Electrochemical treatment of residual ammonia nitrogen in biologically pretreated coking wastewater with three-dimensional electrodes

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ABSTRACT

The electrochemical oxidation of the residual ammonia nitrogen contained in biologically pretreated coking wastewater using three-dimensional electrode system was studied. The results show the Ti/RuO₂/IrO₂ anode plates and the coke have good surface characteristics for the purpose of this study. In addition, studies also show that the three-dimensional electrode system should be able to give a satisfied solution to the residual bio-refractory ammonia nitrogen in biologically pretreated coking wastewater in comparison to conventional two-dimensional electrodes. At coke size of 10–20 mesh, electrode distance of 1.0 cm and current density of 4.5 mA/cm², the residual ammonia nitrogen in the three-dimensional electrode system was almost completely removed in 60 min.

INTRODUCTION

With the rapid development of coal and steel industry, large quantities of wastewater discharged by coke plants have been causing severe environmental problems (Zhao et al. 2009; Zhu et al. 2009). Although the biological methods are very effective for the disposal of the coking wastewater (Zhang et al. 1998; Li et al. 2005; Marañón et al. 2008), they already have some difficulties to achieve the strict requirements of NH₃-N < 25 mg L⁻¹ (Wei et al. 2007). The ammonia nitrogen in wastewater may promote eutrophication, which is fatal to aquatic life, as well as an offensive smell and carcinogenesis (Kim et al. 2006). Therefore, great efforts have been directed toward new techniques for biologically pretreated coking wastewater treatment on ammonia nitrogen.

For the aforementioned reasons, the three-dimensional electrode technology based on electrochemical oxidation has been attracting much more attention due to its extensive specific surface area and high capacity to generate free hydroxyl radicals in comparison to conventional two-dimensional electrodes in the present study (Bockris & Kim 1997; Kong et al. 2006; Wang et al. 2007). Some researchers showed that coating of RuO₂ and IrO₂ on the titanium surface exhibited a good effect on electrochemical oxidation and wastewater treatment and could enhance the stability and prolong the life of plates (Yavuz & K卵巢al 2006; Wang et al. 2007; Costa et al. 2008). In addition, coke was chosen as the particle electrodes in this study for the low cost and the similar properties of active carbon which is always selected as particle electrodes in the three-dimensional electrode technology (Kristof et al. 1997; Li et al. 2005; Szpyrkowicz et al. 2005; Kapalka et al. 2008). In order to achieve a better implementation of the electrolysis, RuO₂ and IrO₂ coated on titanium plates used as anodes with coke particles as the third-dimensional electrodes were selected for this study.

MATERIALS AND METHODS

Reagents and coking wastewater

The coking wastewater and the cokes used for this study were obtained from a secondary sedimentation tank at a coking plant in North China. The wastewater was first treated biologically at the plant using A/O technology. The wastewater
A sample of 1 L was used in each test, with the characteristics of pH 5.9–6.5, chemical oxygen demand 304.09 mg/L, NH$_3$-N 131.31 mg/L, chloride ions concentration 748.85 mg/L, and turbidity 4.80 NTU. The bulk volume of the coke used in each test is 0.2 L, with the properties of C% (atomic) 94.14%, pore volume 0.02168 nm; average pore diameter 6.58 cm$^3$/g and specific surface area 13.18 m$^2$/g. Before the experiment, the coke sample was dried at 378 K in an oven for 2 h and then immersed in the coking wastewater for 12 h to avoid the effect of absorption.

Preparation of Ti/RuO$_2$-IrO$_2$ electrode

The titanium plates were subjected to surface pretreatment with corundum sandblasting and hot hydrochloric acid pickling. After pretreatment, the Ti/RuO$_2$-IrO$_2$ electrodes were obtained by brush painting with β-RuCl$_3$ and H$_2$IrCl$_6$·nH$_2$O followed by heating at 378–393 K and burning at 773 K in several cycles. The electrodes were then burned for 1 h at the same temperature. After the burning, the stems of the supports were polished to remove TiO$_2$ layer formed in the burning process.

The electrolytic system

The electrolytic cell was made of synthetic glass with a dimension of 140 × 90 × 130 mm and an effective volume of 1.3 L. Stainless steel plates (130 × 65 × 1 mm) and Ti/RuO$_2$-IrO$_2$ plates (130 × 65 × 1 mm) were used as cathodes and anodes, respectively. A pump offered air at 0.36 m$^3$/h and a DC power supply (MPS702, Beijing, China) provided constant currents and the corresponding voltages. During the experiments, samples were drawn from the cell at every ten minutes and were analyzed.

