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Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry

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HIGHLIGHTS

- Biochar adsorbed 60% NH_4^+-N from piggery slurry.
- Absorption was sensitive to changes in particle size, pH and temperature.
- NH_4^+-N adsorption from slurry followed the Langmuir and Pseudo second order models.
- Monolayer chemisorption was the major NH_4^+-N adsorption mechanism from piggery slurry.

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ABSTRACT

Due to its high adsorption capacity, the use of biochar to capture excess nutrients from wastewater has become a central focus in environmental remediation studies. In this study, its potential use in adsorption and removal of ammonium in piggery manure anaerobic digestate slurry was investigated. The adsorbed amount of NH_4^+-N ($mg \cdot g^{-1}$) and removal percentage as a function of adsorbent mass in solution, adsorbent particle size, NH_4^+-N concentration in the effluent, contact time, pH and temperature were quantified in batch equilibrium and kinetics experiments. The maximum NH_4^+-N adsorption from slurry at 1400 $mg\ N \cdot L^{-1}$ was $44.64 \pm 0.602\ mg \cdot g^{-1}$ and $39.8 \pm 0.54\ mg \cdot g^{-1}$ for wood and rice husk biochar, respectively. For both biochars, adsorption increased with increase in contact time, temperature, pH and NH_4^+-N concentration but it decreased with increase in biochar particle size. Furthermore, the sorption process was endothermic and followed Langmuir ($R^2 = 0.995$ and 0.998) and Pseudo-second order kinetic models ($R^2 = 0.998$ and 0.999). Based on the removal amounts, we concluded that rice husk and wood biochar have potential to adsorb NH_4^+-N from piggery manure anaerobic digestate slurry, and thus can be used as nutrient filters prior to discharge into water streams.

1. Introduction

Over the years the promotion of scaled piggery farms in China has greatly helped in closing the gap between products supply and demand. However, the huge amounts of manure and related wastes produced are causing an unforeseen environmental pollution (Huaitalla et al., 2013). Piggery farms generate solid manure (feces), raw manure slurry (urine and wash water), and digestate slurry after biodigester treatment. These three waste streams are renowned for containing high nutrients mainly nitrogen and phosphorus compounds but also contain high Chemical and Biological Oxygen Demanding organics (COD and BOD) that often pollute the environment (FAO, 2006). In the past decade, manure nutrients could be efficiently recycled back to because of the high integration of livestock production with cropping cycles (Chen, 1997). To date, the threshold for piggery production has shifted from small scale rural farming communities to large scaled production in the suburbs of major cities. Consequently, the manure nutrients and wastewater produced by the peri-urban farms are far more than can be recycled as fertilizer on nearby land (Chen et al., 2012). The agricultural recycling loop has been ruptured by the extra cost of transporting large volumes of nutrients slurry from urban farms to rural crop farming areas. Furthermore, the rapid development in rural China has increased land fragmentation and as a result, the rural farming methods have gradually changed with now more farmers preferring the use of mineral fertilizers over manure for intensive production on small cropping areas. This shift in farming methods has greatly reduced the potential of agricultural assimilation of large scale nutrients and implying the need for other alternatives to land disposal that could reduce environmental pollution risks.

In China at present the entire livestock industry still lacks adequate manure treatment facilities and pollution is further driven by the weak pollution reinforcement (Gale et al., 2012; Yang et al., 2012). Traditionally, it is common to store the daily generated manure slurry

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in large open lagoons for while to allow for aerobic degradation and after the effluents with their residual nutrients are discharged into the environment. Besides lagoons, anaerobic digestion (AD) with biogas supply is gradually gaining ground as a large scale manure treatment procedure (Chen et al., 2012). The production of biogas has an added advantage of lowering farm energy costs through utilization of the gas directly or for electricity generation. However, considering that during anaerobic digestion limited nitrification occurs, the digestate remains rich in NH_4^+-N in addition to the residual COD, BOD and phosphorous compounds and therefore the disposal challenge of residual slurry remains unsolved. Often times depending on animal stocking density and the digester capacities, the cost of slurry handling and transportation becomes economically unfeasible and farms tend to discharge their waste without any secondary pretreatment to nearby water streams causing heavy pollution.

According to the China pollution source census carried out in 2010, the COD, total nitrogen (TN) and phosphorus from the livestock breeding industry accounted for 96%, 38% and 56% of the total pollutants from agricultural sources respectively and were 2.3 times that of industrial sources. By no surprise, the highest values for this form of pollution were reported in commercial piggery farming areas in Sichuan, Shandong, Guangdong, Henan and Zhejiang provinces (China Ministry of Environmental Protection, 2010). In these provinces, massive eutrophication has caused heavy algae blooms killing fish and other aquatic life. Human life has also been endangered through reduced amount of usable water and reduced aquatic food supply (Nielsen et al., 2013). Therefore, in order to balance livestock production with human welfare and the environment it is imperative to control pollution from manure nutrients and definitely as earlier discussed agricultural recycling and anaerobic digestion alone without recovery of nutrients in the residual slurry is no longer a solution.

