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Effect of clinoptilolite on ammonia emissions in integrated vertical-flow constructed wetlands (IVCWs) treating swine wastewater

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A B S T R A C T

Constructed wetlands (CWs) is an effective way to removal nitrogen (N) from swine wastewater, which accompanying with the process of ammonia (NH_3) volatilization. However, the removal pathway of NH_3 volatilization has adverse impacts on the natural biogeochemical cycle of N. Here, this paper presents the first attempt to investigate the potential use of clinoptilolite in reducing NH_3 volatilization in integrated vertical-flow constructed wetlands (IVCWs) treating swine wastewater. The NH_3 volatilization flux was measured via steady-state chambers. Results showed that the removal rate of TAN (total ammonia nitrogen, NH_3 and NH_4^+-N) in clinoptilolite system was 96.1%, where 93.01% of that was removed by substrate adsorption, it was significantly higher ($p < 0.05$) than that in quartz sand system (29.6%). Moreover, the microporous structure of zeolite is not conducive for the growth of denitrifying microorganisms. The NH_3 volatilization flux covered a range of 0.02–3.00 mg N m^{-2} h^{-1}, which was lower than the reported date. Furthermore, the proportion of NH_3 volatilization in Clite was 0.99%, which was obviously lower ($p < 0.05$) than that in control (9.01%), and the ammonia volatilization quantities decreased by 180.7% in this study. Results suggest that clinoptilolite plays an important role in reducing NH_3 volatilization to the atmosphere.

1. Introduction

China is an agricultural country, and more than 1 billion tons of wastewater produced from livestock each year, which is far more than that in industrial wastewater and domestic wastewater. Swine wastewater is a mixture of feces (45%), urine (55%) and washing water, and characterized by a high content of organic matter, nutrients, ions and other compounds (Villamar et al., 2012). Among that, ammonium (NH_4^+-N) is the main nutrients pollution in wastewater with the concentration of 0.9–4.3 g/L (Plaza de los Reyes et al., 2014), which is an important source of ammonia (NH_3) volatilization. Based on statistics, over 80% of the total NH_3 emissions in Europe and US were produced by animal wastes (Battye et al., 2011). However, the excessive emission of NH_3 had adverse impacts on natural biogeochemical cycle of N, which could cause broad concern due to its environmental and health impacts (Gu et al., 2014, Fowler et al., 2013). It may give rise to the acidification of water and soil. Basically, NH_3 is present in the troposphere with a low concentration, ranging from 1 to 25 ppb (Renard et al., 2004). However, NH_3 could react with atmospheric acids to form ammonium sulfate, ammonium bisulfate or ammonium nitrate (Hristov et al., 2011), which are considered as PM 2.5 (particles with aerodynamic diameter less than or equal to 2.5 mm). The statistics data of International Agency for Research on Cancer in 2014 showed that these particles could responsible for 30% of lung cancer deaths·NH_3 volatilization is a reversible physicochemical process. At the same time, the water quantity of livestock wastewater fluctuates greatly with high COD and TAN (total ammonia nitrogen, NH_4^+-N and NH_3). Inappropriate treatment methods or indiscriminate discharge of swine wastewater could cause haze (Shen et al., 2014) and offensive odour. Thus, how to effectively reduce NH_3 volatilization in wastewater with high concentration of TAN was a public concern.

Constructed wetland (CW) is recognized as a low-cost technology for the treatment of wastewater (Faulwetter et al., 2009), which was widely used for its lower construction and operation costs, convenient management and excellent removal efficiency. It has been successfully used to remove NH_4^+-N in swine wastewaters (Klomjek, 2016, Plaza de

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los Reyes et al., 2014). The flux of NH_3 was mainly determined by the partial pressure of NH_3 (P_{NH3}), as to CW, it was related to wastewater characteristics (TAN, pH, temperature) (Harper et al., 2004). For TAN, according to the relationship of Henry's Law and the equilibrium between NH_3 and NH_4^+, lower concentration of TAN will get lower partial pressure of NH_3 (VanderZaag et al., 2008), which could discharge less NH_3 to the atmosphere. Therefore, rapid reduction of the concentration of NH_4^+ is an effective way to control the volatilization of NH_3. Free ammonia increased ($p < 0.05$) with the increasing of pH (Ortíz et al., 2014), when the pH of the influent is between 7.8 and 8.4 (Stelt et al., 2007), the aqueous NH_4^+-N shifting into NH_3 accelerates the volatilization rate of NH_3 to the atmosphere.

Integrated vertical-flow constructed wetland (IVCW) is a combination of vertical down-flow cell and vertical up-flow cell with high removal efficiency of nutrition. It has become one of the main CW types in China owing to its high purification efficiency to organics in water (Du et al., 2017). Zeolite is a positive ion exchange compound with high affinity and selectivity for NH_4^+ ions because of its crystalline, hydrated properties resulting from its infinite, 3-dimensional structures (Mumpton and Fishman, 1977). Malekian et al. (2011) suggested that the zeolite is a suitable ion-exchanger for NH_4^+ ion, with the potential of being a controlled-release NH_4^+ fertilizer. It has been widely used in reducing ammonia emission from poultry manure. Specifically, it has been used as an air scrubber packing material to improve the quality of sewage sludge (Wang et al., 2017), as a sorbent to mitigate the volatilization of NH_3 during slurry composting. Giacomini et al. (2014) reported that the clinoptilolite could reduce 24–76% NH_3 emissions during pig slurry composting and their efficiency was directly related to the applied rate.

