The Mechanism and Performance of Zeolites for Ammonia Removal in the Zeolite Packed Electrolysis Reactor

Yuanxing HUANG, Cuihong SONG, Liang LI,* and Yuemei ZHOU

School of Environment and Architecture, University of Shanghai for Science and Technology,
No. 516 Jungong Road, Shanghai, P. R. China

* Corresponding author: liliang@usst.edu.cn

ABSTRACT

Electrolytic removal of ammonia was investigated by using zeolite packed electrolysis reactor in batch mode. The results showed that 27.8 mg N/L ammonia could be removed to a concentration as low as 0.3 mg N/L within 1 h. Nitrite, nitrate and chloramines were determined to be 0.02 mg N/L, 3.9 mg N/L and 15.8 mg Cl/L, respectively, which accounted for a total nitrogen removal of 80% after 1.5 h of electrolysis. The main components and crystalline structure of the packed zeolite were found to be unchanged after long time of electrolysis. The specific surface area and pore volume of zeolite increased from 15.9 m²/g and 0.05 cm³/g to 42.6 m²/g and 0.08 cm³/g, respectively, which might be caused by the removal of impurities and formation of new channels and cavities during electrolysis. The adsorption capacities of zeolite for ammonia before and after electrolysis were close.

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1. Introduction

As one of the main nitrogenous contaminants, nowadays ammonia is frequently detected in industrial, agriculture, municipal wastewaters and landfill leachate.^{1,2} Oxygen depletion and algae blooming are common phenomena occurred when large amount of ammonia is released into surface water, which will accelerate the eutrophication process of estuaries, lake or coastal seas. Therefore removal of ammonia from wastewater is a critical issue especially in sensitive and fragile area.

Methods including nitrification/denitrification, chemical precipitation, air stripping, ion-exchange, photocatalytic oxidation and plasma treatment are available for ammonia removal from wastewater.^{3–8} Among them, air stripping process is usually effective for wastewater with high ammonia concentration. Biodegradation is a preferable choice to treat municipal sewage with low ammonia concentration and low toxicity under mesophilic temperature. Chemical precipitation usually produces large amount of chemical sludge that is difficult to handle. Photocatalytic oxidation and plasma treatment of ammonia is usually more effective in alkaline solution since hydroxyl radical reacts fast with NH₃ instead of NH₄⁺.

In term of ion exchange or adsorption, zeolite was proved to have high cation exchange capacity and great affinity for ammonia compared with other natural materials.^{9–11} According to Halim and his co-workers,¹² ammonia adsorption capacity of zeolite can reach up to 17.5 mg N/g, and activated carbon is only 6.1 mg N/g. In addition, zeolite adsorption was preferred by many researchers due to its easy operation, low cost and independence of temperature. Accordingly, regeneration of saturated zeolite by biological or chemical means is a hot research area. Lei et al. proved that saturated zeolite can be regenerated using electrochemical method and the adsorption capacities of regenerated zeolite were almost the same as unused zeolite.¹³

Strong oxidants such as hydroxyl radicals, hypochlorite acid etc. generated during electrochemical oxidation process can oxidize various pollutants in wastewater. For traditional two dimensional (2D) electrode reactor, area-volume ratio, mass transfer and current efficiency were the main limitations for its wide application.

Therefore three dimensional (3D) electrode was developed to overcome these shortcomings. In recent years, 3D electrode reactors had been successfully applied to the treatment of landfill leachate, tannery wastewater, textile wastewater etc.^{14–16} Granular activated carbon (GAC) was often used as particle electrode in many researches due to its large surface area, high adsorption capacity for various organic compounds and catalytic properties within electric field, which had been successfully applied to the treatment of phenol,¹⁷ acid orange 7,¹⁸ p-nitrophenol¹⁹ etc. Apart from GAC, modified kaolin was successfully prepared and used as packed bed particle electrode for removal of anionic surfactants by Kong et al.²⁰ Foaming nickel was also investigated as the particle electrode by Liu et al., which showed high removal efficiency (99%) for rhodamine B at neutral pH in 30 mins.²¹

Compared with activated carbon, zeolite, known as silica-rich heulandite, has great affinity for ammonia. In this research, natural zeolite without any modification was packed in the electrolysis reactor, which provided special large surface area and active sites for ammonia removal from aqueous phase. Mechanism, main products and the change of zeolites' specific characteristics before and after electrolysis were investigated respectively for electrocatalytic ammonia removal by using zeolite packed electrolysis reactor.

