at low reaction temperature. It is well



**Figure 5** | Effect of catalyst dosage on activity of catalyst in terms of *p*-nitrophenol conversion (%) and residual COD with CM-5 resin (a) *p*-nitrophenol conversion (%) (b) Residual COD (mg/L) condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, 85°C.



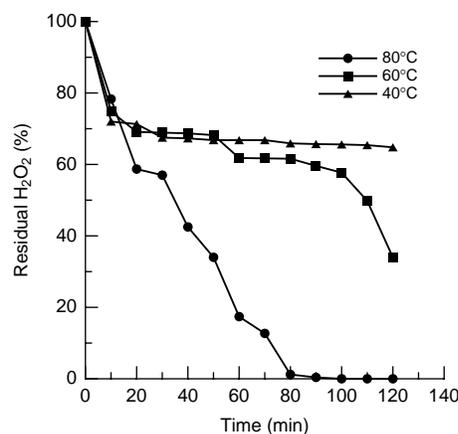
**Figure 6** | Effect of temperature on activity of catalyst in terms of *p*-nitrophenol conversion (%) and residual COD with CM-5 resin (a) *p*-nitrophenol conversion (%) (b) residual COD (mg/L), condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, resin 3 g/l.

known that the thermal decomposition of H<sub>2</sub>O<sub>2</sub> significantly affects the residual H<sub>2</sub>O<sub>2</sub> concentration in the catalytic oxidation. It is proposed that the oxidation of PNP and intermediates strongly depended on the concentration of H<sub>2</sub>O<sub>2</sub> in oxidation. Therefore, the oxidation of PNP or COD of solution should be considered in the competition between catalytic oxidation by H<sub>2</sub>O<sub>2</sub> and thermal degradation of hydrogen peroxide. Due to the strong dependence of thermal decomposition of hydrogen peroxide on temperature, it is about 20% thermal decomposition of hydrogen peroxide at 70°C (Santos *et al.* 2007). In a heterogeneous catalytic oxidation, the heterogeneous catalytic oxidation with H<sub>2</sub>O<sub>2</sub> could also be accelerated in the solution. In this case, the reaction was carried out at 80°C. Therefore, the optimum dosage of residual H<sub>2</sub>O<sub>2</sub> was

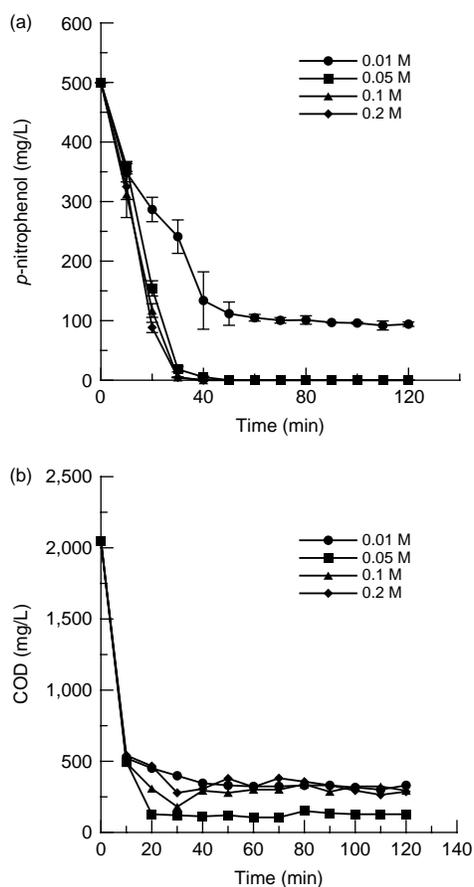
necessary to achieve complete conversion of PNP. Figure 7 shows the effect of reaction temperature on residual H<sub>2</sub>O<sub>2</sub> in oxidation. It can be seen that the residual H<sub>2</sub>O<sub>2</sub> dramatically decreased in the oxidation at 80°C oxidation. After 80 minutes reaction, all the H<sub>2</sub>O<sub>2</sub> was eliminated in the reactor. As shown in Figure 6(a), it is indicated that complete phenol conversion could be achieved in 40 minutes. It can be concluded that the increase in operating temperature accelerated the oxidation of *p*-nitrophenol and the thermal decomposition of H<sub>2</sub>O<sub>2</sub> could be ignored at the test conditions.

