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# Treatment of chitin-producing wastewater by micro-electrolysis-contact oxidization*

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**Abstract:** The technique of micro-electrolysis-contact oxidization was exploited to treat chitin-producing wastewater. Results showed that Fe-C micro-electrolysis can remove about 30% $COD_{cr}$, raise pH from 0.7 to 5.5. The $COD_{cr}$ removal efficiency by biochemical process can be more than 80%. During a half year's operation, the whole system worked very stably and had good results, as proved by the fact that every quality indicator of effluent met the expected discharge standards; which means that chitin wastewater can be treated by the technique of micro-electrolysis, contact oxidization.

**Key words:** Chitin-producing wastewater, Wastewater treatment, Micro-electrolysis, Contact oxidization
**Document code:** A **CLC number:** X52; X131

## INTRODUCTION

1, 4 connected 2-acetylamino-2-deoxide-*β*-D-glucose, commonly known as chitin (chemical formula $C_8H_{13}NO_5$) with molar weight of 203.19, exists as white or pale yellow plates in the industrial pure product. A polyose with natural amount next to that of cellulose on the earth, it can be found in insects, crusts of crustacean, and the cell wall of fungi. It has steady chemical property and no toxicity; and can be biodegraded by lysozyme, indicating good bio-affinity. However, it can only be dissolved in hydrochloric acid, sulfuric acid, acetic acid, and 78%–97% phosphoric acid, but is barely degradable in water, weak acid, alkali, ethyl alcohol, or other organic solvents. Recognized for many specific properties such bio-adaption, hydroscopicity, moisture retaining capacity, membrane formation, porosity, viscosity, gelation, flocculation, and complexation with metals, it has been broadly applied in many industries; chemical engineering, medicine, agriculture, food, etc. However, its production by wastewater treatment is problematic (Wanasen *et al.*, 2001).

Iron-carbon internal electrolysis in water may effectively eliminate the color of the wastewater, and improve the result of the biochemical treatment of the wastewater and has a certain effect on the removal of $COD_{cr}$. Iron-carbon internal electrolysis has been widely used in treatment of dye-stuff wastewater, pesticide, and herbicide industries wastewater (Sun *et al.*, 2001; Jin *et al.*, 2002). The iron-carbon internal electrolysis reactions are proposed as follows:

Anode reaction:

$$\mathrm{Fe} - 2\mathrm{e} \rightarrow \mathrm{Fe}^{2+} \qquad E^0\ (\mathrm{Fe}^{2+}/\mathrm{Fe}) = -0.44\ \mathrm{V}$$

Cathode reaction:

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$$2H^+ + 2e \rightarrow 2[H] \rightarrow H_2 \qquad E^0\ (H^+/H_2) = 0.00\ V$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad E^0\ (O_2) = 1.23\ V$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad E^0\ (O_2/OH^-) = 0.40\ V$$

During iron-carbon internal electrolysis reaction, color and organic matter were effectively eliminated by oxidant and reductive reaction.

Usually chitin is extracted from the crusts of crabs and shrimps through the following procedure: Carbonates contained in crusts are first decomposed by hydrochloric acid, while the protein and fat are removed by sodium hydroxide; then the product is obtained after decolorization. In this experiment, the wastewater came from a chitin-producing factory in Zhejiang Province, and the raw material for extracting chitin was comprised of crusts of crab and shrimp. As the crusts were treated beforehand, most of the wastewater therefore came from the late extraction process, and so, was relatively lightly polluted. Its characteristics are shown in Table 1.

Table 1 shows that chitin-producing wastewater is mainly characterized by strong acidity and high $Cl^-$ concentration.

**Table 1 Characteristics of chitin-producing wastewater**

| | Amount of water ($m^3$/d) | pH | $COD_{cr}$ (mg/L) | $Cl^-$ (mg/L) |
|---|---|---|---|---|
| Direct wastewater | 1 | 2.0–3.0 | 12000–15000 | 6000–10000 |
| Other wastewater | 120 | 0.6–1.0 | 1000–1500 | 3000–6000 |

## EXPERIMENTAL PROCEDURE AND METHOD

### Fe-C micro-electrolytic treatment

The wastewater was first treated by the micro-electrolytic method as it was strongly acidic with pH being around 0.6–1.0. If microbial treatment is adopted for the late process, pH should be adjusted to around 7. Because of the high cost of alkali, Fe-C micro-electrolytic method was employed because it can remove part of the COD, and need relatively less alkali for neutralizing the wastewater; thus reducing the treatment cost. The experiment was aimed to study the relationships between the micro-electrolytic time and COD removal efficiency and pH variation, from which proper electrolytic time can be concluded (Chen, 1999; Cai, 1999; Chai and Gao, 2000; Yang *et al.*, 2002).

