Simultaneous capture removal of phosphate, ammonium and organic substances by MgO impregnated biochar and its potential use in swine wastewater treatment

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ABSTRACT:

Metal oxide-biochar composites have been used for removing pollutants from aqueous systems. In this work, optimized MgO-impregnated porous biochar was prepared using an integrated adsorption-pyrolysis method for absorption of phosphate, ammonium and organic matter (humate). Results revealed that the MgO-biochar was comprised of nano-sized MgO flakes and nanotube-like porous carbon. Mg content had significant effects on the development of the nanotube-like porous carbon structure in MgO impregnated biochar and its adsorption capacity for phosphate, ammonium and humate. The adsorption isotherms fitted by Langmuir model illustrated that the optimized adsorbent, 20% Mg-biochar, exhibited maximum adsorption capabilities of more than 398 mg /g for phosphate, 22 mg/g for ammonium, and 247 mg/g for humate, respectively. The phosphate adsorption fitted the pseudo-second-order kinetic model, while ammonium and humate adsorption were best described by the intra-particle diffusion model. The existence of Cl^- , NO_3^- , SO_4^{2-} , K^+ , Na^+ and Ca^{2+} ions had no significant impacts on humate adsorption, but the presence of SO_4^{2-} and Ca^{2+} affected the phosphate adsorption, and the presence of K^+ , Na^+ and Ca^{2+} ions inhibited ammonium adsorption. Characterization of adsorbents by X-ray diffraction (XRD), field-emission scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) before and after treating swine wastewater revealed that struvite crystallization, electrostatic attraction, and π - π interactions contributed to the adsorption of phosphate, ammonium and humate. The results demonstrated that the optimized MgO-biochar could be employed as an effective adsorbent for the simultaneous removal and recovery of phosphate, ammonium and organic substances from nutrient-rich livestock wastewaters.

Keywords: Phosphate, ammonium, dissolved organic matter, adsorption, MgO-biochar

1. Introduction

With the rapid growth in the global demand for meat consumption, China has become the biggest livestock producing country in the world (Li et al., 2012). Accordingly, the overproduction of swine wastewater, which contains high concentrations of phosphate, ammonia nitrogen, and organic substances generated from the pig-feeding process, has led to a great environmental concern (Huang et al., 2016). The proper treatment and disposal of swine wastewater in China is becoming increasingly urgent as the nitrogen, phosphorus, and COD (an indicator of dissolved organic substance content) from the livestock production industry now account for 38%, 56% and 96% of the total pollutants from agricultural sources, respectively (China Ministry of Environmental Protection, 2010).

Different treatment technologies including biological, physical, and chemical or a combination of these methods have been employed to treat wastewaters for complying with the allowable effluent discharge limits (Delgadillo-Mirquez et al., 2016; Escudero et al., 2015; Liu et al., 2013; Xia et al., 2016). Current biological approaches have focused on the treatment of swine wastewater through anaerobic fermentation, biofilm reactors, sequentially combined aerobic and anaerobic batch reactors (SBR), and denitrification in constructed wetlands etc., whereas physical and chemical approaches have emphasized on recovering nitrogen and phosphorus from livestock wastewaters based on precipitation and adsorption mechanisms (Escudero et al., 2015; Xiao et al., 2016). Large scale application of biological processes for wastewater treatment is often technically limited by the high microbial sensitivity to shock loadings and pH changes in wastewaters, which would require repeated pH corrections and potentially more nitrate generated that necessitates further removal (Delgadillo-Mirquez et al.,

2016; Ye et al., 2016). Various physical and chemical methods employing adsorbents including activated carbon (Huggins et al., 2016), ion exchange resins (Liu et al., 2013), zeolites (Farhad and Mohsen, 2016), attapulgite (Yin and Kong, 2014), diatomite (Xia et al., 2016), and raw biochar (Kizito et al., 2015) for ammonia and phosphate removal have been explored. Despite the reported success, the challenge with all the above mentioned technologies still remain, due to the high cost and/or limited removal performance (Tao et al., 2016).

Alternatively, it is known that metals like magnesium, aluminum, and calcium etc. play an important role in the removal of ammonium and phosphate from livestock wastewater (Xia et al., 2016). However, the economic feasibility of this method is strongly controlled by the cost of soluble metal salts and alkali reagents (Romero-Güiza et al., 2015; Xia et al., 2016; Ye et al., 2016). Some researchers pointed out that solid metal oxides like MgO and CaO could be used as sinks of metal source with many benefits because they are environmental materials and essential for biological growth, and their alkaline nature can neutralize acids and provide a suitable pH range for nutrient recovery (Xia et al., 2016; Yao et al., 2013). For example, Xia et al. (2016) prepared the mesoporous MgO modified diatomite adsorbent with the maximum removal capacity of 77.05 mg/g for ammonium and 160.94 mg/g for phosphate from aqueous solutions. Yin and Kong (2014) also used a calcium-rich attapulgite for ammonium and phosphate adsorption. However, these mineral adsorbents generally have very limited adsorption capacity for dissolved organic substances. Recently, researchers have shifted the sight to a low cost emerging material, biochar, which refers to a carbonaceous solid produced by pyrolyzing biomass under oxygen limited condition. While regular pristine biochar has excellent adsorption capacity for organic substances, it exhibits very limited adsorption capacity for phosphate and anions in general (Chen et al., 2011; Jeong et al., 2012; Li et al., 2016; Tan et al., 2015). Aiming

to improve biochar's phosphate adsorption capacity, some lanthanum, magnesium, iron and aluminum oxides grafted biochar composites are produced to enhance biochar's sorption ability for phosphate, especially the MgO modified biochar composites (Agrafioti et al., 2014; Chen et al., 2011; Jung and Ahn, 2016; Li et al., 2016; Wang et al., 2015; Yao et al., 2013; Zhang and Gao 2013). However, the knowledge gaps still exist in optimization of biochar with nano-sized MgO for adsorption of phosphate, ammonium and organic substances. In addition, the potential use of these biochar composites for simultaneous removal of phosphate, ammonium and organic substances from swine wastewater has not been investigated.

Therefore, the objectives of this work were to (1) prepare nano-sized MgO impregnated porous biochars with varying contents of Mg by using an integrated adsorption and pyrolysis method, (2) optimize Mg addition in Mg-biochar composite for maximum phosphate, ammonium and organic substance adsorption, and (3) investigate the potential of Mg-biochar for swine wastewater treatment through a batch experiment.