### Influence of H<sub>2</sub>O<sub>2</sub> concentration

Figure 8 shows the results obtained in terms of *p*-nitrophenol conversion (Figure 8(a)) as well as the evolution of COD removal (Figure 8(b)) in the experiments carried out with various H<sub>2</sub>O<sub>2</sub> concentrations and Fe(III)-resin. Complete *p*-nitrophenol conversion was reached at H<sub>2</sub>O<sub>2</sub> concentration higher than 0.05 M with Fe(III)-resin catalyst. It can be also seen that the residual *p*-nitrophenol concentration substantially decreased with increasing H<sub>2</sub>O<sub>2</sub> concentration in the solution except at 0.01 M H<sub>2</sub>O<sub>2</sub>. Incomplete conversion of *p*-nitrophenol is due to insufficient oxidant in the reactor. It is interesting to note that the increase in H<sub>2</sub>O<sub>2</sub> concentration up to 0.05 M (mole/L) owned over 97% *p*-nitrophenol conversion. When the H<sub>2</sub>O<sub>2</sub> concentration was up to 0.1 M (mole/L), over 99% *p*-nitrophenol conversion could be achieved in 30 minutes.



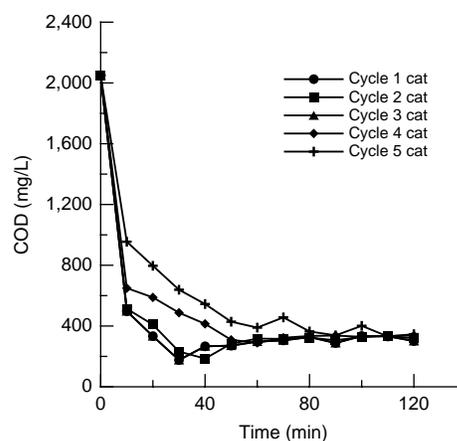
**Figure 7** | Effect of temperature on residual H<sub>2</sub>O<sub>2</sub> during catalytic oxidation with CM-5 resin. condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, resin 3 g/l, 85°C.



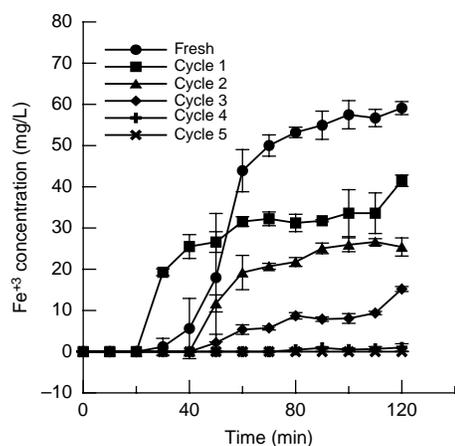
**Figure 8** | Effect of H<sub>2</sub>O<sub>2</sub> concentration on activity of catalyst in terms of *p*-nitrophenol conversion (%) and residual COD with CM-5 resin. (a) *p*-nitrophenol conversion (%) (b) residual COD (mg/L) condition: *p*-nitrophenol 500 mg/L, resin 3 g/l, 85°C.

This result indicates that the increase in the concentration of H<sub>2</sub>O<sub>2</sub> strongly enhanced the *p*-nitrophenol conversion. This result is similar to a previous report (Chou *et al.* 1999) in CWPO system for *p*-nitrophenolic wastewater treatment. They found that the decomposition rate of H<sub>2</sub>O<sub>2</sub> was found to be proportional to both H<sub>2</sub>O<sub>2</sub> and catalyst concentration in the reactor. The *p*-nitrophenol conversion is usually proportional to H<sub>2</sub>O<sub>2</sub> concentration in the oxidation. The *p*-nitrophenol conversion is also dominated by the competition between the rate of *p*-nitrophenol and H<sub>2</sub>O<sub>2</sub> decomposition. It has been shown that the decomposition rate of *p*-nitrophenol is slower than the rate of HO· radical formation (Chou *et al.* 1999). They also suggested that the large amount of HO· radical decomposed from H<sub>2</sub>O<sub>2</sub> cannot be beneficial to the complete oxidation of

