Ammonia Nitrogen Adsorption using Spent Mushroom Substrate Biochar (SMSB)

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ABSTRACT

The objective of this study is to elucidate sorption mechanism of ammonia-N by Spent Mushroom Substrate Biochar (SMSB), produced from pyrolysis process of Spent Mushroom Substrate (SMS) at 550°C for two hours. Surface functional group, ash contents, and elemental compositions were analysed using Boehm titration, furnace and Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) respectively. Sorption parameters (i.e., sorbent dosage, input ammonia-N concentration, and contact time) were optimised, and the sorption data were analysed using kinetic models (i.e., pseudo-first-order and pseudo-second-order), and isotherm models (i.e., Langmuir, Freundlich, and Dubinin-Radushkevich (D-R)). The surface of SMSB consists of carboxylic (0.3 mmol/g), phenolic (0.5 mmol/g), and basic functional groups (0.2 mmol/g). Sorption of ammonia-N was best described by the pseudo-second-order kinetic model and the Dubinin-Radushkevich (D-R) isotherm model. The D-R sorption capacity for SMSB was 12.6 mg/g, and correlates well with the amount of acid functional groups (i.e., carboxylic and phenolic groups) in SMSB (i.e., 14.4 mg/g). The low Freundlich constant ($n = 0.754$), and low D-R mean free energy per mol of the adsorbate ($E = 4.4$ kJ/mol) indicates a physical sorption process, and ammonia-N binds with acid functional groups through weak forces. The result shows great potential of SMSB for removing ammonia-N in wastewater.

Keywords: Activated carbon, ammonia, ammonium, charcoal, nutrient, sewage wastewater

INTRODUCTION

Sewage wastewater contains ammonia-N due to microbial degradation of nitrogen–rich organic matter such as urine, faeces, and by-products in the industrial effluents. Ammonia-N is a plant nutrient and is the major constituent in fertiliser. Ironically, excessive use of fertiliser has contributed to

high ammonia-N in wastewater, causing eutrophication and harming living organism (Aziz, Adlan, Zahari, & Alias, 2004). An aqueous ammonia concentration of 0.2 mg/L may be hazardous to aquatic organisms (Lin, Chan, Jiang, & Lan, 2007). Moreover, high concentration of ammonia-N decreases the biological treatment performance in a sewage treatment plant from increased algae growth (Bashir, Aziz, Yusoff, & Adlan, 2010). Ammonia-N in sewage wastewater may be recycled by zeolite for fertilising agricultural soils (Saleh, Mahmoud, & Rashad, 2013). However, direct application may cause sedimentation in wastewater treatment plant, incurring additional maintenance cost. Spent Mushroom Substrate (SMS) may be used for adsorbing ammonia-N from wastewater. For every 1 kg production of mushrooms, approximately 5 kg of SMS is produced. Most of the SMS is disposed into landfill or composed as agricultural fertiliser (Finney, Ryu, Sharifi, & Swithenbank, 2009). Studies had examined the potentials of SMS for environmental decontamination, such as treatment for acid mine drainage (Cheong, Das, Roy, & Bhattacharya, 2010), bioremediation, and as a biosorbent (García-Delgado, Yunta, & Eymar, 2015). Spent mushroom compost may be pyrolysed at a low oxygen environment to produce a relatively stable, carbon-rich material called biochar, minimise microbial degradation that releases pollutants from SMS into the environment. Spent mushroom compost is recommended as feedstock for biochar production because it contains carbon-rich sawdust (Liu, Zhang, Li, Feng, & Zhang, 2014).

Partial degradation of cellulosic materials and adding lime in SMS has given it unique chemical and physical properties compared with rubber wood sawdust. In fact, SMS has been converted to biochar and it's sorption for ammonia-N from aqueous system has been reported (Liu et al., 2013). However, the sorption capacity for SMSB and its link to the surface functional groups in SMSB has not been reported. Greater understanding of surface interactions between SMSB and ammonia-N may provide more information for possible application of SMSB for recycling ammonia-N from wastewater streams. This study aims to (i) determine the elemental composition and surface functional groups in SMSB; (ii) optimise the sorption parameters (i.e., sorbent dosage, contact time, and input ammonia-N concentration) on sorption capacity of ammonia-N by SMSB; (iii) elucidate the ammonia-N sorption mechanism by SMSB.

MATERIALS AND METHOD

Spent mushroom substrate was autoclaved, oven-dried at 105°C for one week, and sieved to 710 µm using a 25-mesh screen. The dried SMS was pyrolysed at 550°C, 2 hours, and at nitrogen atmosphere to produce SMSB. Inorganic ash component in SMSB was eliminated by agitation with 0.05 M HCl, deionised water, and 0.05 M $CaCl_2$ solution (Chen, Zhou, & Lin, 2015). Then, SMSB was oven-dried again at 105°C for 24 hours, and sieved using a 25-mesh screen. All sieved SMSB was stored in an air-tight container containing anhydrous calcium chloride.

