



Decomposition of Ammonia Nitrogen from Biologically Pretreated Coking Wastewater with Electrochemical Three-dimensional Ti/RuO₂/IrO₂ Electrodes

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ABSTRACT

In this research, the electrochemical oxidation with a three-dimensional electrode system, with coke serving as packed bed particle electrodes, was applied for the removal of ammonia nitrogen in biologically pretreated coking wastewater. Surface characteristics of the anode plate and the coke were analysed. The results showed that there had been few cracks on the coating surface of anode and the coating layer had been compact before electrolysis, while the coating surface became relatively rough after electrolysis and small cracks appeared on anode surface. Meanwhile, the surface of prepared coke was porous at the beginning, which enabled it to have adsorption effect, while after electrolysis, the surface of the used coke became dense, which made it function better as packed bed electrodes. In addition, operating variables of retention time, plate spacing, area/volume, current density, pH and chloride concentration were investigated respectively to check their influence on ammonia nitrogen removal. Meanwhile, the results showed that the electrochemical three-dimensional Ti/RuO₂/IrO₂ electrodes could remove ammonia nitrogen efficiently, and when plate distance was 1.0cm, retention time was 40min and current density was 4.5mA/cm², the highest ammonia nitrogen removal rate of about 95% was achieved, which was much higher than the removal rate of the system when Ti/RuO₂/IrO₂ electrodes were used in single under the same condition.

INTRODUCTION

With the rapid development of coal industry, enormous amount of coke has been consumed, so large quantities of wastewater were discharged by coke plants into natural water receptors, which has been causing severe environmental problems. As part of our systematic investigation on wastewater treatment, the present study describes the contamination contained in biologically pretreated coking wastewater (Zhang et al. 2012, Xie et al. 2014, Ma et al. 2015, Yu et al. 2015), it was found that most of its constituents were refractory, toxic, mutative, and carcinogenic. So it needs to be treated to reduce their possible impacts on the aquatic environment.

There are several conventional coking wastewater treatment methods, including solvent extraction of phenolic compounds, steam stripping of ammonia, and biological treatment (mostly the activated sludge process), and many other treatment processes, which have been studied. Although the biological methods are very effective for the disposal of wastewater (Zhang et al. 1997, Yu et al. 1997, Lee et al. 1998, Yu et al. 2005, Lai et al. 2008), it is still difficult to achieve the strict requirements of the National Discharge Standard of China (COD < 150 mg L⁻¹, NH₃-N < 25 mg L⁻¹) through

these methods (Wei et al. 2007), and the cost was also very high. Therefore, great attention has been directed towards new techniques for coking wastewater treatment.

For the aforementioned reasons, the method of electrochemical oxidation, for treatment of the contaminants contained in wastewater has become the focus of research in recent years (Yavuz & Koparal 2006, Abdelwahab et al. 2009). The three-dimensional electrode technology has been attracting much more attention due to its strong ability to mineralize a variety of bio-refractory ammonia nitrogen with its extensive specific surface area and the high capacity to generate free hydroxyl radicals in comparison to conventional two-dimensional electrodes (Bock & Kim 1997, Ma & Wang 2006, Kong et al. 2006, Wang et al. 2007).

Some researches showed that titanium substrate coating anode plates had good effect on electrochemical oxidation and wastewater treatment (Xiong et al. 2003). Meanwhile, inter layer with RuO₂ and IrO₂ oxide paint-coat could enhance the stability and prolong the lifetime (Comminellis 1994, Foti et al. 1999, Li et al. 2005, Costa & Olivi 2009). In order to get a better implementation of the comprehensive utilization of waste, the Ti/RuO₂/IrO₂ anode with coke particle as the third-dimensional electrode was selected.

MATERIALS AND METHODS

Experimental apparatus: Electrolysis was carried out relying on the electrolytic device which consisted of coke, the electrolytic cell, electrode plates and DC power supply (MPS702). Electrochemical plates consisted of stainless steel cathode plates and titanium substrate anode plates coated with noble metal oxide, which included RuO_2 and IrO_2 . The electrolytic cell was made of synthetic glass with a dimension of $140\text{mm} \times 90\text{mm} \times 130\text{mm}$ and an effective volume was 1.3L. Specification of each plate was $130\text{mm} \times 65\text{mm} \times 1\text{mm}$. The schematic diagram of the main apparatus is shown in Fig. 1.

