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Short Communication

The Adsorption and Oxidation of Ammonia in Granular Activated Carbon Packed Three-Dimensional Electrode Reactor

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The adsorption and oxidation of ammonia was investigated by using a granular activated carbon packed three-dimensional electrode reactor under continuous mode. Experimental results showed that 30.7 mg N/L ammonia can be reduced to 1.2 mg N/L by electrolysis under 2.0 A and 10.6 min HRT. 76% total nitrogen removal was achieved at the same time with nitrate and chloramines as the residue in aqueous phase. Prolonged ammonia retention time and decomposition of H_2O_2 to hydroxyl radical on the surface of activated carbon might be the two main reasons for enhanced ammonia removal. Higher current, chloride concentration and longer HRT were beneficial for this process. Treatment of actual wastewater showed that 28.0 mg N/L ammonia can be fully removed by electrolysis under 2.0 A and 10.6 min HRT, which can meet strict discharge limit.

Keywords: Ammonia; Adsorption; Electrolysis; Three-dimensional electrode

1. INTRODUCTION

Electrolysis is a frequently used advanced oxidation process for treatment the of ammonia, nitrate, organic compounds in the wastewater due to its characteristics of effective removal for various contaminants, easy operation and maintenance, no sludge production etc. Despite of these merits, there are still some drawbacks limiting its real application. For example, mass transfer is limited in two-dimensional (2D) electrode reactor, which results in a low current density and high energy cost [1].

Recently, three-dimensional (3D) electrode reactor has attracted more and more attention since the particle electrode can provide large surface area and active sites for both reactive species and pollutants, leading to an increased current efficiency and decreased energy cost. Beside the frequently discussed mechanism of direct oxidation and indirect oxidation, adsorption/electrosorption of contaminants on the particle electrode plays an important role for their removal. Furthermore, many

researches confirmed the production of hydroxyl radicals on particle electrode due to the presence of polyaromatic moieties and functional groups [2, 3]. Electrode materials, structure, current density, hydraulic retention time (HRT), initial concentration had been proved to be related to the treatment efficiency as well as energy cost.

Various materials such as activated carbon, zeolite, foamed nickel etc. have been used as the packing materials inside the electrolysis reactor to treat acid orange 7[4], anionic surfactants [5], heavy metals [6], rhodamine B [7], oil refinery wastewater [8] and phenolic compounds [9]. Those packing materials can be polarized during electrolysis and acted as a micro-electrolytic cell, which is beneficial for both direct and indirect electro-oxidation. Enhanced contaminants removals were frequently observed due to shorter mass transfer distance, higher specific surface area and area-volume ratio, leading to better efficiency and promising environmental applications [10].

Granular activated carbon (GAC) is an excellent material for particle electrode especially for the electrolytic oxidation of organic compounds since it is a non-polar adsorbent as well as a semi-conductor. Enhanced removal of organic compounds was observed when activated carbon was packed into 2D electrode reactor [11]. However, to the best of our knowledge, there are rare reports on the treatment of ammonia by activated carbon packed electrolysis reactor. This research provides an insight on the ammonia removal in electrostatic field with the presence of GAC. Possible mechanism and pathway were investigated through adsorption and electrolysis experiments, respectively. Single factor tests were employed to study the impact of different influencing factors such as current, HRT, chloride and initial ammonia concentration etc. Finally, the possibility of real application was tested by electrolysis with municipal wastewater.

2. MATERIALS AND METHODS

2.1. Batch adsorption experiment

GAC with 2-3 mm diameter was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The adsorption of ammonia on GAC was performed by batch test in a shaking water bath with constant temperature ranging from 15 to 45 ^{o}C. GAC was pre-washed with deionized water and then dried in 50 ^{o}C oven until constant weight. 5.0 GAC adsorbent was measured and mixed with 200 mL ammonia solution prepared with ammonia sulfate and deionized water. During adsorption, pH was kept near 7.0±0.5, similar to most municipal wastewater. Samples were periodically taken and analyzed to determine the adsorption of ammonia with time.