In literature, several methods ranging from biological, physical, chemical or a combination of these have been explored to manage pollution from livestock sources. The chemical approach has focused on the use of struvite to recover N and P from livestock liquid manure (Ganrot et al., 2007; Nelson et al., 2003; Song et al., 2011; Turker and Celen, 2007; Wrigley et al., 1992) Biologically, ammonium removal using membrane reactors, anaerobic ammonium oxidation (ANAMMOX), sequential combined aerobic and anaerobic batch reactors (SBR) and denitrification in constructed wetlands have received reasonable research attention (Değermenci et al., 2012; Harrington and Scholz, 2010; Healy et al., 2007; Molle et al., 2008). Likewise, adsorption methods with activated carbons, ion exchange resins and zeolites for ammonia removal have been widely explored (Huang et al., 2010; Nguyen and Tanner, 1997; Sica et al., 2014; Thornton et al., 2007). Despite the reported success, the challenge with all the above mentioned methods still remains the high cost of raw materials and the initial process set up especially for large scale projects (Song et al., 2011). In addition, full scale application of biological processes for ammonium removal is technically limited by the high microbial sensitivity to shock loadings and pH changes in the waste water which require pH correction while the more nitrate generated necessitates further removal (Sica et al., 2014).

In the present study, the potential use of biochar is proposed as an alternative treatment for NH_4^+-N removal from piggery manure anaerobic digestate slurry. Biochar is described as porous solid carbonaceous material producible through pyrolysis of a wide range of biomass in anoxic conditions at temperatures ranges of 300–1500 °C (Ahmedna et al., 1997b). Due to its favorable characteristics such as high surface area, high porosity, cation exchange capacity and pH buffering ability, biochar has received overwhelming attention in agronomic studies for soil amendment and carbon sequestration (Mukherjee et al., 2014; Mukherjee and Zimmerman, 2013; Novak et al., 2010; Rajkovich et al., 2011; Spokas et al., 2011; Taghizadeh-Toosi et al., 2012b). Biochar has also emerged as a potential biomaterial for adsorption of nutrients and different organic pollutants from domestic, agricultural and industrial waste waters (Amuda et al., 2007; Chen et al., 2011; Kim et al., 2013; Mizuta et al., 2004; Sarkhot et al., 2013; Zheng et al., 2010; Zhu et al., 2012). However, from our literature survey, the application of biochar to treat piggery manure anaerobic digestate slurry for nutrient recovery and water recycling has not been fully researched. This study therefore focuses on (a) understanding the effects of biochar dosage, particle size, pH, effluent concentration, temperature and adsorption time on the NH_4^+-N removal efficiency from the slurry and (b) evaluating the process kinetics and thermodynamics of NH_4^+-N adsorption onto biochar derived from wood residues and rice husks. This work is part of a larger research project aimed at developing on-farm livestock wastewater treatment technologies based on biochar adsorption to recycle nutrients and re-use water. Therefore, the preliminary results on adsorption dependent factors and kinetics will provide empirical information useful for the design of future adsorption facilities on a pilot scale.

2. Materials and methods

2.1. Biochar characterization

The biochar was produced from mixed wood cuttings and rice husks under slow pyrolysis at 600 °C for a retention time of 10 h. Proximate analysis was done to measure moisture content, fixed carbon, volatiles and ash content according to ASTM D-1762-84 standard for analysis of charcoal (ASTM, 2007). In brief, the moisture content was determined on dry matter basis after drying the samples in open crucibles at 105 °C for 24 h. The ash content was determined by combustion of biochar samples in an open ceramic crucible at 700 °C for 6 h. Volatile matter content was determined as weight loss after combustion in a ceramic crucible with a loose ceramic cap at 950 °C for 10 min while the fixed carbon was calculated by difference. The elemental composition of carbon, hydrogen, nitrogen, oxygen and sulfur of biochar samples was done based on the dry combustion method using a CHNS/O Elemental Analyzer (Vario MACRO, Germany). The biochar bulk density, pH and electro-conductivity were determined with slight modification of the method described by Ahmedna et al. (1997). Briefly, five tubes of 10 ml volume capacity were filled with dry ground biochar and gently tamped to a constant volume. The bulk density was then calculated by dividing the weight of each tube by the volume of the packed biochar material. To measure the pH and electro-conductivity, suspensions of biochar were prepared by diluting 1 g biochar with 20 ml de-ionized (Milli-Q pore) water. The suspensions (in triplicate) were then shaken at 90 °C in an end to end shaker for 2 h to allow the dissolution of the soluble biochar components, after which the pH was measured with a pH-meter (Metler Toledo) and the electro-conductivity was read using a EC meter (Orion Model 115A, Thermal Fisher Scientific, USA). Brunauer–Emmett–Teller method with N_2 adsorption at 77 K was used to investigate the surface area and porosity of the biochar. Scanning electron microscopy technique was used to study the morphology of the adsorbent while surface and structural chemical functional groups in the biochar were studied using the Fourier Transform Infrared technique (FT-IR, Spectrum 100, Perkin Elmer) with an intensity of 4000–400 cm^{-1} (Fu et al., 2012). Table 1 gives a summary of the measured parameters.

2.2. Sampling and slurry characterization

Pretreated slurry samples were collected from a mesophilic biogas plant digesting solely piggery manure with an anaerobic digestate slurry capacity of 10 m^3 day^{-1}. The plant is located in Dong Hua Shan Village, Beijing. The collection time was from November 2013 to February 2014. Prior to use, the slurry was centrifuged at 12,000 rpm for 15 min and the supernatant was filtered through a 0.45 μm cellulose acetate membrane to remove residual colloidal matter. One part of the filtrate was used in determination of the organic and inorganic parameters while the other part was stored at 3 ± 1 °C prior to sorption