Methodology

The NH$_3$-N concentration was obtained via a Nessler’s reaction using a 752 N spectrophotometer (Shanghai Jingke, China). The Ti/RuO$_2$-IrO$_2$ anode and the coke were examined using SEM. The electrolysis tests were carried out in order to optimize the three-dimensional electrode process. Table 1 presents the details on experimental conditions that were changed in separate experiments.

### RESULTS AND DISCUSSION

#### The SEM study of Ti/RuO$_2$-IrO$_2$ electrode and the coke

The morphology of Ti/RuO$_2$-IrO$_2$ electrode analyzed by SEM is presented in Figure 1. The cracks on the surface of the anode are common on the coated surfaces of chlorine-evolution electrodes, which could improve electrochemical efficiency and prolong service life of electrodes (Zhang 2009). The significant compactness and low porosity observed indicate that incorporation of RuO$_2$ and IrO$_2$ components can improve the coating structure effectively which may contribute to prolong the electrodes’ lifetime.

The SEM micrograph of the coke samples shows that the surface structure of the coke is stable and slightly porous (Figure 2). The coke sample before the electrolysis exhibits...
porous structures that have absorption effect and dense surface that may function as a particle electrode in reaction.

The effect of coke on the electrolysis

As shown in Figure 3, the degradation efficiencies of ammonia nitrogen all increased with the retention time (Experiments 1 and 2). The removals increase relatively slowly when the retention time increases to a certain degree, suggesting that the ability of generating active substances of plate reaches a plateau. The ammonia nitrogen degradation using the three-dimensional electrodes was 97.4% in 60 min, while the degradation using the two-dimensional electrodes was only about 72.5%. Recent researches have demonstrated that the particle electrode improved the electrolysis efficiency as many small coke particles form charged microelectrodes under the influence of electric field, which could generate additional free hydroxyl radicals and greatly improve the ammonia nitrogen removal rate (Kong et al. 2006; Zhou et al. 2009). All of these indicate that the coke particle electrode in the three-dimensional electrode system may be able to provide a more satisfied solution to degrade the residual ammonia nitrogen from the biological treatment process in comparison to the conventional two-dimensional electrodes.

The effect of operating variables on ammonia nitrogen degradation

Coke size

Table 2 shows the results of Experiment 3 for NH₃-N degradation of coking wastewater in 40 min. The degradation efficiency of NH₃-N increased with the decrease of coke size except for 20–40 mesh and the ammonia nitrogen degradation efficiency of 20–40 mesh was very low at only 66.5% in 40 min. The NH₃-N degradation efficiency of 10–20 mesh was 98.7% in 40 min, the highest among these tests. This is because many small particles put into the three-dimensional electrode system form charged microelectrodes under the influence of electric field (Bockris & Kim 1997). The coke in 10–20 mesh may have larger effective electrode area to improve the current efficiency of electrolysis, and can avoid the by-path current and short-circuit current coming from coke in less than 5 mesh. All in all, the optimal coke size is 10–20 mesh.

Electrode distance

The results of NH₃-N degradation rate and energy consumption in 40 min with the electrode distance ranging from 0.5 to 2 cm are shown in Table 2 (Experiment 4). The electrode distance had a clear impact on NH₃-N removal, but the increase in the rate of NH₃-N reduction was insignificant when the spacing was less than 1 cm. The NH₃-N reduction rate and energy consumption of 1.0 cm in 40 min was 96.9% and 305.1 kwh/kgNH₃-N, respectively, which was the best among these tests. To sum up, the best electrode distance is 1 cm.

The ratio of plate area to the volume of wastewater (A/V)

In the electrolysis tests, various A/V were adjusted by changing plate areas with constant volume of the wastewater. As shown in Table 2, at 33.8, 67.6, 101.4, and 135.2 m²/m³, the
ammonia nitrogen removals are about 36.2, 79.2, 85.5, and 98.7%, respectively in 40 min. The ammonia nitrogen concentration decreases generally with the increase of A/V at 6 mA/cm². All of this shows that the optimum A/V is 135.2 m²/m³ among these tests.

Current density

The degradation of ammonia nitrogen at various current densities is presented in Table 2 (Experiment 5). The removal of ammonia nitrogen increases with the current density and the retention time. At 4.5, 6.0, and 7.5 mA/cm², the residual NH₃-N was almost completely removed in 40 min. However, at current densities of 6.0 and 7.5 mA/cm², the electrolyte temperature increased significantly from 289.5 to 308 K and 316 K, which affected the efficiency of the electrodes and increasing power consumption. Therefore, the optimum current density for the ammonia nitrogen removal is considered to be 4.5 mA/cm².