2.2. Electrolysis

The GAC packed 3D electrode reactor consisted of RuO_2/Ti anode, stainless cathode and GAC particle electrode. The same dimension of 176×38 mm was applied for both anode and cathode inside a cylindrical cell with 62 mm inner diameter and 248 mm height. Before use, GAC was prewashed with deionized water to remove the impurities and then dried in a 50 ^{o}C oven until constant weight. After packing with GAC, the void volume of the electrolysis reactor was determined to be 270 mL.

Electrolysis experiments were performed under continuous mode with upflow ammonia-containing wastewater by using peristaltic pump (YZ1515X, Baoding Longer Precision Pump Ltd, China). Different HRTs were achieved by adjusting the flow rates. A direct current power source (WYJ, Shanghai Wenkai Power Supply Equipment Ltd, China) was used to supply current in the range of 0-2.0 A. Samples were taken periodically and analyzed immediately according to standard procedure.

Mechanism and pathway of the electrolytic removal of ammonia was investigated through the analysis of transformation of element nitrogen and chlorine during electrolysis under the reference conditions of 2.0 A current, 10.6 min HRT, 30.0 mg N/L ammonia and 300 mg Cl/L chloride. Besides that, important impact factors were tested using single factor experiments by changing the targeting factor and fixing other parameters in reference condition. Finally, actual wastewater from municipal wastewater treatment plant was taken and electrolyzed to test the performance of GAC packed 3D electrode reactor.

2.3. Analysis procedure

Ammonia was determined by Nessler's method [12]. The analysis of nitrate was done by UV spectrophotometry [13]. Nitrite was analyzed through N-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometric method [14]. Free chlorine (HOCl, Cl_2 and ClO^-) and total chlorine (free chlorine and chloramines) were both determined by DPD ferrous titrimetric method [15]. Chloride ion was measured through titrimetric method with silver nitrate [16]. Total nitrogen and pH were measured by TOC/TN analyzer (Multi N/C 3100, Analytikjena Company, Germany) and pH meter (PHS-2C, Leici Company, Shanghai, China), respectively [17].

3. RESULTS AND DISCUSSION

3.1. Adsorption of ammonia on GAC

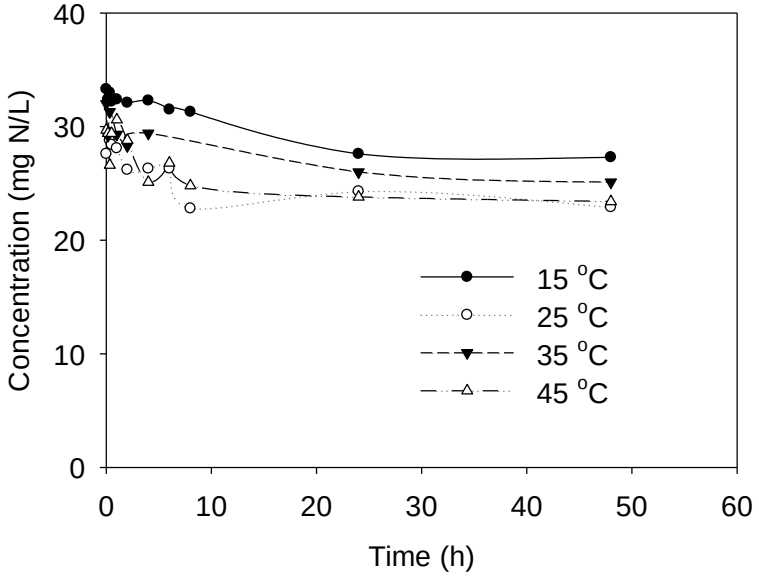

Figure 1. Adsorption of ammonia by granular activated carbon

Before packing into the reactor, the adsorption capacity of GAC was investigated by batch experiments, and results were plotted in Figure 1. The results showed that ammonia can be adsorbed by GAC and the 48 hours' adsorption capacities were 0.24, 0.28, 0.19 and 0.25 mg/g under 15, 25, 35 and 45 ^{o}C, respectively. Temperature had little effect on the adsorption process. Generally speaking, activated carbon is not an effective adsorbent for ammonia compared with zeolite. Wang and Peng [18] reviewed the application of zeolite for the adsorption of ammonia as single adsorbent with adsorption capacities in the range of 2.7-30.6 mg/g. Low adsorption capacity of ammonia by GAC might be explained by the non-polar structure as well as low ion exchange ability of activated carbon.