Materials: The coking wastewater used for this study was obtained from a secondary sedimentation tank at the Tangshan coking plant in P.R. China. The characteristics of the wastewater are given in Table 1.

The coke was obtained from a coke bin in coking plant at Tangshan city, and the property of coke is shown in Fig. 2 and Table 2.

Methodology: In order to optimize the three-dimensional electrode process using $\text{Ti}/\text{RuO}_2/\text{IrO}_2$ anode and the coke particles, electrolysis of coking wastewater was carried out under different current density, pH and temperature. Moreover, we examined the properties of $\text{Ti}/\text{RuO}_2/\text{IrO}_2$ anode cell and modified coke particles through SEM and EDS briefly. Finally, the removal mechanisms of ammonia nitrogen in the three-dimensional electrode process using $\text{Ti}/\text{RuO}_2/\text{IrO}_2$ anode and the modified coke particles were investigated.

RESULTS AND DISCUSSION

The study of $\text{Ti}/\text{RuO}_2/\text{IrO}_2$ electrode: As is shown in Fig.

Table 1: Characteristics of wastewater used in the experiments.

Parameter	Unit	Concentration
pH	-	5.94
Chemical oxygen demand (COD)	mgL^{-1}	304.09
Ammonia nitrogen ($\text{NH}_3\text{-N}$)	mgL^{-1}	131.31
Total nitrogen (TN)	mgL^{-1}	132.25
chloride ions concentration	mgL^{-1}	748.85
Turbidity	NTU	4.80

Table 2: The element percentage spectrum of coke particle used in the experiments.

Element	Weight %	Atomic %
C	85.55	90.87
O	8.22	6.56
Al	2.16	1.02
Si	1.70	0.77
S	0.34	0.14
Ca	2.02	0.64

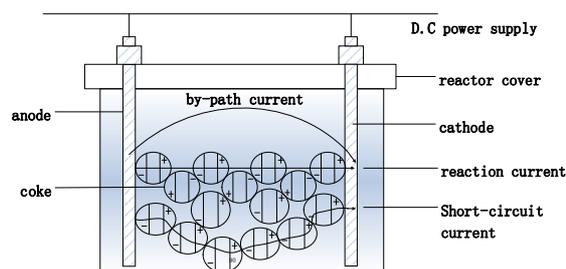


Fig. 1: Schematic diagram of the experimental apparatus.

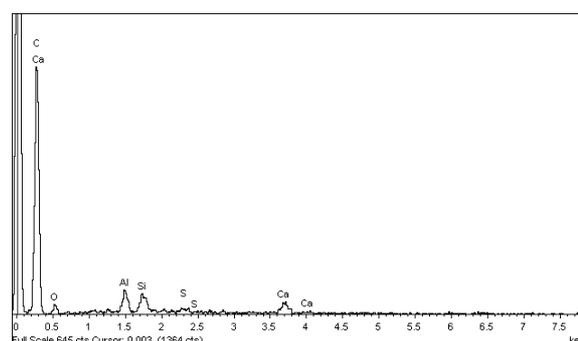
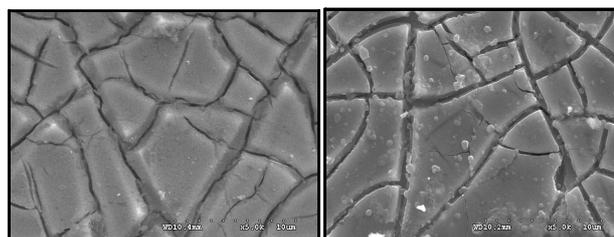


Fig. 2: EDS of coke particle.



(a) before use (b) after use

Fig. 3: Scanning electron micrographs of $\text{Ti}/\text{RuO}_2/\text{IrO}_2$ electrode before (a) and after (b) electrochemically advanced treatment coking wastewater.