2. Material and Methods

2.1. Materials

Sugarcane harvest residue (leafy trash) obtained from Louisiana State University Agricultural Center Sugar station at St. Galniel, LA was used as the feedstock biomass. The biomass materials were cut into <5 cm pieces and sequentially washed by tap and deionized water (DI, 18.2 MΩ) to minimize the presence of dust followed by oven-drying at 55 °C overnight. The dry sugarcane leaves were crushed by a high-speed rotary cutting mill pass through a screen smaller than 0.12 mm and used for biochar preparation. The swine wastewater used in this study was collected from a pig farm located in the suburb near the campus. Prior to

use, the swine wastewater and was pretreated by passing it through a 0.22 μ m filter membrane to remove suspended solids. The characteristics of this pretreated swine wastewater were pH 7.86, alkalinity (as CaCO₃) 1377.2 mg/L, COD 2080.4 mg/L, total ammonium 388.1 mg/L, total phosphorus 91.3 mg/L, K⁺173.6 mg/L, Ca²⁺ 21.2 mg/L, and Na⁺ 13.1 mg/L, respectively. All chemicals, magnesium chloride, sodium phosphate monobasic monohydrate, sodium hydroxide, nitric acid, sulfuric acid, hydrogen peroxide, ammonium chloride, and sodium humate of analytical grade were purchased from Sigma-Aldrich and used as received. All chemical solutions were prepared using DI water in the experiment.

2.2 Biochar preparation

The MgO particle-impregnated porous biochar composite was produced from sugarcane crop harvest residue using a modified adsorption and pyrolysis method (Liu et al., 2013). In brief, 50 g of sugarcane crop harvest residue (leafy trash) powder and 1000 mL of MgCl₂ solutions in varying concentrations were mixed in respective flasks and the mixtures were shaken at a constant-temperature oscillator at 120 rpm for 24 h. The mixtures were then heated at 80 °C until the supernatant evaporated, and dried at 105 °C for 6 h. After that, each dried mixture was transferred into a porcelain crucible and placed in a muffle furnace under N₂ flow at 400 mL min⁻¹ for 30 min to remove air from the system. Thereafter, the mixture in the muffle furnace was pyrolyzed at 550 °C for 1 h under N₂ flow of 200 mL min⁻¹. After the pyrolysis, the resulting biochar products were gently crushed and passed through < 0.12 mm nylon sieve, washed, and oven-dried at 105 °C for 6 h before characterization. Biochar with and without magnesium salt addition were made. For the convenience of discussion, *x*Mg-biochar will be used to express MgO impregnated biochar where *x* represents the specific Mg content in percentage.

2.3. Biochar characterization

Total C, H and N contents in different biochar samples were determined using an elemental analyzer (Elementar Analysensysteme GmbH, Germany), and total Mg content was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SPECTRO Plasma 3200, Germany) after biochar samples were digested using concentrated H_2SO_4 and H_2O_2 at about 300 °C. Dissolved organic carbon (DOC) content was measured by a TOC analyzer (Shimadzu TOC-V) after extracting 1.0 g biochar sample with 20 mL DI water (stirred at 120 rpm for 48h) and filtered using a 0.22 μm nylon membrane filter (GE cellulose nylon membrane). The BET surface area (S_{BET}), total pore volume (V_{tot}) and pore size distribution of the biochar samples were evaluated based on N_2 adsorption at 77 K using a V-Sorb 2800P analyzer (App-one, China). The microscopic features and morphology were characterized using a field emission gun scanning electron microscopy (FEG-SEM, JEOL 6335F, Japan) equipped with an energy-dispersive X-ray (EDX) spectroscopy and a transmission electron microscopy (JEOL 200CX TEM, Japan). X-ray diffraction (XRD) analysis was also carried out to identify any crystallographic structure in the samples using a computer-controlled X-ray diffractometer (Philips Electronic Instruments). In addition, Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS, Kratos, UK) were carried out to characterize surface interactions of biochar samples before and after surface loadings of solutes.

2.4. Adsorption performance tests

The optimization of Mg addition on the adsorption of Mg-biochar composite was investigated with phosphate, ammonium and organic substance solutions. Due to the fact that natural water and wastewater contains various dissolved organic substances that makes it

difficult to identify all existing ones, water solution containing dissolved organic matter was prepared from sodium humate as described by Delgado-Moreno et al. (2015). It should be noted that the DOC content of biochar samples used in this study was less than 0.20 mg/L. Therefore for evaluation of humate adsorption, the dissolved organic matter content of biochar samples was neglected. In doing so, 0.05 g biochar sorbent samples were mixed with a series of 40 mL solutions containing 50 mg/L of phosphate, ammonium or humate, respectively, in centrifuge tubes on a shaker platform operating at 120 rpm for 24 h under room temperature (22.5 ± 0.2 °C). After 24 h shaking, the supernatants were filtered through 0.22 μ m nylon membrane filters (GE cellulose nylon membrane) and analyzed with the standard methods (APHA, 1998). Phosphate was analyzed by using a spectrophotometer (Thermo Scientific EVO 60) at wavelength of 880 nm, ammonium content was determined by a segmented flow analyzer (Technicon Autoanalyzer II System, Germany), and humate concentrations in the supernatants were quantified by an automated TOC analyzer (Shimadzu TOC-V). Adsorption experiments were performed over an initial pH range of 4.0 to 10.0, and adsorption isotherms were conducted with varying initial concentrations of phosphate (as phosphorus at 1 ~ 500 mg/L), ammonium (5~200 mg/L) and humate (5~1000 mg/L). Adsorption kinetics of phosphate, ammonium and humate on the Mg-biochar composite were evaluated by mixing a series of 0.5 g 20 % Mg biochar with 400 mL phosphate solution (pH 4.03, 50 mg/L phosphorus), 400 mL ammonium solution (pH 7.05, 50 mg/L) and 400 mL humate solution (pH 7.83, 50 mg/L) in plastic bottles. The mixtures were magnetically stirred at 120 rpm at room temperature. At selected time intervals, aliquots of the mixtures were collected, filtered, and analyzed. All adsorption experiments were triplicated.

Langmuir and Freundlich isotherm models were used to simulate the adsorption isotherm experimental data. Two isotherm models were used to simulate the experimental data and the governing equations can be written as equation (1) and (2) (Li et al., 2016).

$$\text{Langmuir model, } q_e = KQC_e/(1+KC_e) \quad (1)$$

$$\text{Freundlich model, } q_e = K_f C_e^{1/n} \quad (2)$$

Where q_e is the equilibrium adsorption capacity (mg/g), K and K_f represent the Langmuir bonding term related to interaction energies (L/mg) and the Freundlich affinity coefficient ($\text{mg}^{(1-n)}\text{L}^n \text{g}^{-1}$), respectively, Q denotes the Langmuir maximum capacity (mg/g), C_e is the equilibrium solution concentration (mg/L) of the sorbate, and n is the Freundlich linearity constant.