2. Experimental

2.1 Set-up and procedure

Electrochemical experiment was performed in recycling mode at laboratory scale in a cylindrical cell (2) (62 mm inner diameter, 248 mm height) made of stainless steel. RuO₂/Ti and stainless steel with the same dimension of 176 × 38 × 1 mm were used as anode and cathode, respectively. Natural zeolite (9) was clinoptilolite with diameter of 2–3 mm, which was purchased from Jinyun County, Zhejiang Province, China. The zeolite was packed into the electrolysis reactor, which resulted in a void volume of 350 mL. Anode and cathode were connected to a direct current (DC) power supply (1) (WYJ, Shanghai Wenkai Power Supply Equipment Ltd, China) with maximum output of 10 A and 30 V. As shown in Fig. 1, wastewater containing ammonia was stocked in feed tank (5), and

Figure 1. The schematic diagram of zeolite packed electrolysis reactor. 1. DC power supply; 2. electrolytic reactor; 3. peristaltic pump; 4. magnetic stirrer; 5. feed tank; 6. gas washer; 7. gas collector; 8. sampling port; 9. natural zeolite.

pumped by a peristaltic pump (3) (YZ1515X, Baoding Longer Precision Pump Ltd, China) into electrolytic reactor (2) at constant flow rate of 150 mL/min. Magnetic stirrer was used to mix the solution in order to make homogenous concentration distribution in feed tank. The total volume of aqueous solution in the system is 4 L so the retention time is 2.3 and 24.3 min in electrochemical cell and feed tank respectively. In a gas washer (6), boric acid solution was used in order to evaluate the gas stripping contribution for ammonia removal. Water samples were taken from sampling port (8) and analyzed immediately.

2.2 Chemicals and materials

The synthetic wastewater was prepared by dissolving analytical reagents into deionized water. The chemicals used in this research were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The composition of the synthetic wastewater was as follows: $(\text{NH}_4)_2\text{SO}_4$, 131 mg/L; NaCl, 544 mg/L. 1 mol/L NaOH and 0.5 mol/L H_2SO_4 were used to adjust the pH of the synthetic wastewater. In addition, 30% boric acid was prepared as adsorption solution in the gas washer to determine the volatilization of ammonia.

2.3 Analysis

According to standard methods,²² ammonia was determined by Nessler method. The analysis of nitrate was done by UV spectrophotometry. Nitrite was analyzed through N-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method. Free chlorine (including HOCl , Cl_2 and ClO^-) and total chlorine (including free chlorine and chloramines) was determined by DPD ferrous titrimetric method. Chloride ion was measured through titrimetric method with silver nitrate. pH was measured by a pH meter (PHS-2C, Leici Company, Shanghai, China). Total nitrogen

was measured by a TOC/TN analyzer (Multi N/C 3100, Analytikjena Company, Germany).

X-ray powder diffraction (XRD) of all samples was performed in reflection mode by Bruker D8 Advance X-ray diffractometer under voltage 40 kV and current 30 mA with a $\text{Cu K}\alpha$ radiation, which employed a scan rate of 8° per min in 2θ ranging from 10 to 50° . Nitrogen adsorption-desorption isotherms were collected on Micromeritics ASAP 2020 surface area and porosity analyzer at 77 K after the sample had been degassed at 200°C for 5 h. The Brunauer-Emmett-Teller (BET) surface area was calculated from the linear part of BET plot ($P/P_0 = 0.04\text{--}0.16$). Morphological features of the zeolite before and after electrolytic process were analyzed by a scanning electron microscope (SEM, S4800, Hitachi, Japan).

3. Results and Discussion

After experiment, the concentration of ammonia in gas washer was measured and the result showed that ammonia volatilization was less than 1%. So the amount of ammonia removed through volatilization can be ignored.