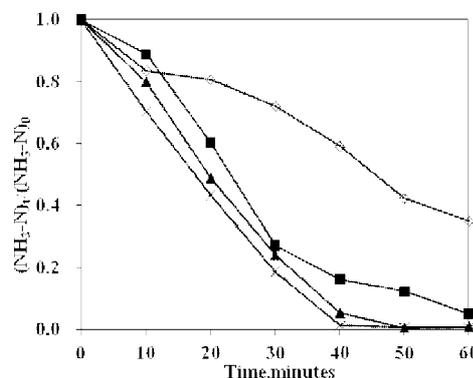


Fig. 4: The effect of different coke particle diameter on removal efficiency of $\text{NH}_3\text{-N}$: (●) ≥ 5 mesh, (◻) 5~10 mesh, (×) 10~20 mesh, (◐) 20~40 mesh.

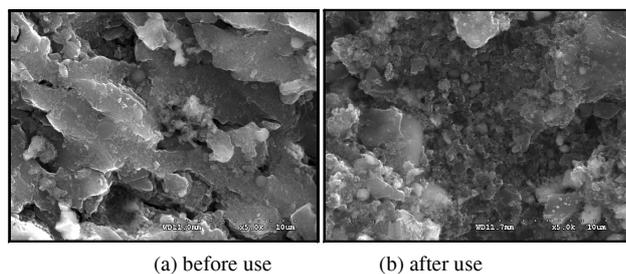


Fig. 5: Scanning electron micrographs of the coke surface.

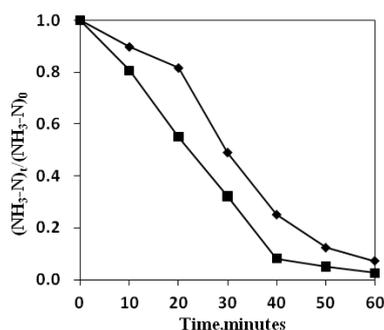


Fig. 6: Two dimensional electrodes(2D) and three dimensional electrodes(3D) on the electrochemical removal of NH₃-N compounds from biologically pretreated coking wastewater for the electrolyses performed at 9mAcm⁻² on the Ti/RuO₂/IrO₂ electrode: (◆) two dimensional electrodes, (■) three dimensional electrodes.

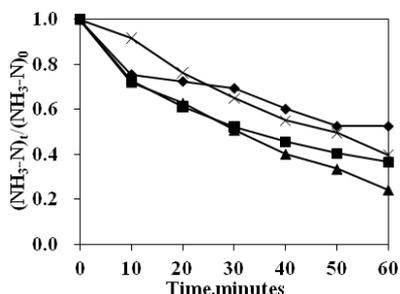


Fig. 7: The remove mate of different plate distance on removal efficiency of NH₃-N: (■) 0.5cm, (▲) 1cm, (×) 1.5cm, (◆) 2cm.

3, each anode plate was coated by RuO₂ foil for approximately 0.2mm in thickness. IrO₂ was also covered in certain ratio in order to keep the stability of the anode plates. The morphology of Ti/RuO₂/IrO₂ electrode has been analysed by SEM in Fig. 4. Fig. 4(a) shows that there are almost no cracks on the coating surface before electrolysis and the coating layer is compact. The significant compactness and low porosity observed indicate that incorporation of ruthenium oxide and iridium oxide components can improve the coating structure effectively, which may contribute to the prolongation of the electrode life. Fig. 4(b) shows that the outer

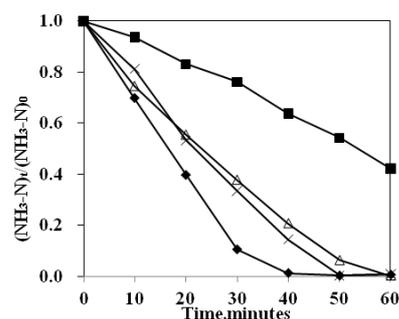


Fig. 8: The effect of area/volume on the electrochemical removal of NH₃-N compounds from advanced treatment of biologically pretreated coking wastewater with three-dimensional electrodes: (■) 33.8m²/m³, (△) 67.6m²/m³, (×) 101.4m²/m³, (◆) 135.2m²/m³.

layer film after electrolysis is relatively rough and little porous. In Fig. 4, after the electrolysis reaction, the plate has not been damaged during reaction, only surface scaling phenomenon. Therefore, from the scanning electron microscope, we can see the plate with strong corrosion resistance can be used for a long.