Possible mechanism and kinetic of degradation of NH₃-N

Some researchers showed that the mechanism of electrochemical treatment in three-dimensional electrodes includes direct and indirect oxidation. In the direct electrochemical process, direct oxidation takes places at the electrode surface (Kong et al. 2006; Wang et al. 2007). Moreover, the NH₃-N compounds could be adsorbed and oxidized on the coke. In the indirect electrochemical treatment, active chlorine could also degrade the NH₃-N contaminants in the bulk of the solution (Zhou et al. 2009).

\[
2\text{NH}_4^+ + 3\text{HOCl} \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^- \tag{1}
\]

Considering that NH₃-N can be removed by several concomitant reactions, its degradation may be impossible to determine experimentally the rate constants and the reaction order simultaneously. To define quantitatively the rate of electro-oxidation of NH₃-N, some assumptions have to be made to lead to a necessary simplification. It is assumed that there is no accumulation of mediators in the solution and the rate of their production and rate of the degradation are equal, the concentration of mediators during electrolysis can be assumed to be constant (Szpyrkowicz et al. 2001). Therefore, the concentration of active chlorine during the electrolysis is assumed to be a constant. The NH₃-N degradation may be simplified to Equation (2):

\[
- \frac{d[\text{NH}_3 - \text{N}]}{dt} = k[\text{NH}_3 - \text{N}]^n \tag{2}
\]

where \(k\) is the observed rate constant, which reflects the contributions of several reactions, including direct and mediated electro-oxidation, and \(n\) is the pseudo-order of reaction, both of which can be measured experimentally. Under the conditions of the present study, most of the results were described by an apparent first-order reaction. Therefore, with Equation (2) above, the values of kinetic constant \(k\) in the electrolysis are calculated in Table 3.

| Table 2 | Different experimental results for NH₃-N degradation of coking wastewater in 40 min |
|---------|----------------------------------|-----|-----|-----|-----|-----|
| Experiment 3 | Coke size (mesh) | ≤5 | 5–10 | 10–20 | 20–40 | – |
| | The removal rate of NH₃-N (%) | 83.80 | 94.67 | 98.74 | 66.47 | – |
| | Energy consumption (kwh/kgNH₃-N) | 306.03 | 300.81 | 302.69 | 458.14 | – |
| Experiment 4 | Electrode distance (cm) | 0.5 | 1.0 | 1.5 | 2.0 | – |
| | The removal rate of NH₃-N (%) | 71.80 | 96.98 | 90.05 | 69.25 | – |
| | Energy consumption (kwh/kgNH₃-N) | 391.61 | 305.05 | 552.32 | 760.56 | – |
| Experiment 5 | A/V(m²/m³) | 33.8 | 67.6 | 101.4 | 135.2 | – |
| | The removal rate of NH₃-N (%) | 36.19 | 79.19 | 85.48 | 98.67 | – |
| | Energy consumption (kwh/kgNH₃-N) | 860.341 | 312.93 | 286.17 | 257.19 | – |
| Experiment 6 | Current density (mA/cm²) | 1.5 | 3 | 4.5 | 6 | 7.5 |
| | The removal rate of NH₃-N (%) | 35.42 | 67.70 | 96.27 | 98.67 | 99.14 |
| | Energy consumption (kwh/kgNH₃-N) | 361.50 | 261.59 | 222.47 | 257.19 | 236.12 |
### CONCLUSIONS

The coated titanium anode plate has good surface characteristics for the purpose of this study. The experimental results indicate that the three-dimensional electrode system should be able to give a satisfied solution to the residual bio-refractory ammonia nitrogen in biologically pretreated coking wastewater in comparison to conventional two-dimensional electrodes. At coke size of 10–20 mesh, electrode distance of 1.0 cm and current density of 4.5 mA/cm², the residual ammonia nitrogen in the three-dimensional electrode system was almost completely removed in 60 min.

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### REFERENCES


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**Table 3** | Pseudo rate constants (k) for the NH3-N removal data

<table>
<thead>
<tr>
<th>Parameters</th>
<th>k (min⁻¹)</th>
<th>Correlation coefficient</th>
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<tbody>
<tr>
<td>Coke</td>
<td>0.006</td>
<td>0.98</td>
</tr>
<tr>
<td>Two-dimensional electrode</td>
<td>0.023</td>
<td>0.97</td>
</tr>
<tr>
<td>Three-dimensional electrode</td>
<td>0.065</td>
<td>0.96</td>
</tr>
</tbody>
</table>

*The standard error and confidence intervals of k in three-dimensional electrode are 0.0076 and 0.050, 0.082, respectively.*