Pseudo-first-order and pseudo-second-order kinetic and intra-particle diffusion models (Lalley et al., 2016) as expressed in equation (3) - (5) were used to fit the adsorption kinetics experiment data, respectively.

$$\text{Pseudo-first-order kinetic model, } \ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\text{Pseudo-second-order kinetic model, } t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (4)$$

$$\text{Intra-particle diffusion model, } q_t = k_p t^{1/2} + C \quad (5)$$

Where k_1 and k_2 are the first-order and second-order apparent adsorption rate constants (1/h and g/mg/h), respectively. k_p is the intra-particle diffusion rate constant ($\text{mg/g/h}^{1/2}$), C is related to the thickness of the boundary layer. q_t and q_e are the amount of sorbate sorbed (mg/g) at time t and at equilibrium, respectively.

The effects of coexisting substances on phosphate, ammonium and humate adsorption were evaluated by mixing 0.05 g 20% Mg-biochar composite with 40mL solutions containing 50 mg/L phosphorus (pH 4.01), 50 mg/L ammonium (pH 7.05), 50 mg/L humate (pH 7.83) , and

equal concentrations of coexisting ions (cations and anions) in polyethylene centrifuge tubes. Solution without co-existing ions was used as blank test. After overnight equilibration, the mixture was filtered through a 0.22 μm GE cellulose nylon membrane filter, and then analyzed for phosphate, ammonium and humate concentrations.

For evaluating treatment potential of swine wastewater, adsorption experiment was carried out by mixing 0.25 g biochar adsorbent with 200 mL of swine wastewater in a 250 mL glass flask and shaking for 24 h using similar procedure as described previously. The experiment was repeated three times. After adsorption was complete, the mixtures were filtered and the filtrates were analyzed for phosphate, ammonium and humate according to the methods described previously. The pH of filtrate solutions was measured. The loaded (used) biochar adsorbent samples were separated and washed by 10 mL DI water, followed by drying at 105 $^{\circ}\text{C}$ for 6 h before characterization.

3. Results and Discussion

3.1. Composition and structure of the MgO particle–impregnated porous biochar

Detailed final Mg contents and elemental composition of prepared biochar samples with corresponding initial MgCl_2 concentrations can be found in Table 1. Elemental analysis showed a generally increasing Mg content with decreasing C content as initial Mg salt was added, implying that there was a blend of C and Mg in these samples (Li et al., 2016). The XRD analysis (Fig.1a) revealed that raw biochar without Mg addition was dominated with a broad diffraction peak at 2 theta of 23.0° , which is attributed to the cellulose (002) crystal plane (Liu et al., 2013). In the Mg–biochar samples with elevating Mg percentage, the XRD pattern displayed increasing intensity of typical reflections of the MgO with five diffraction peaks at 2 theta

around 37.1° , 43.1° , 62.5° , 74.7° and 78.6° , which can be attributed to the (111), (200), (220), (311), and (222) lattice planes of MgO (Fig. 1a), respectively, indicating the formation of MgO crystallite during the slow pyrolysis process (Liu et al., 2013). In addition, Mg–biochar displayed gradually increasing diffraction peaks at 2θ 25.8° and 53.5° , which are attributed to the (002) and (004) lattice planes of carbon nanotube in the biochar (Jagannatham et al., 2015). These results suggest that during the pyrolysis process at 550°C , the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ underwent a drastic dehydration process to form MgO while sugarcane residue turned into solid carbonaceous particles.

Salts such as FeCl_3 , ZnCl_2 and MgCl_2 have been used as activating agents in the carbon preparation in order to produce more pores (Liu et al., 2013). In this study, with elevating Mg level, biochar pore sizes and volume increased significantly (Table 1), especially at 15–20% Mg, which likely corresponded to the emergence of carbon nanotube–like pore structure in the Mg–biochar (Fig. 1a). The average pore size (AVP) enlarged from 2.35 nm in 2% Mg–biochar to 22.38 nm in 20% Mg–biochar (Table 1). Li et al. (2014) also observed the pore diameter increase with kaolin addition in the rice straw biochar preparation, while CaCO_3 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ addition had no effects on the pore variation but increased C content of the biochar. Other researchers also found that exogenous salts such as KCl and K_2CO_3 additions in the biochar production increased C content of charcoal products as well (Jensen et al., 1998; Wang et al., 2012). Besides the increase in pore volume, effect of MgCl_2 addition on C content enhancing was not observed in our study. This could be explained by the fact that different salts and minerals have different thermal properties which affect their interaction with the carbonation process during pyrolysis and consequently influence the outcomes of pore generation and C preservation in the biochars (Li et al., 2014). For example, it is known that at a pyrolysis temperature around

550 °C, FeCl_3 , ZnCl_2 and MgCl_2 could decompose to metal oxides and release HCl in gas phase (Liu et al., 2013), while the salts like KCl, K_2CO_3 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaCO_3 etc. could not at this temperature (Li et al., 2014).

The clear difference in the surface morphology between the original raw biochar (without Mg salt pretreatment) and the Mg-biochar could be observed by SEM analysis. Compared with the raw biochar (Fig. 1b and Fig. 1c), SEM images clearly showed that MgO particles were deposited on the biochar surface or within the matrix of the 20% Mg biochar (Fig. 1d and Fig. 1e). The EDX spectrum mapping revealed a uniform C distribution, whereas Mg was closely associated with O distribution in the same Mg-containing biochar (Fig. 2a~2d). The small peaks for Si, K, and Ca elements were also found in the EDX spectrum (Fig. 2e). In addition, the TEM analysis showed that the surface of raw biochar without MgO was generally smooth (Fig.3a), whereas the ultra-fine 20% Mg biochar composite was homogeneously deposited with MgO flakes across the entire substrate and resulted in a rough and flaky morphology (Fig. 3b). The calculated average thickness of MgO flakes ranged from 12 to 28 nm. The TEM images also indicated the existence of carbon nanotube-like pore structures in the 20% Mg-biochar (Fig.3d), which was consistent with the observation of the (002) and (004) lattice planes of carbon nanotube in XRD analysis (Fig.1a), whereas it was absent in the raw biochar without Mg (Fig.3c).