The study of coke particles: As is shown in Fig. 4, the evolution of NH₃-N concentration is a function of electrolysis time at different particle sizes of coke particles (≥5 mesh, 5~10 mesh, 10~20 mesh and 20~40 mesh). As shown in the Fig. 4, the removal rates of NH₃-N increased with the decrease of particle size, but the increase in the rate of NH₃-N reduction is not significant for over 20 mesh. And the removal rate of 10-20 mesh is the highest of the four kinds of samples. Coke in 10-20 mesh may have a 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. To sum up, the optimal particle size is 10-20 mesh.

As is shown in Fig. 5, SEM of the coke has been obtained to study the morphology of amorphous particles. The porous structures were formed, and which had adsorption effect for prepared coke (Fig. 5a), while dense surface and functioned as packed bed electrodes could be seen in Fig. 5(b) after use. This shows that the surface structure of the coke as a particle electrode in reaction is stable and little porous. Therefore, its surface area does not change much, the wastewater treatment efficiency is stable. However, the surface structure also shows that coking wastewater, in the electrolysis process, easily produce insoluble salts, therefore, coke particle in the course of the need for regular cleaning, to ensure the effective use.

The electrochemical treatment effect: As is shown in Fig. 6, the ammonia nitrogen concentration changed, obviously as a function of electrolysis time in the presence of different

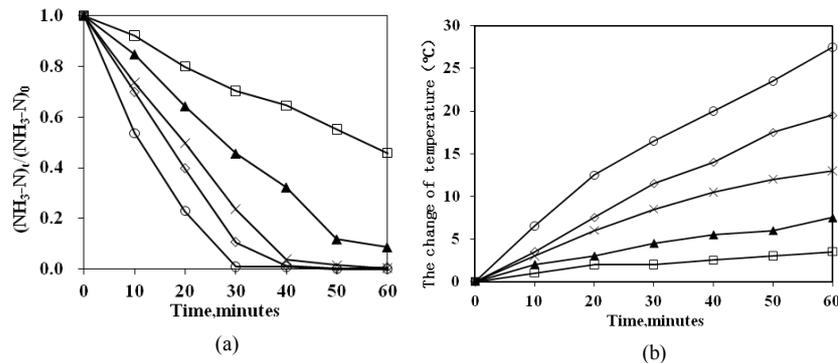


Fig. 9: The effect of current density on the electrochemical removal of $\text{NH}_3\text{-N}$ compounds and the change of temperature from advanced treatment of biologically pretreated coking wastewater with three-dimensional electrodes (\square) 1.5 mA/cm², (\blacktriangle) 3.0 mA/cm², (\times) 4.5 mA/cm², (\diamond) 6.0 mA/cm², (\bullet) 7.5 mA/cm².

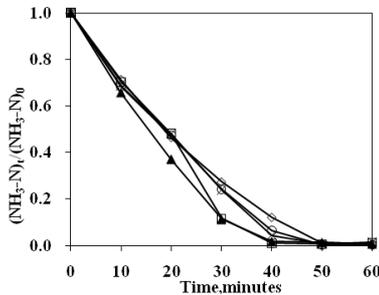


Fig. 10: The effect of pH on the electrochemical removal of $\text{NH}_3\text{-N}$ compounds from advanced treatment of biologically pretreated coking wastewater with three-dimensional electrodes: (\square) pH=3, (\blacktriangle) pH=5, (\times) pH=7, (\diamond) pH=9, (\bullet) pH=11.