3.2. Mechanism and pathway

GAC packed 3D electrode reactor was investigated under continuous mode with synthetic wastewater containing 300 mg Cl/L chloride at pH 7.0. As shown in Figure 2, the change of elements nitrogen and chlorine were analyzed during electrolysis under 2.0 A current and 10.6 min hydraulic retention time (HRT). Obviously, 30.7 mg N/L ammonia decreased to 1.2 mg N/L, and at the same time total nitrogen decreased to 7.7 mg N/L with 3.2 mg N/L nitrate, 0.004 mg N/L nitrite and chloramines as the rest. Chloride decreased from initial 300 mg Cl/L to 270 mg Cl/L with the generation of 0.3 mg Cl/L free chlorine and 19.7 mg Cl/L chloramines, respectively.

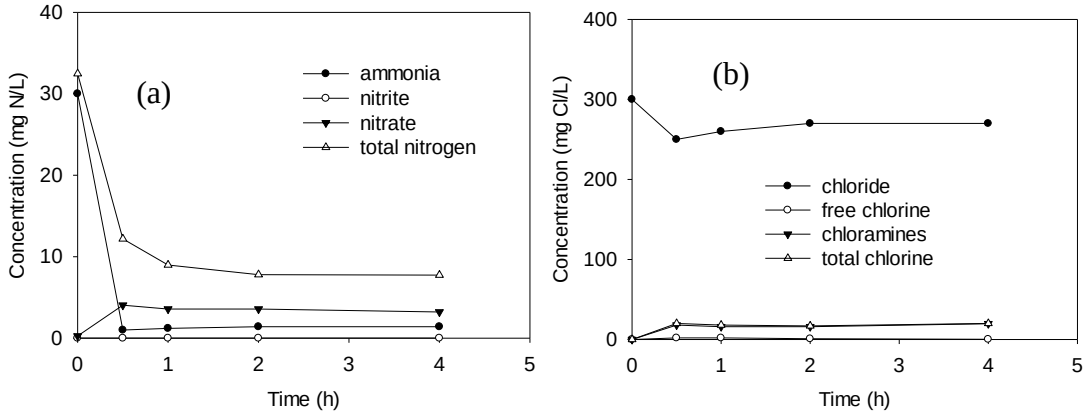

Figure 2. the transformation of different elements during electrolysis at 2.0 A and 10.6 min HRT: (a) nitrogen; (b) chlorine

The direct oxidation of ammonia on electrode or indirect oxidation by hydroxyl radicals was proved to be slow, and indirect oxidation by hypochlorous acid was the main pathway (equation [1] & [2]) as shown in previous research [19]. The additional mechanism might include the adsorption of ammonia on GAC, which increase the ammonia retention time in reactor. The adsorbed ammonia can be simultaneously oxidized as equation [2]. This process can be enhanced in 3D electrode reactor, since many researches [20, 21] proved that H_2O_2 can be decomposed into hydroxyl radicals on the surface of activated carbon, and thus enhance the generation of active chlorine in the presence of chloride in aqueous phase as shown in equation [3] [22, 23].

$2Cl^- - 2e^- \rightarrow Cl_2$ [1]

$HClO + (2/3)NH_4^+ \rightarrow (1/3)N_2 + H_2O + (5/3)\ H^+ + Cl^-$ [2]

$Cl^- + \cdot OH \rightarrow HOCl^-\cdot$ [3]

3.3 Influencing factors

Several important factors such as current, HRT, chloride concentration and initial ammonia concentration were investigated by a single factor method. The experimental results are shown in Figure 3 (a)-(d). For currents 0.5, 1.0, 1.5 and 2.0 A, the effluent ammonia concentrations were 21.2, 12.1, 2.4 and 1.2 mg N/L, respectively, indicating that the current had obvious positive relationship with ammonia removal efficiency.