*p*-nitrophenol because of the lifetime of HO· free radical in the solution. With the large amount of HO· radical decomposed from H<sub>2</sub>O<sub>2</sub> in oxidation, it was indicated that the amount of H<sub>2</sub>O<sub>2</sub> would be rapidly consumed at the start of oxidation and *p*-nitrophenol does not completely oxidize at stoichiometric dosage of H<sub>2</sub>O<sub>2</sub>. As shown Figure 8(b), it can be seen that the residual COD decreased with increasing H<sub>2</sub>O<sub>2</sub> concentration in the oxidation, but the final COD of the solution almost had the same value at high H<sub>2</sub>O<sub>2</sub> concentration (0.05 M and 0.1 M). The residual COD via 0.01 M H<sub>2</sub>O<sub>2</sub> oxidation was much higher than the residual COD via 0.05 M and 0.1 M H<sub>2</sub>O<sub>2</sub> oxidation. The concentration of 0.01 M H<sub>2</sub>O<sub>2</sub> was much lower than the stoichiometric dosage of oxidant. But the higher H<sub>2</sub>O<sub>2</sub> dosage still did not completely oxidize the pollutant and intermediates in the oxidation. It is indicated that the stoichiometric H<sub>2</sub>O<sub>2</sub> dosage could not completely oxidize the *p*-nitrophenol and intermediates to form the final product. Therefore, it can be seen that the high *p*-nitrophenol conversion could be achieved at low oxidant dosage, but low residual COD was obtained in the oxidation. Therefore, poor COD removal can be expected at low H<sub>2</sub>O<sub>2</sub> concentration in the oxidation. It is interesting to note that the increase in H<sub>2</sub>O<sub>2</sub> concentration up to 0.1 M could not further increased the COD removal in the oxidation. It is due to the excess H<sub>2</sub>O<sub>2</sub> reacting with the hydroxyl radical to form water and another product (Caudo *et al.* 2007).



**Figure 9** | Effect of aging on activity of catalyst in terms of residual *p*-nitrophenol concentration and residual COD with CM-5 resin. condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, resin 3 g/l, 85°C.



**Figure 10** | Effect on Fe leaching from catalyst after several times of reusing catalyst in oxidation with CM-5 resin. condition: *p*-nitrophenol 500 mg/L, molar ratio of *p*-nitrophenol/H<sub>2</sub>O<sub>2</sub> = 0.026, resin 3 g/l, 85°C.

### Stability of Fe(III)-resin catalyst

The iron leaching of Fe(III)-resin catalyst was made to evaluate the stability of catalyst at test condition with CM5 catalyst at 0.1 M H<sub>2</sub>O<sub>2</sub>. The effect of reused cycles on the *p*-nitrophenol conversion and COD removal is shown in Figure 9(a, b), respectively. It can be seen that the PNP conversion rate slightly decreased with increasing number of reuse. It can be seen that the COD removal also showed the same trend with increasing number of reuse. But it can be seen that the COD removal could be achieved over 80% even after 5 times of reuse. It is indicated that the iron leaching may be coming from the iron dissolution of catalyst in the oxidation. However, the amount of leaching iron did not dramatically decrease the activity of catalyst on oxidation. Complete PNP conversion and over 80% COD evidenced that the reused resin still owned a high activity in oxidation. Figure 10 shows the leaching iron measurement after various numbers of reuse in oxidation. It is indicated that the leaching iron concentration increased during the oxidation with a fresh catalyst. The leaching iron concentration decreased with increasing number of reuse in the solution. After several tests, the nonbonding irons were mainly washed out in the oxidation. Only the trace iron concentration could be detected in the solution. Though there was some iron leaching from the catalyst, the effective activity of Fe(III)-resin could be obtained in the oxidation. It is suggested that the impregnated iron concentration

should be an economic consideration for resin catalyst preparation.

### CONCLUSION

Fe(III)-resin catalyst was prepared with ion exchange as support, and it was successfully applied for *p*-nitrophenol oxidation in a batch reactor. The catalytic activity of Fe-resin catalyst was determined by studying the oxidation of *p*-nitrophenol and COD removal of solution in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant. The oxidation of *p*-nitrophenol was determined at different molar ratios of H<sub>2</sub>O<sub>2</sub>. It was found that the dosage of oxidant dominated the PNP conversion and COD removal of solution in oxidation. It was worthwhile to note that complete *p*-nitrophenol conversion could be achieved at a basic pH with the Fe(III)-resin catalyst in oxidation. The iron leaching could be detected in the oxidation with a fresh catalyst. The resin support Fe(III) catalyst showed a high catalytic activity for conversion of *p*-nitrophenol. It was suggested that a high catalytic activity catalyst for conversion of *p*-nitrophenol and environment friendly catalyst could be prepared with an optimum impregnated iron concentration.

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