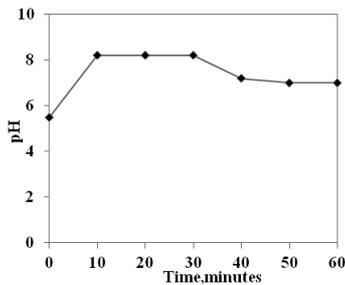


Fig. 11: The effect of retention time on pH from advanced treatment of biologically pretreated coking wastewater with three-dimensional electrodes.

electrodes. Before the experiment, the coke was dried at 105°C in oven for 2 hours and immersed in coking wastewater for 12h respectively, to avoid the effect of absorption. As can be seen from Fig. 3, in the same electrolysis conditions, the ammonia nitrogen of the 3D reactor removal achieved 90% at 40min, while the 2D reactor in the same period is only about 75%. After 60 minutes, the ammonia nitrogen removal of two reactors achieved 97% and 93% respectively. This is because, many small particles, put into

the three-dimensional electrode system, form charged microelectrodes under the influence of electric field. Coke could increase the effective area of electrodes. More importantly, the coke acted as the bipolar electrode for additional free hydroxyl radical generation, which could greatly improve the ammonia nitrogen removal rate. All of these indicate that the three-dimensional electrode system should be able to give a satisfied solution to the remained bio-refractory ammonia nitrogen from the biological treatment process in comparison to conventional two-dimensional electrodes.

Influence of operating variables on ammonia nitrogen:

Influence of plate spacing: When the plate spacing increased from 0.5cm to 2cm, the characteristics of contamination removal rate are shown in the Fig. 7. As can be seen from the figure, with the shorter distance of plates, $\text{NH}_3\text{-N}$ removal efficiency increased gradually. The plate spacing had a clear impact on $\text{NH}_3\text{-N}$ treatment effect, but the increase in the rate of $\text{NH}_3\text{-N}$ reduction was not significant for less than 1cm. This is because the short distance between plates can generate the H_2O_2 , free hydroxyl radicals ($\cdot\text{OH}$) increasingly, which could have an effect on the degradation of ammonia nitrogen. Plates resistance would increase and the current through the plates would decrease if the plate spacing get less than 1cm. To sum up, the best plate spacing was 1cm.

Influence of A/V (area of plates/volume of wastewater):

As shown in Fig. 8, the ammonia nitrogen concentration decreased generally with the increasing of A/V and retention time at 6mA/cm². At the constant current density condition, the increasing of plate area was conducive to the generation of strong oxidizing substances such as H_2O_2 , $\cdot\text{OH}$ and O_3 , etc. Meanwhile, it was easy to assemble pollutant to occur oxidation reaction on the plate surface owing to the large plate area, improving the ammonia nitrogen removal efficiency.

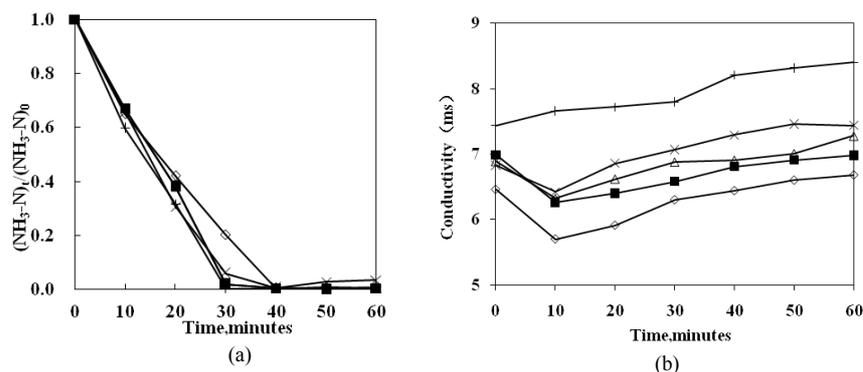


Fig. 12: The effect of chloride concentration on the electrochemical removal of NH₃-N compounds and conductivity from advanced treatment of biologically pretreated coking wastewater with three-dimensional electrodes: (◇) N:Cl=1:8, (■) N:Cl=1:9, (△) N:Cl=1:10, (×) N:Cl=1:11, (+) N:Cl=1:12.