3.2. Effects of Mg content on adsorption

The effects of Mg content on phosphate, humate and ammonium adsorption are illustrated in Fig.4. With increasing Mg content in the MgO biochar composites from 0.44% to 23.07%, ammonium adsorption nearly kept constant (~20 mg/g), whereas phosphate and humate

adsorptions exhibited a strong dependence on Mg content. With MgO impregnation, the Mg-biochar significantly enhanced the affinity for phosphate and humate with more than 660% and 280% increases, respectively, in the amounts of adsorption over the raw biochar without MgO impregnation, which had very low affinity of adsorption (phosphate <5 mg/g, humate < 10 mg/g) (Fig.4). This result was consistent with the findings of the previous studies in which high Mg-containing biochar composites derived from Mg-accumulating tomato tissues (Yao et al., 2013) and MgCl₂ solution soaked brown marine macroalgae (Jung and Ahn, 2016) showed strong affinity for aqueous phosphate. This result was also in agreement with the reports in which MgO modified diatomite (Xia et al., 2016) and lanthanum assisted oak sawdust biochar exhibited strong affinity for aqueous phosphate (Wang et al., 2015). Our study clearly indicates that increasing Mg content in the Mg-biochar composite facilitate much greater percentage of phosphate and humate removal from aqueous solution. The highest phosphate and humate removal (> 99.1%) were observed in the 20% Mg-biochar, indicating the optimization of phosphate and humate adsorption with MgO impregnation.

3.3 Adsorption isotherms and kinetics.

Because the higher phosphate and humate removal (> 99%) were observed in the 20% Mg-biochar, it was selected as the adsorbent in subsequent adsorption isotherm evaluations. The phosphate, ammonium and humate adsorption isotherms of 20% Mg-biochar are given in Fig. 5a. It is evident that with the increasing initial phosphate, ammonium and humate concentrations, the adsorption amounts were increased dramatically and then reached equilibrium gradually. The 20% Mg-biochar showed stronger affinity for phosphate and humate than for ammonium. Further data modeling indicated that the Langmuir model described the sorption process better than the Freundlich model, with R^2 values ranging from 0.9886 to 0.9992 for phosphate,

ammonium and humate (Table 2). For the 20% Mg-biochar, maximum adsorption capacities were 398 mg/g for phosphate, 247 mg/g for humate, and 22 mg/g for ammonium. These adsorption capacities were much higher than most of the reported adsorbents. For example, the maximum phosphate adsorption capacity of the 20% Mg-biochar was more than 1.5-398 times greater than 1.24 mg/g, 1.0 mg/g, 250 mg/g, 160.94 mg/g, and 135.03 mg/g reported for magnetic orange peel biochar (Chen et al., 2011), lodgepole pine wood biochar (Huggins et al., 2016), Mg/Al- LDHs sugarcane biochar (Li et al., 2016), MgO loaded diatomite (Xia et al., 2016), and AlOOH-impregnated cottonwood biochar (Zhang and Gao, 2013) , respectively. It was also more than 5 times greater than 70 mg/g reported for the maximum adsorption capacity of organic substances by lodgepole pine wood biochar (Huggins et al., 2016).

Adsorption kinetics is one of the most important factors in evaluating the efficiency of an adsorbent. The phosphate, ammonium and humate adsorption by 20% Mg-biochar composite as a function of time are presented in Fig. 5b. It is clear that initially phosphate adsorption was fast followed by a relatively slow adsorption, which is similar to other studies (Li et al., 2016; Xia et al., 2016). The phosphate adsorption increased with extended contact time, and more than 99% phosphate was removed within 1h. The initial rapid adsorption might be due to the electrostatic attraction between the positive charged magnesium oxide surfaces and the negative charged phosphate ions (Huang et al., 2016; Li et al., 2016). The kinetic data of phosphate adsorption was further fitted with pseudo-first-order, pseudo-second-order kinetic model and intra-particle diffusion model. The obtained kinetic model parameters indicated that the phosphate adsorption was better described by the pseudo-second-order kinetic model with the greatest correlation coefficient (R^2) among the three models (Table 3). The pseudo-second-order model assumes a monolayer adsorption system and the mechanism of adsorption may be determined by

chemisorption (Lalley et al., 2016). On the other hand, humate and ammonium adsorptions took longer time and reached the equilibrium at about 8 h and 4h, respectively. The fact that the relatively slow adsorption exhibited by humate and ammonium and their best fit using the intra-particle diffusion model indicated that intra-particle diffusion mechanism may be involved since the process of pore diffusion is typically slow and rate-determining (Lalley et al., 2016). The slow phase of humate and ammonium adsorption was perhaps associated with the pore network and surface of the biochar, which helps the dispersion of MgO flakes to efficiently interact with humate and ammonium. The latter could allow humate and ammonium ion pass through pores or interstices of the 20% Mg-biochar composite surface, and further comes into the negative charged carbon matrix by a combined process of intra-particle diffusion and film diffusion.

3.4. Effect of solution pH and coexisting substances on adsorption.

pH is a critical factor that influences the adsorption ability of an adsorbent in solution. The effects of solution pH on phosphate, ammonium and humate adsorption and the relation to the resulting final pH after adsorption are shown in Fig.6a. As expected, the phosphate sorption capacity decreased with the solution pH increasing from 4.0 to 10.0, likely responding to the diminishing of positive charges by MgO impregnation of the biochar surface. And at pH 4.0, nearly all phosphate was adsorbed by 20% Mg-biochar. Different from phosphate, the humate adsorption capacity slightly increased with pH rise and remained more or less constant (~ 40 mg/g) at pH above 5.5. This suggests that humate did not respond to the surface charge change of the biochar. Instead, the pH rise facilitated the strong interaction with the Mg-biochar matrix, which could be due to better dispersion of a more linear physical form of humate that tends to exist at high pH (Ghosh and Schnitzer, 1980). Thus, the Mg-biochar can be used as an efficient adsorbent for humate removal at relatively higher pH values. Han et al. (2015) also found KOH

activated peanut shell biochar could effectively remove organic pollutants from aqueous solutions. Obviously, the ammonium adsorption capacity was increased when the pH rose to 7.0 and remained more or less constant (~ 21 mg/g) at pH 7.0 – 8.5, suggesting that ammonium was responding to the diminishing positively charged Mg-biochar surface. Only after pH above 8.5, the ammonium adsorption capacity decreased dramatically from around 21 mg/g to 2.2 mg/g (pH 10.02), which was likely due to the gaseous loss of NH_4^+ as NH_3 at high pH. The result was in accordance to the findings reported by Xia et al. (2016), who used MgO-loaded diatomite as an adsorbent for ammonium removal.