3.1 Mechanism of ammonia removal

Figures 2(a) and 2(b) illustrated the changes of nitrogen and chloro species in water during the electrolysis of ammonia solution with 330 mg/L Cl^- at pH 7.0 and current density 13.8 mA/cm^2 , respectively. As shown in Fig. 2(a), concentration of ammonia decreased quickly from 27.8 mg N/L to 0.3 mg N/L in 1 h. After 1.5 h of electrolysis, total nitrogen decreased from 30.1 mg N/L to 5.8 mg N/L, and nitrate concentration increased from 0 to 3.9 mg N/L. Nitrite concentration was always below 0.02 mg N/L. With regard to the variety of chloride ions, free chlorine and total chlorine, the transformation of element Cl was shown in Fig. 2(b). The concentration of Cl^- decreased from 330 to 300 mg/L after 1.5 h of electrolysis of synthetic wastewater. During the same time period, free and total chlorine was detected out in aqueous phase with concentration range of 0–1.3 and 0–17.1 mg Cl/L, respectively. Consequently, the reduction of Cl^- could be attributed to the formation of total chlorine in water and Cl_2 escaped from the solution in gaseous form. The variety of Cl^- was in accordance with the results obtained by Rosilda et al.²³ Moreover, the electrolytic removal of ammonia was effective for both NH_3 and NH_4^+ , which was different from the photocatalytic oxidation.⁸ Oxidation by hydroxyl radical was considered to be the main mechanism for ammonia removal in photocatalytic oxidation, which was more effective in alkaline solution for NH_3 instead of NH_4^+ .

Additional experiment was done by using the same synthetic wastewater and experimental setup without passing current. The results showed that ammonia concentration decreased from

Figure 2. Concentration profiles during electrolysis process of ammonia solution with 330 mg/L Cl^- at pH 7.0 and current density 13.8 mA/cm^2 : (a) different nitrogens and (b) chloro species.

29.5 mg/L to 13.6, 12.7, 11.6, 9.4 mg/L after 0.25, 0.5, 1.0, 1.5 hours, respectively. The removal of ammonia without passing current can be ascribed to the adsorption on zeolite. It was obviously that adsorption was very fast during the first 0.25 h and slowed down when the zeolite became saturated, which was different from the situation of passing current. Compared with the previous experiment, it can be concluded that electrolysis accelerated the removal of ammonia which gave a lower effluent ammonia concentration.

For 2D electrode, many researches proved that direct anode oxidation, indirect oxidation by hydroxyl radicals and hypochlorite acid were the mechanisms for ammonia removal. In chloride mediated system, oxidation-reduction reaction between ammonia and hypochlorite acid was the main passway. The possible reactions were shown in Eqs. (1)–(4):²⁴

Chlorine gas, which will be easily dissolving in water and forming strong oxidants such as HClO, ClO^- , can be generated on anode surface in the chloride system. Then, ammonia will be oxidized to nitrogen gas. However, not all of the ammonia will be oxidized to nitrogen gas. Some side reactions could occur in the solution as shown in Eqs. (5)–(8). Due to the formation of chloramines and elution of chlorine gas, the chloride concentration decreased after electrolysis for a period of time.

In addition, part of the HClO, ClO^- would be transferred to chloride ions on the cathode as shown in Eqs. (9)–(10). Strong oxidants were reduced, leading to the decrease of ammonia oxidation efficiency.

As for the zeolite packed electrolysis reactor in this experiment, adsorption by zeolite was important at the early stage when free chlorine concentration was low. When electrolysis proceeded, the generated strong oxidants HClO, ClO^- did not only oxidize ammonia in the solution but also regenerate zeolite simultaneously. According to Li Miao's research,¹³ the electrochemical method can regenerate saturated zeolite and the adsorption capacities of regenerated zeolite were recovered almost completely. So combined mechanism of adsorption and electrocatalytic oxidation played an essential role in ammonia removal in the zeolite packed electrolysis reactor.

3.2 Characterization of the packed zeolite before and after electrolysis

The XRD patterns of natural zeolite before and after electrolysis were depicted in Fig. 3. Clinoptilolite, quartz and mordenite were found from the profiles, which had no change after electrolysis. Significant increase in the relative intensities at 20.9° , 26.7° and 39.5° (2θ) for quartz, at 26.0° , 30.0° (2θ) for clinoptilolite were observed after electrolysis. This could be ascribed to the loss of impurities on the surface and pore wall of natural zeolite after electrolysis. On the other hand, as can be seen from diffraction patterns of the samples, a new peak at 15.8° (2θ) was observed for clinoptilolite in zeolite after

Figure 3. XRD patterns of natural zeolite: (a) after electrolysis; (b) before electrolysis (C: clinoptilolite; Q: quartz; M: mordenite).