Iron-carbon internal electrolysis experiments were performed in a beaker. The schematic diagram of the experimental set-up used in this study is shown in Fig.1. At the beginning, 500 ml pH 7.0 wastewater and 3400 mg/L $COD_{cr}$ were added to reaction facility, followed by some Fe-C filings. In the meantime, air was pumped into the beaker. At certain intervals samples were taken out and filtered to measure the values of pH and COD.

### Microbial treatment experiment

The high concentration of $Cl^-$ in the wastewater inhibits somewhat the microorganisms. To obtain theoretical background for engineering design, effects of microbial treatment were investigated under $Cl^-$ concentrations of 3000–6000 mg/L.

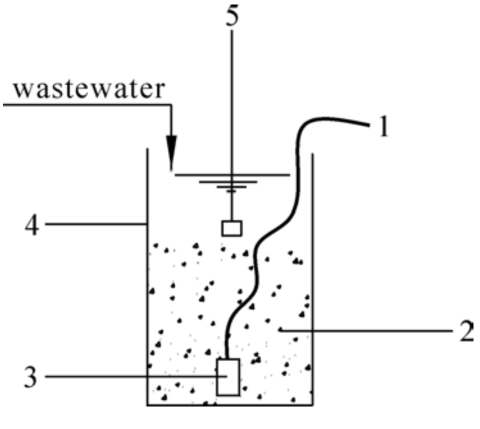

**Fig.1 Schematic diagram of Fe-C reaction facility**
1: air; 2: scrap iron; 3: air release;
4: reactor; 5: pH instrument

## RESULTS AND ANALYSIS

### Micro-electrolytic treatment

The results are shown in Fig.2 and Fig.3 showing that when pH rises to 1.5 after electrolysis for 2 hours, the COD removal efficiency is 33.6%; when pH increases to 4.5, it is 29.6%; after 6 hours, it is 29.7% at pH=5.5. Though at 2 hours the removal efficiency is the highest, pH is very low. To reduce alkali for neutralization in late processes, 6-hour electrolysis is preferred, which can be adopted as parameter for engineering design.

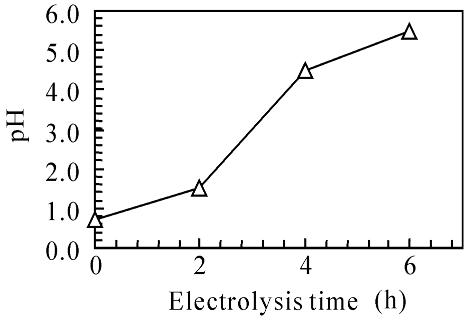

**Fig.2 pH change vs electrolysis time**

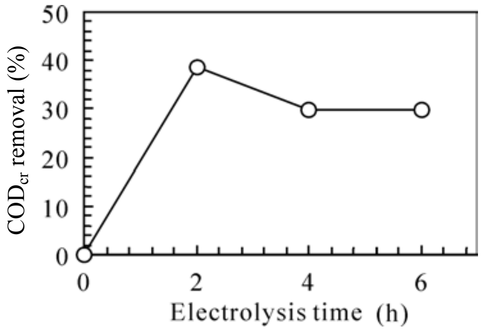

**Fig.3 $COD_{cr}$ removal vs electrolysis time**

### Microbial treatment experiment

The experiment was aimed to investigate the effects of microbial treatment under high $Cl^-$ concentration. The wastewater for the experiment was micro-electrolyzed, adjusted to around 7 pH and $Cl^-$ was around 5000 mg/L. Fig.4 shows the $COD_{cr}$ removal efficiency under different microbial treatment duration. At hour 12, it was more than 80%, which means under such $Cl^-$ concentration there is little inhibition effect on the microbial growth, and such $Cl^-$ concentration feasible for microbial treatment.