After adsorption, all solution final pHs were around 9.6 to 10.4 (Fig.6b) indicating that the MgO surface was still positively charged, which could be caused by the positive charge development following biochar surface protonation of MgO (Li et al., 2016). This reaction can be simply described as $\equiv\text{MgO} + \text{H}_2\text{O} \rightarrow \equiv\text{MgOH}^+ + \text{OH}^-$, resulting an alkaline pH in solution. In this study, the initial phosphate solution pH was maintained in the range of 4.0 ~ 10.0 with the negatively charged H_2PO_4^- and HPO_4^{2-} as the main species (Li et al., 2016). The MgO on the biochar surface was expected to be positively charged under the experimental aqueous conditions, due to the point of zero charge (PZC) of MgO at around 12 (Parks and Bruyn, 1962) and to exhibit strong affinity for negatively charged phosphate at lower pH values (Fig.6a). Although in view electrostatic attraction, the positive surface of the adsorbent might not favor the positive ammonium adsorption, the ammonium adsorption capacity remained acceptable at pH 7.0 – 8.5, which probably indicated that the phosphate and ammonium adsorptions were controlled by different processes. In consideration of removal efficiency and operational feasibility, the initial pH of 4.0, 7.0 and 10.0 were selected for the investigation of co-existing substances on phosphate, ammonium and humate adsorption.

Various cations and anions that normally coexist in wastewater would interfere with the removal of phosphate, ammonium and humate by 20% Mg-biochar through competing adsorption. The influences of the potential presence of coexisting substances were evaluated and the results are given in Fig. 6c. Comparing with the blank, the existence of Cl^- , NO_3^- , SO_4^{2-} , K^+ , Na^+ and Ca^{2+} ions had no effect on humate adsorption. Similarly, the presence of Cl^- , NO_3^- , K^+ and Na^+ ions did not influence phosphate adsorption removal by 20% Mg-biochar. On the other hand, SO_4^{2-} led a slight decrease of phosphate removal, while Ca^{2+} promoted phosphate sorption slightly. This could be explained by the fact that Ca^{2+} could react with phosphate to form amorphous calcium phosphate (Karapinar 2009). And the presence of SO_4^{2-} could compete for the positively charged site of the adsorbent surface due to similar ionic radii of SO_4^{2-} (0.230 nm) and H_2PO_4^- (0.238 nm) (Li et al., 2016). In addition, anions such as SO_4^{2-} , Cl^- and NO_3^- showed no effect on the ammonium adsorption, whereas the presence of equal concentration of cations (K^+ , Na^+ and Ca^{2+}) in solution would compete with ammonium leading to a remarkable decreased ammonium removal rate from 48.85% to 32.53%.

3.5. The efficacy of 20% Mg-biochar on swine wastewater treatment and sustainable benefits.

The adsorption performances of phosphate, ammonium and COD onto 20% Mg-biochar composite in treating swine wastewater are presented in Fig. 7. Nearly 100% phosphate, 25.77% ammonium and 20.96% COD were removed from the swine wastewater, and the wastewater was significantly clarified (Fig. 7). These results suggest that 20% Mg-biochar composite has great potential to be used for adsorption removal of phosphate, ammonium and dissolved organic substances from swine wastewater. Besides treating livestock wastewater, it also could be used for phosphate and ammonium recovery from nutrient-rich surface waterbodies. It should be pointed that it is very attractive from both environmental and economic aspects to use the MgO-

impregnated porous biochar derived from the pyrolysis of MgCl_2 preloaded agricultural biomass residue for contamination control. The low-cost agricultural biomass residue is readily available and could be obtained with large quantity through local agricultural processes. The chemical reagent MgCl_2 also could be easily obtained since the resource is abundant in the world, for example, from seawater, which contains huge amounts of easily available MgCl_2 . On the other hand, while agricultural biomass wastes are readily available from local agricultural processes, many parts of the world still perform random and open-field burning of these biomass materials for various reasons, which cause significant resource losses and air quality concerns (Jeong et al., 2016). Therefore, the thermal conversion of these biomass wastes into useful products as MgO impregnated porous biochar not only leads to the alleviation in CO_2 emission due to open field burning but also improves the agricultural solid waste disposal (Jeong et al., 2016; Zhang and Wang, 2016). In addition, the fact that MgO impregnated porous biochar exhibits strong affinity for phosphate and its ability to “clarify” the livestock wastewater by simultaneous recovery of phosphate, ammonium and organic substance suggests its potential use as a fertilizer to be applied to soil for agricultural crop production. The latter has great importance in resource conservation, nutrient cycling, and sustainable development of the environment.

3.6. Mechanisms on the 20% Mg-biochar treatment of swine wastewater.

In order to elucidate the adsorption mechanism in this study, the surface morphology of the 20% Mg -biochar composite after swine wastewater treatment was compared with that of the original 20% Mg -biochar composite (Fig. 8). It can be clearly seen from the SEM images that the ultra-fine MgO flakes disappeared and some new solids appeared meanwhile after the composite was utilized for swine wastewater treatment (Fig. 8a). The EDX spectrum analysis further proved the presence of N and P elements in the solid particles of the 20% Mg -biochar composite

after swine wastewater treatment (Fig. 8b). The XRD analysis showed spectral peaks of not only the preexisting Mg oxides but also the new crystal with a series of strong signals at 15.04(110), 15.85(020), 16.50(011), 20.91(111), 21.50(021), 27.13(130), 30.66(211), 31.97(040) and 33.29(022) after the 20% Mg biochar composite was treated with swine wastewater (Fig. 8c). These signals are consistent with $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ crystal structure (JCPDS 15-762), which confirmed the formation of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) on the MgO-biochar composite surface. The dissolving MgO at the composite surface likely served as the seeding place where struvite grows. Therefore, in swine wastewater, the following reactions may be involved at the composite surface:

It is well known that the alkali environment (pH 8–10) is suitable for the precipitation of struvite (Zhang and Wang, 2016). In this study, the reactions among ammonium, phosphate ions and the MgO particles on carbon surfaces within the biochar matrix, which result in the formation of struvite crystals, were consistent with the observed final solution pH range between 8.49 and 9.92 (Fig. 6b). It should be pointed out that in view of the struvite formation reaction, ammonium and phosphate ions would be expected to have equal stoichiometric ratios in struvite. In this study, however, the maximum amounts of adsorbed ammonium and phosphate ions were found not in agreement with the 1:1 molar ratio, rather more ammonium (~ 6 mmol) adsorbed than phosphate (~ 4 mmol) per gram of biochar. This result could indicate that ammonium adsorption was not only governed by the struvite formation but probably also controlled by other processes, which could be the electrostatic attraction between positive ammonium ion and the inner negatively charged biochar carbon surface. The later was inferred from the result in that

ammonium adsorption kinetic process was consistent with the intra-particle diffusion model (Table 3).