Influence of current density: As is shown in Fig. 9(a), the removal rates of ammonia nitrogen changed obviously with retention time at various current densities. The electrolytic oxidation removal of ammonia nitrogen increased generally with the current density and the retention time. At a current density of 4.5 mA/cm², 6.0 mA/cm², 7.5 mA/cm² and retention time 40 min, the ammonia nitrogen removals were about 96.2%, 98.6% and 99.9%, respectively. The residual NH₃-N was almost completely removed in all solutions. Gradually increasing from a low current intensity, electrolysis was generated in the process. Meanwhile, ·OH concentration was increased, and the ammonia nitrogen removal increased. As shown in Fig. 9(b), at a current density of 6.0 mA/cm² and 7.5 mA/cm², with the current intensity of the sustained, increased in the final mixture temperature at 43°C and 35°C respectively. In addition, the efficiency of the electrodes with the treatment effect changed generally while increasing power consumption. Therefore, the best current density was 4.5 mA/cm².

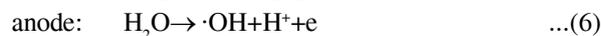
Influence of initial pH: As is shown in Fig. 10, pH was a crucial parameter that played an important role in the treatment, because it influenced the form of the electro-generated active chlorine species (Eqs. (1)-(3)) and its oxidation potential. Meanwhile, the active chlorine substances were mainly composed of chlorine molecules and hypochlorite ions, which could degrade the ammonia nitrogen concentration in the solution.



In addition, there was not a significant difference on ammonia nitrogen removal when using three-dimensional electrodes under the combining process at different initial pH conditions of acid (pH 3, 5), neutral (pH 7) and alkaline

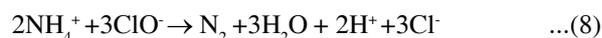
(pH 9, 11). The discrepancy may be attributed to the different electrolytes employed.

Moreover, as is shown in Fig. 11, pH had a sharp increase in the beginning of electrolysis, and it achieved at 8.5 within 10 minutes and the solution was alkaline. Meanwhile, the longer the electrolysis time, the less of pH, and pH decreased to about 7 after 30 minutes. Because of the high chloride concentration in the wastewater, reactions may possibly happen in electrodes as follows (Eqs. 4-7):



In addition, hydrogen extraction played a great role in improving water pollutant degradation at initial stage. Large amounts of dissolved oxygen were deoxidized to H₂O₂, OH⁻ were created after H⁺ absorption, which resulted in high level of pH. As the temperature increased, cathode and deoxidized metal ions made reaction to generate ·OH with high oxidation. Meanwhile, oxygen evolution and chloride evolution in anode region played a significant role in reaction gradually, and large amounts of H⁺ were created, which made pH decreasing. And the effluent pH was of about 7, the initial pH was not adjusted, which could meet the demand of Iron and Steel Industry Discharge Standard (pH=6~9).

Influence of the chloride concentration: The results showed that the higher the chloride concentration, the higher the production active chlorine species, and higher ammonia nitrogen removal rates were achieved. When NaCl was introduced to the anode compartment, anions in the water were mainly Cl⁻ ions. Active chlorine species could react with ammonia nitrogen by addition, substitution and electrons transferred. These species were powerful oxidant agents which were able to oxidize ammonia nitrogen (Eqs. 1-3 & 8):



However, higher ammonia nitrogen removals also were achieved by increasing the chloride concentration. The presumption could be explained by the following factors: (a) elevated chloride concentrations could result in products that are more easily mineralized by hydroxyl radicals generated on the electrode surface; (b) Cl^\cdot radicals, which were also able to promote mineralization of ammonia nitrogen compounds, could be formed in the process. But the increase in salt concentrations resulted in a decrease of the electrical conductivity and current density.

Furthermore, as is shown in Fig.12, the decreasing of conductivity at first 10 minutes was due to a decrease in the concentration of dissolved ionic species, which was caused by the formation of precipitates at cathode region. Thereby, a much lower current was resulted. Considering the removal rate as the cost and safety in all aspects, the optimal concentration of nitrogen and chlorine ratio was 1:9.

CONCLUSIONS

In this paper, the three-dimensional electrodes in combined process could effectively decompose ammonia nitrogen. For plate distance of 1.0cm, retention time of 40min and current density of $4.5\text{mA}/\text{cm}^2$, the highest removal efficiency of nitrogenous compounds was achieved; ammonia removals were about 95%; the titanium substrate coating anode plate has nice surface characteristics which could make it become good electrode material, and the cokes served as packed bed particle electrodes exhibited good electrical conductivity.

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