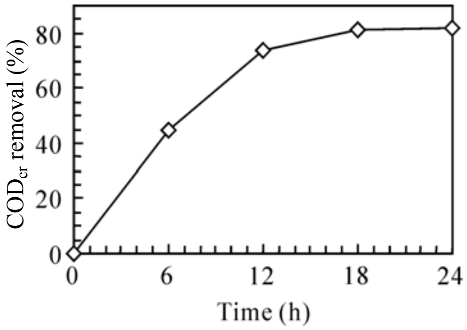

**Fig.4 $COD_{cr}$ removal vs biochemical treamtment time**

## ENGINEERING DESIGN

### Water flow and water quality

The wastewater flow was about 150 $m^3$/d, had average content of pH=1.0 $COD_{cr}$ of around 1500 mg/L and $Cl^-$ was 5280 mg/L. The effluent had to meet GB8978-96 first degree discharge standard whose major pollutant indicators are pH 6–9, $COD_{cr}$<100 mg/L, $BOD_5$<30 mg/L, SS<70 mg/L (SS: suspended solid).

### Technological process

The treatment process has to consider the chitin wastewater factors such as low pH value, high concentration of chloride and $COD_{cr}$ which fluctuates within a wide range, etc. And the technique exploited should put emphasis on the effects of pH adjustment, maintain wastewater treatment stability and removal of organic pollutants. Treatment flow of chitin-producing wastewater is shown in Fig.5.

The wastewater was discharged to the micro-electrolysis tank, with addition of iron filings, for the micro-electrolysis reaction. In the meantime, the tank can function as a adjustment tank, to adjust chitin-producing flux and quality. Then the wastewater was lifted by pump to the neutralizing tank where pH was adjusted to around 8–9 by $Ca(OH)_2$. After precipitation, the supernatant liquor spontaneously flowed to the A/O tank to perform for aero-

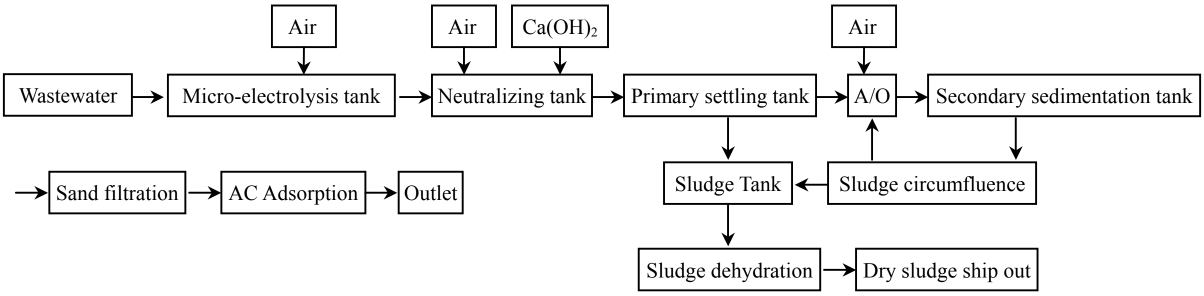

**Fig.5 Flow scheme of chitin-producing wastewater treatment**

bic treatment. After the contact oxidation process, the effluent flowed through the secondary sedimentation tank for precipitation, sand filtration, and activated carbon absorption. Then it was measured and discharged. Part of the sludge in the secondary sedimentation tank re-circulated to the A/O tank; the rest along with the sludge from the primary settling tank were discharged to the sludge pond, dehydrated by the press filter and moved out. And the water returned to the collecting tank.

Designing parameters for the treatment units: Micro-electrolysis tank: HRT=6 h; Neutralizing tank: HRT=15 min; Primary settling tank: Surface load 0.8 $m^3/m^2h$; A/O tank: HRT=48 h; Anaerobic: 6 h; Oxidation: 32 h; Secondary sedimentation tank: Surface load 0.6 $m^3/m^2h$.

## Technique characteristics

This treatment system can be divided into three units: (1) Pre-treatment unit. The pH was raised by the micro-electrolysis method in order to reduce addition of alkali for neutralization reaction; meanwhile, it removed part of the $COD_{cr}$, which made it easier for biodegradation. Air was pumped to accelerate the effects of aerobic treatment. The effluent after micro-electrolysis process was (by addition of alkali) adjusted to meet the pH requirements of influent for microbial treatment. (2) Microbial treatment unit. A/O method was exploited to remove most of the COD. (3) After-treatment unit. The quality of the effluent from the secondary sedimentation tank was controlled by sand filtration and activated carbon absorption. During these processes, its chromaticity color caused by $Fe^{3+}$, SS and part of the $COD_{cr}$ was removed before discharge.