It is well known that the mechanism responsible for the significant adsorption increase of dissolved organic substances by carbon adsorbent was mainly attributed to the appearance of porous carbon structure, since the more the developed porous structure in a carbon adsorbent surface the more the dissolved organic substances were adsorbed (Parker et al., 2012). The FTIR spectra of 20% Mg-biochar before and after reacting with swine wastewater are shown in Fig. 8d. The bands at 3438 cm^{-1} and 1662 cm^{-1} are due to -OH stretching vibration of hydroxyl groups or adsorbed water (Leng et al., 2015), and the peaks at 3580 cm^{-1} and 3743 cm^{-1} are stretching vibration of Mg-OH (Lichtenberger et al., 2016). The peaks around $2926\sim 2948\text{ cm}^{-1}$ are related to the C-H bond vibration (Wu et al., 2011). The benzene ring C=C stretching peaks at 1560 cm^{-1} indicate the existence of aromatization substance (Leng et al., 2015). The peaks around 1370 cm^{-1} and 1050 cm^{-1} are assigned to N=C double bond stretching vibration and N-C single bond stretching vibration, whereas the peak at 1129 cm^{-1} is related to the -CH_3 group symmetry vibration and the signals located at $695\sim 887\text{ cm}^{-1}$ are assigned to the $\text{-CH}_2\text{-}$ and C=C-H bond stretching vibrations (El-Qanni et al., 2016). Further, the peak around 500 cm^{-1} is assigned to the Mg-O bond stretching vibration (Xia et al., 2016). After adsorption, the FTIR spectrum of the used 20% Mg-biochar showed some drastic differences as compared to that of the original 20% Mg-biochar. The strengthening of peaks at 3438 cm^{-1} , 1560 cm^{-1} , 887 cm^{-1} and 793 cm^{-1} , the appearance of peaks at 2948 cm^{-1} , 1444 cm^{-1} and 1129 cm^{-1} as well as the decrease in the peak at 500 cm^{-1} could well define the pollutant adsorption from swine wastewater by the 20% Mg-biochar. The strong peaks located at 1444 cm^{-1} and 1002 cm^{-1} (overlapped the peak at 1050 cm^{-1}) indicate the adsorption of ammonium and phosphate,

respectively. The shifting of the aliphatic C–H asymmetric stretching vibration peaks at 2926 cm^{-1} to 2948 cm^{-1} , and the benzene ring C=C stretching peak at 1560 cm^{-1} to 1585 cm^{-1} suggest the involvement of π – π interaction during the adsorption of dissolved organic substances (Chen et al., 2011). While the π – π interaction with the increased porosity on biochar matrix by MgO impregnation might be the primary mechanism for the adsorption of dissolved organic substances in swine wastewater, it is important to state that the biochar carbon matrix surfaces were masked by MgO impregnation in this study. Therefore, based on the result from the kinetic study, it can be postulated that dissolved organic substance molecules in swine wastewater pass through the pores or interstices of the 20% Mg biochar composite surface, and further come into the carbon matrix by a combined intra-particle diffusion and film diffusion process with the driving force of π – π interaction. Based on the evidence presented in this paper, three mechanisms that control the adsorption of phosphate, ammonium and organic substance from swine wastewater by 20% Mg-biochar composite may be proposed and they are illustrated in scheme 1.

3.7. Future work

It is interesting to note relatively higher ammonium:phosphate molar ratio (3:2) than the 1:1 molar ratio that would be expected for the ideal formation of struvite [$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O (s)}$] and the evidence of adsorption kinetics pointing to the intra-particle diffusion of at least partial NH_4^+ followed by possibly electrostatic interaction with biochar C matrix. Since increasing Mg level in biochar matrix affects little on amount of ammonium adsorption (Fig. 4) and the struvite formation is more used to target the recovery of phosphate rather than ammonium, our result suggests preferred benefits of using MgO impregnated biochar to recover more NH_4^+ -N through both struvite formation and biochar matrix ammonium adsorption in treating livestock wastewater over direct application of Mg salts. Future work is needed to evaluate the

bioavailability of these captured ammonium and phosphate to plants in soil application. In addition, other co-adsorbed or co-precipitated nutrients or pollutants captured by MgO impregnated biochar during the livestock wastewater treatment process need to be examined in order to further best utilize this innovative product.

4. Conclusions

MgO-impregnated porous biochar composite was prepared by MgCl_2 adsorption followed by a carbonization process, optimized and employed as an adsorbent for the removal of phosphate, ammonium and organic substances from swine wastewater solution. The optimized composite, 20% Mg-biochar, exhibited strong affinity for phosphate, ammonium and organic matter with maximum capacities of 398 mg/g, 22 mg/g and 247 mg/g, respectively. The phosphate adsorption fitted the pseudo-second-order kinetic model, while ammonium and humate adsorptions were best described by intra-particle diffusion model. The co-existing ions have no impacts on humate adsorption, but the presence of SO_4^{2-} and Ca^{2+} affect the phosphate adsorption, and the presence of K^+ , Na^+ and Ca^{2+} ions hinder ammonium capture. The capture mechanism study implicated that the struvite crystallization, electrostatic attraction, and π - π interactions contributed to the swine wastewater treatment process for the removal of phosphate, ammonium and organic substances. The results illustrated that the 20% Mg-biochar could be employed as an effective adsorbent for the simultaneous removal and capture of phosphate, ammonium, and organic substances from nutrient-rich livestock wastewaters. The presented work has significant implications towards cleaner production. The MgO impregnated porous biochar not only could “clarify” the livestock wastewater for potential reuse but also, with simultaneous capture removal of phosphate and ammonium, yield a nutrient-rich product as

potential fertilizer for soil application in agricultural production. In addition, the conversion of readily available agricultural biomass waste reduces agricultural waste disposal as well as minimizes CO₂ emission from otherwise open-field burning of the waste biomass. All these facilitate resource conservation, nutrient cycling, and sustainable development of the environment.

Acknowledgements

This project was funded by USDA–NRCS#69–3A75–10–156 and partly supported by China Fundamental Research Funds for the Central Universities (No.2014YB064).

References

- Agaroti E., Kalderis D., Diamadopoulos E., 2014. Ca and Fe modified biochars as adsorbents of arsenic and chromium in aqueous solutions, *J. Environ. Manag.* 146, 444–450.
- APHA, 1998. Standard methods for the examination of water and wastewater, Nineteenth ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.
- Chen, B., Chen, Z., Lv, S., 2011. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate, *Bioresour. Technol.* 102, 716–723.
- China Ministry of Environmental Protection, First national census on pollution sources. China Government Press; 2010. [February 9, 2010].
- Delgadillo-Mirquez, L., Lopes, F., Taidi, B., Pareau, D., 2016. Nitrogen and phosphate removal from wastewater with a mixed microalgae and bacteria culture, *Biotechnology Reports*, 11, 18–26.