Figure 4. Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of the natural zeolite before (B) and after (A) electrolysis.

electrolysis. Based on those results, it can be concluded that there was no transformation in zeolite's main crystalline structure after long time of electrolysis.

The specific surface area and porosity of the natural zeolite were investigated by using nitrogen adsorption and desorption isotherms. As shown in Fig. 4(a), curve A and B showed the nitrogen adsorption-desorption isotherms of the natural zeolite after and before electrolysis, respectively. The isotherms of zeolite before and after electrolysis are types IV according to the Brunauer-Emmett-Teller (BDDT) classification, which classified the majority of physisorption isotherms into six types.²⁵ As for hysteresis loop, both of them have a H3 hysteresis loop indicating their pore-size distributions are in mesoporous regions. The BET specific surface areas of the natural zeolite before and after electrolysis were 15.9 and 42.6 m²/g respectively, which were calculated from nitrogen-adsorption isotherms with data in the relative pressure (P/P_0) range of 0.04–0.16. As shown in Fig. 4(b), the corresponding pore-size distributions (PSD) of the zeolite before and after electrolysis were described by curve A and B, respectively. The PSD curve B was bimodal with smaller (~ 3.7 nm) and larger (~ 18.3 nm) mesopores for zeolite before electrolysis. For zeolite after electrolysis, the PSD curve A was changed to unimodal with smaller (~ 4.0 nm) mesopores. By using Barret-Joyner-Halenda desorption method, the average pore volume of zeolite before and after electrolysis can be calculated to be 0.05 and 0.08 cm³/g, respectively. The significant increase of surface area and pore volume might be caused by two

Figure 5. Adsorption of ammonia by zeolite: B represents zeolite before electrolysis; A represents zeolite after electrolysis.

Figure 6. SEM micrographs of zeolite: (left) before electrolysis; (right) after electrolysis.

reasons: one is the removal of impurities through chemical reactions and mechanical action, the other is the formation of new channels/cavities caused by hydraulic as well as mechanical shearing force during electrolysis.

The adsorption of ammonia on zeolite before (B) and after (A) electrolysis were evaluated with synthetic ammonia solution under batch mode as shown in Fig. 5. Before electrolysis, the adsorption capacities of zeolite were 1.18, 1.98 and 3.09 mg N/g zeolite for initial ammonia concentrations of 29.8, 51.2 and 94.7 mg N/L, respectively. After electrolysis, 1.16, 2.00 and 2.85 mg N/g adsorption capacities were observed with the initial ammonia concentrations of 29.2, 50.8 and 96.9 mg N/L, respectively. No significant change of ammonia adsorption was observed after electrolysis. This phenomenon was not consistent with the obvious increase of surface area. So the adsorption of ammonia on natural zeolite was mainly through the chemical process of ion exchange rather than physical adsorption.

The SEM micrographs in Fig. 6 visually illustrated the same trend obtained by XRD, specific area and porosity analysis. The appearance of zeolite before electrolysis is relatively smooth with clear layer shape. After electrolysis, some fragments chipped off the main body of zeolite. Many fractures, caused by the coaction of hydrodynamic collisions and chemical corrosive effects, appeared on the zeolite surface to make it look more coarse, and thus reflected the generation of new channels and cavities, which lead to increase the surface area and pore volume. However, the laminated structure

of zeolite kept unchanged, which was in accordance with the XRD results.

4. Conclusions

Zeolite packed electrolysis reactor with RuO_2/Ti as anode and stainless steel as cathode could enhance ammonia removal rate significantly in wastewater treatment. The mechanism for ammonia removal by zeolite packed electrolysis reactor included the combined action of ion-exchange, electrochemical oxidation and simultaneously electrocatalytic regeneration of zeolite. Nitrite, nitrate, chloramines and gaseous products were found to be main products of ammonia oxidation. After electrolysis, the main components and crystalline structure of zeolite had no change, the surface area and pore volume increased significantly, which might be caused by the removal of impurities and formation of new channels/cavities during electrolysis. However, the adsorption capacity of zeolite for ammonia kept almost the same before and after electrolysis.

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