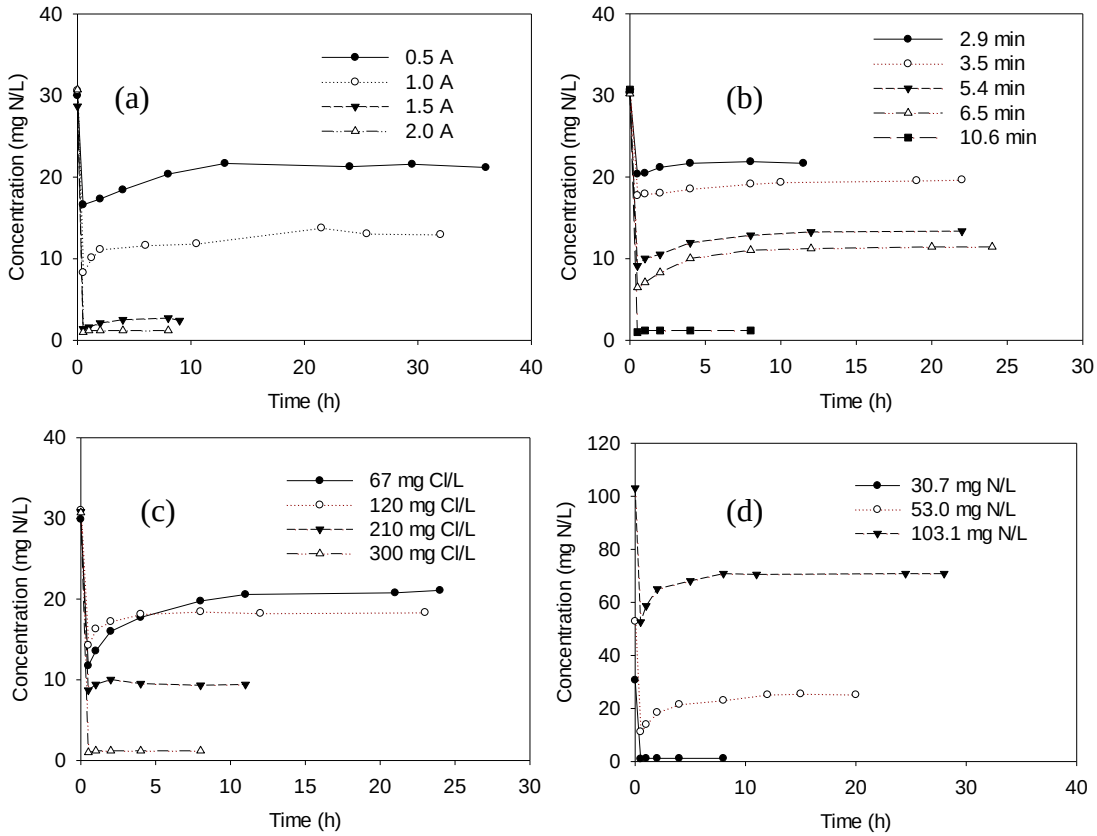

Figure 3. the effect of different factors on electrolytic removal of ammonia: (a) current; (b) HRT; (c) chloride concentration; (d) initial ammonia concentration

The increase of current density was found to enhance the chlorine/hypochlorite production [24], leading to high ammonia removal rate through indirect oxidation. Furthermore, different ammonia effluent concentrations of 21.7, 19.7, 13.4, 11.4 and 1.2 mg N/L were observed for HRTs 2.9, 3.5, 5.4, 6.5 and 10.6 min, respectively, which was less effective than zeolite packed reactor under similar conditions [25]. This might be explained by the affinity for ammonia on zeolite. Ammonia removal efficiencies increased significantly with HRT. As for the effect of chloride concentration, effluent ammonia concentrations of 21.1, 18.3, 9.4 and 1.2 mg N/L were got under the conditions of 67, 120,

210 and 300 mg Cl/L, respectively. High chloride concentration was beneficial for ammonia removal due to the higher yield of active chlorine. Similar phenomenon with ammonia removal proportional to the NaCl level was observed during electrolysis of swine wastewater by Cho et. al. [26] For different initial ammonia concentrations of 30.7, 53.0, and 103.1 mg N/L, effluent ammonia concentrations were found to be 1.2, 25.2 and 70.8 mg N/L. It was interesting to notice that when initial ammonia concentration increase for 3.4 times, the amount of removed ammonia varied for only 6%.