- El-Qanni, A., Nassar, N.N., Vitale, G., Hassan, A., 2016. Maghemite nanosorbents for methylene blue adsorption and subsequent catalytic thermo-oxidative decomposition: Computational modeling and thermodynamics studies, *J. Colloid Interf. Sci.* 461, 396–408.
- Escudero, A., Blanco, F., Lacalle, A., Pinto, M., 2015. Struvite precipitation for ammonium removal from anaerobically treated effluents, *J. Environ. Chem. Eng.* 3, 413–419.
- Farhad, M., Mohsen, J., 2016. Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions, *J. Environ. Chem. Eng.* 4, 1664–1673.
- Ghosh, K., Schnitzer, M., 1980. Macromolecular structure of humic substances. *Soil Sci.* 129, 266–276.
- Han, X., Chu, L., Liu, S., Chen, T., Ding, C., Yan, J., Cui, L., Quan, G., 2015. Removal of methylene blue from aqueous solution using porous biochar obtained by KOH activation of peanut shell biochar, *BioResources*. 10, 2836–2849.
- Huang, H., Zhang, P., Zhang, Z., Liu, J., Xiao, J., Gao, F., 2016. Simultaneous removal of ammonia nitrogen and recovery of phosphate from swine wastewater by struvite electrochemical precipitation and recycling technology, *J. Clean. Prod.* 127, 302–310.
- Huggins, T.M., Haeger, A., Biffinger, J.C., Ren, Z.J., 2016. Granular biochar compared with activated carbon for wastewater treatment and resource recovery, *Water Res.* 94, 225–232.
- Jagannatham, M., Sankaran, S., Prathap, H., 2015. Electroless nickel plating of arc discharge synthesized carbon nanotubes for metal matrix composites, *Appl. Surf. Sci.* 324, 475–481.
- Jensen, A., Dam-Johansen, K., Wojtowicz, M.A., Serio, M.A., 1998. TG-FTIR study of the influence of potassium chloride on wheat straw pyrolysis, *Energy Fuels*. 12, 929–938.
- Jeong, C.Y., Dodla, S.K., Wang, J.J., 2016. Fundamental and molecular composition characteristics of biochar produced from sugarcane and rice crop residues and by-products, *Chemosphere* 142, 4–13.
- Jeong, C.Y., Wang, J.J., Dodla, S.K., 2012. Effect of biochar amendment on tylosin adsorption/desorption and transport in two different soils, *J. Environ. Qual.* 41, 1185–1192.

- Jung, K., Ahn, K., 2016. Fabrication of porosity-enhanced MgO/biochar for removal of phosphate from aqueous solution: Application of a novel combined electrochemical modification method, *Bioresour. Technol.* 200, 1029–1032.
- Karapinar, N., 2009. Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions, *J. Hazard. Mater.* 170, 1186–1191.
- Kizito, S., Wu, S.B., Kirui, W.K., Lei, M., Lu, Q.M., Bah, H., Dong, R.J., 2015. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery manure anaerobic digestate slurry. *Sci. Total Environ.* 505, 102–112.
- Lalley, J., Han, C., Li, X., Dionysiou, D.D., Nadagouda, M.N., 2016. Phosphate adsorption using modified iron oxide-based sorbents in lake water: Kinetics, equilibrium, and column tests, *Chem. Eng. J.* 284, 1386–1396.
- Leng, L., Yuan, X., Zeng, G., Shao, J., Chen, X., Wu, Z., Wang, H., Peng, X., 2015. Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption, *Fuel.* 155, 77–85.
- Li, F., Cao, X., Zhao, L., Wang, J., Ding, Z., 2014. Effects of mineral additives on biochar formation: carbon retention, stability, and properties, *Environ. Sci. Technol.* 48(2014)11211–11217.
- Li, R., Wang, J.J., Zhang, Z., Shen, F., Zhang, G., Qin, R., Li, X., Xiao, R., 2012. Nutrient transformations during composting of pig manure with bentonite, *Bioresour. Technol.* 121, 362–368.
- Li, R., Wang, J.J., Zhou, B., Awasthi, M.K., Ali, A., Zhang, Z., Gaston, L.A., Lahori, A.H., Mahar, A., 2016. Enhancing phosphate adsorption by Mg/Al layered double hydroxide functionalized biochar with different Mg/Al ratios, *Sci. Total Environ.* 559, 121–129.
- Lichtenberger, J., Hargrove-Leak, S.C., Amiridis, M.D., 2006. In situ FTIR study of the adsorption and reaction of 2'-hydroxyacetophenone and benzaldehyde on MgO, *J. Catal.* 238, 165–176.

- Liu, J., Su, Y., Li, Q., Yue, Q.Y., Gao, B.Y., 2013. Preparation of wheat straw based superabsorbent resins and their applications as adsorbents for ammonium and phosphate removal, *Bioresour. Technol.* 143, 32–39.
- Liu, W., Jiang, H., Tian, K., Ding, Y., Yu, H., 2013. Mesoporous carbon stabilized MgO nanoparticles synthesized by pyrolysis of MgCl_2 preloaded waste biomass for highly efficient CO_2 capture, *Environ. Sci. Technol.* 47, 9397–9403.
- Parker, H.L., Hunt, A.J., Budarin, V.L., Shuttleworth, P.S., Miller, K.L., Clark, J.H., 2012. The importance of being porous: polysaccharide-derived mesoporous materials for use in dye adsorption, *RSC Adv.* 24, 8992–8997.
- Parks, G.A., Bruyn, P.L.D., 1962. The zero point of charge of oxides, *J. Phys. Chem.* 66, 967–973.
- Romero-Güiza, M.S., Tait, S., Astals, S., del Valle-Zermeño, R., Martínez, M., Mata-Alvarez, J., Chimenos, J.M., 2015. Reagent use efficiency with removal of nitrogen from pig slurry via struvite: a study on magnesium oxide and related by-products, *Water Res.* 84, 286–294.
- Tan, X., Liu, Y., Zeng, G., Wang X., Hu, X., Gu, Y., Yang, Z., 2015. Application of biochar for the removal of pollutants from aqueous solutions, *Chemosphere*. 125, 70–85.
- Tao, W., Fattah, K.P., Huchzermeier, M.P., 2016. Struvite recovery from anaerobically digested dairy manure: A review of application potential and hindrances, *J. Environ. Manage.* 169, 46–57.
- Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., Wang, L., Xiao, H., Deng, S., 2015. Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH_4^+), nitrate (NO_3^-), and phosphate (PO_4^{3-}), *Chemosphere* 119, 646–653.
- Wang, Z., Wang, F., Cao, J., Wang, J., 2012. Pyrolysis of pine wood in a slowly heating fixed-bed reactor: Potassium carbonate versus calcium hydroxide as a catalyst, *Fuel Process. Technol.* 91, 942–950.
- Wu, X., Zhu, W., Zhang, X., Chen, T., Frost, R.L., 2011. Catalytic deposition of nanocarbon onto palygorskite and its adsorption of phenol, *Appl. Clay Sci.* 52, 400–406.