To date, the researches about NH_3 emissions in CWs were focused on the wetland types (VanderZaag et al., 2008; Poach et al., 2004), vegetation species (Zhang et al., 2016), diversity (Luo et al., 2016), seasonality (Reyes and Vidal, 2015) and water characteristics (He et al., 2016). As far as we know, the research about the role of clinoptilolite in reducing NH_3 emissions in CW has never been reported. The present research was conducted to provide more detailed information about the effect of clinoptilolite on NH_3 volatilization in IVCWs treating swine wastewater. The specific objective of this paper was to observe the temporal variation of NH_3 volatilization in IVCWs and identify the main influencing factors and analysis the mechanism on how zeolite regulate the NH_3 volatilization. This research will expand the application areas of CWs and provide insight into N cycling in treating animal wastewater.

2. Materials and methods

2.1. Constructed wetland

Two sets of organic glass tanks (40 cm length, 20 cm width, and 40 cm depth) were built as microcosms IVCWs. A piece of glass plate with holes in the bottom was fixed in the middle of each tank to form two series systems, which were called down-flow cell and up-flow cell. *Arundo donax* was planted in each cell of wetland sequentially. 35 cm of clinoptilolite and quartz sand were filled in IVCWs, which were called Clite and Ctrl system for short. The design of the system for determining the volatilization of NH_3 in IVCWs was following the method described by Stelt et al. (2007) with some modifications (Fig. 1). Plastic chamber (40 cm length, 20 cm width, and 60 cm height) was employed to cover on the surface of constructed wetland and sealed with tape. A small beaker was placed on the surface of the substrate of IVCWs in advance. 100 mL 0.01 M H_2SO_4 was added in the beaker to trap the volatilized NH_3, as volatilized NH_3 will be converted into ammonium when it contacts with the H_2SO_4 solution.

The experiment was carried out in a stable wetland feeding with swine wastewater, which was taken from the digestion tank of swine feedlots (in Wuhan, China). The influent water quality were as follows:

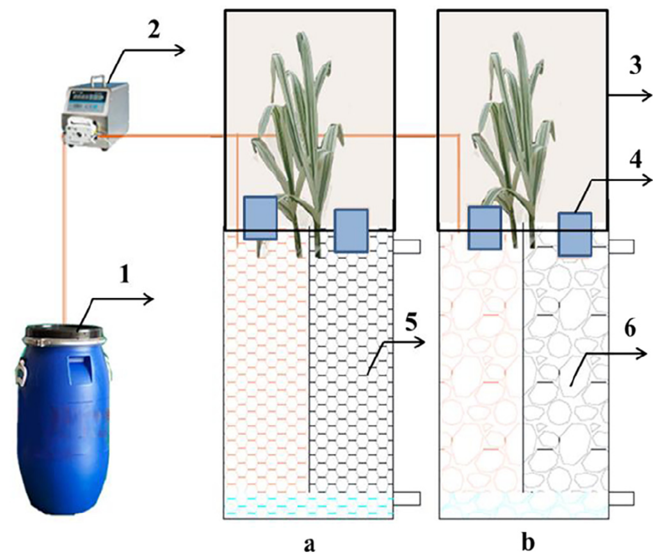

Fig. 1. Schematic representation of IVCWs (a) Clite, (b) Ctrl 1-wastewater tank, 2-pump, 3-sealing cover, 4-beaker, 5- clinoptilolite, 6-sand.

pH, 8.0 ± 0.3; COD, 251.06 ± 42.63 mg/L; total nitrogen (TN), 454.65 ± 52.75 mg/L; ammonium (NH_4^+), 405.81 ± 34.20 mg/L; nitrate (NO_3^-), 48.32 ± 6.24 mg/L and NO_2^- was not detected. The chemical composition of employed clinoptilolite were silicium (SiO_2, 68–70%), aluminium (Al_2O_3, 13–14%), calcium (CaO, 1.8–2.2%), sodium (Na_2O, 0.6–1.6%), potassium (K_2O, 1.6–3.9%), iron (Fe_2O_3, 1–1.8% and magnesium (MgO) = 0.9–1.4%. The quartz sand medium is mainly composed of SiO_2. The systems were operated for 3 batches, each batch was held for 10 days, and the effluents were detected every day at the same time. The activity of urease was measured following the method of Kandeler and Gerber (1998). Potential nitrification and denitrification rates were measured following the preliminary research of our group (Hu et al., 2016). The experiment was conducted in Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan, China.

2.2. Water sampling and analysis

Water samples of the inflow and outflow were collected every day at the same time, temperature and pH in influent and effluent were measured immediately using portable Orion Star meter (520M-01A, Thermo, USA) equipped with a pH electrode (8107UWMMD, Thermo, USA). Water samples were collected to analyze TN (alkaline potassium persulfate digestion spectrophotometry method), NH_4-N (Nessler's Reagent Spectrophotometry), NO_3-N (UV spectrophotometric determination) and NO_2-N (N-(1-naphthyl)-ethylenediamine dihydrochloride spectrophotometry method). Before that samples were filtered with a coarse filter to eliminate suspended solids, and then persevered with concentrated sulfuric acid to keep pH = 2 in water and kept at 4 °C until analysis.

2.3. Substrate sampling and analysis

Substrate samples were collected at the end of batch 2 and batch 3 for measuring the adsorption amount of N in the substrate for one batch. It was collected from the top 5–10 cm and 25–30 cm height of each up-flow cell and down-flow cell, roots and macro-fauna were removed by hand and then placed in a sterile sealing bag. The wetland substrate samples were stored at −20 °C until analyses. The concentration of TN in substrate was determined by persulphate digestion method.