## Adjustment results

The adjustment stage of this project started at the beginning of March, 2001. At the initial stage, to the biochemical treatment tank was added 2-ton dehydrated sludge, and nutrients like urea, phosphate manure, glucose and flour. After two day's fermentation, some wastewater was introduced into the tank while it was supplied with substrates like fecal matter. After operation for 15 days, the effluent started to stick to the membrane. However, in the following one month, the quality of the effluent continuingly fluctuated greatly, i.e., effluent $COD_{cr}$ always was higher than 2000 mg/L, sometimes even above 10000 mg/L. In addition, because of the unstable addition of $Ca(OH)_2$ into the neutralizing unit, the pH value of the biochemical effluent fluctuated from 3.5 to 10, leading many microorganism deaths in the A/O tank. The treatment results were far from satisfactory. On the basis of this situation, the effluent pH of the biochemical treatment tank was further regulated and, as a result, stayed around 8–9. And it was refilled with active sludge. After a period, some membranes formed on the fillers; the effluent quality was apparently improved until the beginning of June when it basically met the standard requirements. Fig.6 shows the effluent quality of collecting tank and biochemical treatment tank during the adjustment late stage; Fig.7 shows the effluent quality of the secondary sedimentation tank and the primary discharge hole during the adjustment late stage. These two figures show that the biochemical treatment unit (A/O) de-

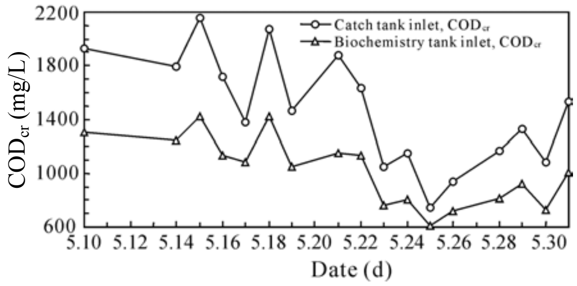

**Fig.6 Treatment effect of micro-electrolysis ($COD_{cr}$)**

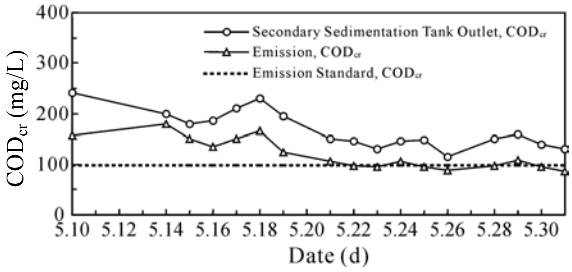

**Fig.7 Treatment effect of contact oxidation and three class treatment ($COD_{cr}$)**

graded in average about 83.3% of the $COD_{cr}$.

## CONCLUSION

During a half year's operation, the whole system worked very stably and yielded good results, as proved by the fact that every effluent quality indicator met the expected discharge standards, which means that chitin wastewater can be treated by the technique of micro-electrolysis, contact oxidization, filtration and absorption. The key points to operate stably the system are the optimal time for micro-electrolysis and pH control in the tanks.

### Micro-electrolysis control

The actual operation results showed that 6-hour is optimal for micro-electrolysis. On one hand, this raised the pH values of the wastewater, resulting in reducing the addition of alkali in late stages and high removal rate of COD. But if the electrolysis time is too long, although the pH will be higher, $Fe^{2+}$ contained in the wastewater will be greatly increased. Thus, it will be hard to be biodegraded; and, in order to remove those iron ions, more $Ca(OH)_2$ has to be added. On the other hand, the iron filings in the electrolysis tank should be a little in excess. Besides, as the reaction continuously consumes iron, more iron fillings have to be added periodically and the whole system should be maintained aerobically to enhance the treatment effects.

### pH control of biochemical effluent

The pH control of the effluent to the biochemical treatment system is critical to the treatment results. The pH control functions in two aspects: Firstly, the biochemical treatment is sensitive to the pH value. Normally, the effluent pH should be 6 to 9; Secondly, the micro-electrolysis produced a lot of $Fe^{2+}$. If too much $Fe^{2+}$ enters the biochemical system, it would be oxidized to $Fe^{3+}$ aerobically, which results in high chromaticity color. Therefore, the pH of the neutralizing tank should be kept at 8 to 9 in order to remove excess $Fe^{2+}$ contained in the wastewater. In the real operation, the automatic pH adjustment system has more advantages over the manual one which is very unstable.

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