- Xia, P., Wang, X.J., Wang, X., Song, J.K., Wang, H., Zhang, J., Zhao, J.F., 2016. Struvite crystallization combined adsorption of phosphate and ammonium from aqueous solutions by mesoporous MgO-loaded diatomite, *Colloid. Surf. A: Physicochem. Eng. Asp.* 506, 220–227.
- Yao, Y., Gao, B., Chen, J., Zhang, M., Inyang, M., Li, Y., Alva, A., Yang, L., 2013. Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: Characterization and phosphate removal potential, *Bioresour. Technol.* 138, 8–13.
- Yao, Y., Gao, B., Fang, J., Zhang, M., Chen, H., Zhou, Y., Creamer, A.E., Sun, Y., Yang, L., 2014. Characterization and environmental applications of clay-biochar composites, *Chem. Eng. J.* 242, 136–143.
- Ye, Y.Y., Ngo, H.H., Guo, W.S., Liu, Y.W., Zhang, X.B., Guo, J.B., Ni, B.J., Chang, S.W., Nguyen, D.D., 2016. Insight into biological phosphate recovery from sewage, *Bioresour. Technol.* 218, 874–881.
- Yin, H., Kong, M., 2014. Simultaneous removal of ammonium and phosphate from eutrophic waters using natural calcium-rich attapulgite-based versatile adsorbent, *Desalination*, 351, 128–137.
- Zhang, M., Gao, B., 2013. Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite, *Chem. Eng. J.* 226, 286–292.
- Zhang, J.S., Wang, Q.Q., 2016. Sustainable mechanisms of biochar derived from brewers' spent grain and sewage sludge for ammonia-nitrogen capture, *J. Clean. Prod.* 112, 3927–3934.

Figure Captions

Fig. 1. (a) XRD spectra of biochar samples. (b) and (c) SEM images of raw biochar. (d) and (e) SEM images of 20% Mg-biochar.

Fig. 2. EDX spectrum patterns of 20% Mg-biochar. (a) The selected area of 20% Mg-biochar for EDX analysis. (b) Carbon distribution map. (c) Magnesium distribution map. (d) Oxygen distribution map. (e) Elements content of the selected area in EDX analysis.

Fig. 3. (a) TEM image of raw biochar. (b) TEM image of 20% Mg-biochar. (c) TEM image of carbon substrate in the raw biochar. (d) TEM image of the nanotube structure carbon in 20% Mg-biochar.

Fig. 4. Effects of Mg content on adsorption.

Fig. 5. Adsorption isotherm (a) and kinetics (b).

Fig. 6. (a) Effect of solution pH on adsorption. (b) pH change during adsorption. (c) Impact of co-existing substance on adsorption.

Fig. 7. Potential of 20% Mg-biochar on swine wastewater treatment.

Fig. 8. (a) SEM images of Mg-biochar before and after adsorption, (b) EDX spectra of biochar before and after adsorption, (c) XRD patterns of Mg-biochar before and after adsorption, (c) XRD patterns of Mg-biochar before and after adsorption, (d) FT-IR spectra of Mg-biochar before and after adsorption.

Scheme1. Schematic illustration of the phosphate, ammonium and organic matter adsorption in swine wastewater by 20%Mg biochar.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Scheme 1

Table 1

Table 1. The physiochemical properties of the raw material and biochar

Material	Mg (%)	C (%)	H (%)	N (%)	S_{BET} (m ² /g)	V_{tot} (cm ³ /g)	AVP (nm)
Sugarcane leaves	ND	45.85 ± 0.22	6.16 ± 0.17	0.55 ± 0.02	ND	ND	ND
Biochar	0.44 ± 0.02	66.28 ± 1.68	2.15 ± 0.02	0.90 ± 0.02	27.9	0.038	4.89
2% Mg biochar	2.14 ± 0.17	62.52 ± 0.48	1.54 ± 0.02	1.84 ± 0.05	218.9	0.061	2.35
5% Mg biochar	5.07 ± 0.53	60.11 ± 0.43	1.37 ± 0.03	1.74 ± 0.29	144.2	0.117	3.67
8% Mg biochar	8.72 ± 0.12	47.34 ± 0.89	1.25 ± 0.08	2.12 ± 0.01	100.4	0.122	4.34
15% Mg biochar	14.71 ± 0.03	41.55 ± 0.07	2.32 ± 0.07	2.24 ± 0.00	61.2	0.204	12.20
20% Mg biochar	23.07 ± 2.61	27.17 ± 0.22	2.37 ± 0.06	1.47 ± 0.03	40.6	0.372	22.38

Note: ND means no detection.

Table 2. Isotherm model parameters obtained from adsorption

Adsorbate	Langmuir model			Freundlich model		
	K (L/mg)	Q (mg/g)	R^2	K_f	n	R^2
Phosphate	0.030	398.71	0.9948	14.32	1.64	0.9650
Humate	0.049	247.67	0.9992	13.57	1.88	0.8426
Ammonium	0.018	22.10	0.9886	20.13	5.82	0.8849

Table 3

Table 3. Kinetics model parameters obtained from adsorption.

Kinetics model	Parameters	Phosphate	Humate	Ammonium
Pseudo-first-order	$q_{cal}(g/mg)$	8.72	22.54	51.29
	$k_1 (h^{-1})$	7.14	0.37	1.22
	R^2	0.8675	0.9627	0.8709
Pseudo-second-order	$q_e(g/mg)$	40.04	41.32	35.17
	$k_2(g\ mg^{-1}\ h^{-1})$	1.69	0.046	0.039
	R^2	0.9993	0.9761	0.9682
Intra-particle diffusion	$k_p(mg\ g^{-1}\ h^{-0.5})$	7.21	15.26	23.50
	$C (g/mg)$	29.02	8.31	0.595
	R^2	0.8370	0.9974	0.9984