3.4 Treatment of municipal wastewater

The GAC packed 3D electrode reactor was further investigated by using municipal wastewater after primary settling under the conditions of 2.0 A current and 10.6 min HRT. As shown in Figure 4, 28.0 mg N/L ammonia decreased to less than 0.02 mg N/L. Compared with synthetic wastewater, no significant decrease of ammonia removal was observed for 3D electrode reactor, which was different from 2D electrode reactor with 26-28% lower ammonia removal rate [27]. This phenomenon can be explained by that reductive organic compounds were adsorbed on the surface of GAC, which hindered its influence on ammonia oxidation. Furthermore, total nitrogen decreased from 31.5 to 3.5 mg N/L. 3.0 mg N/L nitrate was determined in the effluent. Nitrite was always less than 0.01 mg N/L. The rest total nitrogen might exist in the form of chloramines. The chloride ion decreased from the initial 300 mg Cl/L to 270 mg Cl/L, which was converted to free chlorine and chloramines, respectively. The energy consumption (EC) can be estimated through equation (1), which was calculated to be 2.2 kJ/mg N ammonia in this case.

$$EC = \frac{V \times I \times HRT}{(C_0 - C_e) \times V} = \frac{V \times I}{(C_0 - C_e) \times Q} \qquad (1)$$

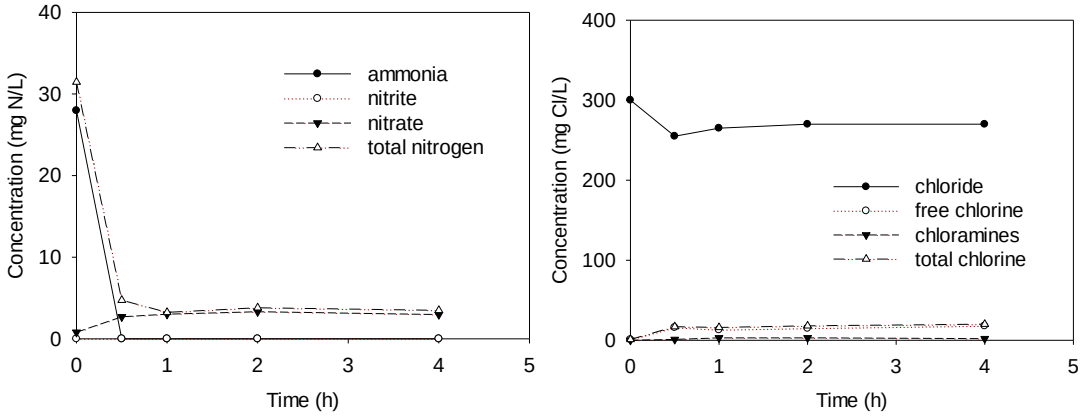

Figure 4. Electrolytic removal of ammonia from actual wastewater at 2.0 A current and 10.6 min HRT

4. CONCLUSION

In this research, GAC packed 3D electrode reactor was used for the removal of ammonia from aqueous phase. 30.7 mg N/L ammonia was reduced to 1.2 mg N/L under 2.0 A current and 10.6 min

HRT. At the same time, total nitrogen decreased from 32.5 to 7.7 mg N/L, in the form of nitrate and chloramines in the effluent. High current, chloride concentration and long HRT were found to be beneficial for ammonia removal. The treatment of municipal wastewater showed that GAC packed 3D electrode reactor was effective for ammonia removal from 28.0 mg N/L to less than 0.02 mg N/L, which can meet strict discharge standards.

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