A proximate analysis was conducted to determine the contents of moisture, ash, and fixed carbon for SMSB through gravimetric approach. The moisture in SMS samples (0.05 g) was removed by drying them in an oven at 105°C for 24 hours. The dried SMS samples were then

combusted in the furnace at 600°C for 6 hours to produce ash. The dried SMS and its ash was cooled in a desiccator for about one hour before being weighed with a calibrated analytical balance. Fixed carbon was determined from the yield of SMSB. The volatile matter for SMSB was determined by the difference of the initial weight for SMS, and with the weights of moisture, ash and fixed carbon. The pH value, compositions of elements and surface functional groups were determined on SMSB. Elemental analyses were conducted using the carbon-hydrogen-nitrogen-oxygen (CHNO) elemental analyser, and inductively coupled plasma-optical emission spectroscopy (ICP-OES). For analysis using ICP-OES, 0.05 g of ash samples from SMS and SMSB were digested in 1 mL of 37% HCl and 7 mL of 65% HNO_3 at 200°C for an hour. The digested mixture was then filtered, diluted and analysed for various metal contents (Ca, Cd, Cr, Cu, K, Mg, Mn, Pb and Zn). The surface functional groups for SMSB was determined using method described elsewhere (Boehm, 2008).

Ammonia-N stock solution (1000 mg/L) was prepared by dissolving 1.908 g ammonium chloride (NH_4Cl) in 500 mL of deionised water. The initial ammonia-N concentration for all sorption experiments (except for sorption isotherm) is 50 mg/L. Initial solution pH for all sorption experiment was 6.2. For optimisation of sorbent dosage, SMSB samples at various weights were added to 50 mL of ammonia-N solution to make 0.5, 1.0, 2.0, 5.0 g/L in sorbent dosage, and agitated for 120 minutes. Sorption kinetics experiment was conducted at 1.0 g/L of SMSB dosage, and sorption data was collected at seven contact times (i.e., 10, 20, 30, 40, 50, 60 and 70 minutes). For sorption isotherm experiment, SMSB samples were agitated with ammonia-N solutions at various ammonia-N concentration (i.e., 2.6, 11, 32, 55, 78 mg/L), 1.0 g/L sorbent dosage, and 60 minutes contact time. The mixtures of SMSB and ammonia-N solutions were sealed in conical flasks and agitated with an orbital shaker at 150 rpm. The mixtures were centrifuged, and the supernatants were filtered with 0.45 µm syringe filters. The pH values for ammonia solution were recorded using a calibrated pH meter before and after contact with SMSB. The residual ammonia-N in the solution was determined via calorimetric method using Nessler's reagent. Ammonia-N removal percentage (%) and sorption capacity, q_t (mg/g) for SMSB were calculated using Eq [1] and Eq [2], respectively. All sorption data was analysed with linearised kinetic models (i.e., pseudo-first-order & pseudo-second-order) and isotherm models (i.e., Langmuir, Freundlich, D-R) (Table 1).

$$\mathrm{Re}\,moval\% = \frac{\left[NH_3\right]_i - \left[NH_3\right]_f}{\left[NH_3\right]_i} \times 100 \qquad [1]$$

$$q_t = \frac{\left[NH_3\right]_i - \left[NH_3\right]_f}{m_{SMSB}} \times V_{NH3} \qquad [2]$$

Table 1
Linearised kinetic models (pseudo-first-order & pseudo-second-order) and isotherm models (Langmuir, Freundlich and D-R)

Kinetic/isotherm models	Linearized equation
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \dfrac{k_1 t}{2.303}$
Pseudo-second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \left(\dfrac{1}{q_e}\right) t$
Langmuir	$\dfrac{1}{q_e} = \left(\dfrac{1}{K_L q_{max}}\right)\dfrac{1}{C_e} + \dfrac{1}{q_{max}}$
Freundlich	$\ln q_e = \dfrac{1}{n}\left(\ln C_e\right) + \ln K_F$
D-R	$q_e = q_{max} - K\varepsilon^2$ $\varepsilon = RT \ln\left(1 + \dfrac{1}{C_e}\right)$ $E = \dfrac{1}{\sqrt{2K}}$

$[NH_3]_i$ and $[NH_3]_f$ are the initial and final concentrations for ammonia-N (mg/L); m_{SMSB} is the mass for SMSB (g); V_{NH3} is the volume for ammonia-N solution (L); t is the contact time between SMSB and ammonia solution (minute); q_e is the equilibrium sorption capacity (mg/g), k_1 (min^{-1}) and k_2 (g/mg min) are the rate constant for the pseudo-first-order and pseudo-second-order equation respectively; q_{max} is the maximum sorption capacity of SMSB in the Langmuir or D-R models (mg/g); n is the empirical constant for Freundlich model (L/mg); K_L, K_F and K are the constants for Langmuir (L/mg), Freundlich (mg/g), and D-R model (mol^2/J^2) respectively; ε is Polanyi potential (J/mol) related to equilibrium concentration C_e; R is gas constant (8.314 J/mol) and T is the absolute temperature; and E is the mean free energy of adsorption per mol of the adsorbate (kJ/mol).

Sewage wastewater was collected from a sewage treatment plant at Nilai. The water parameters of the effluent (i.e., pH, temperature, salinity, electric conductivity, and dissolved oxygen) were measured immediately using the YSI 556 multiprobe system. One litre of effluent was preserved with 2 mL of concentrated HCl (37% w/w) and stored at <4°C. Sorption experiment was conducted by agitating 0.03 g and 0.06 g SMSB with 30 mL effluent in 50 mL centrifuge tubes for 60 minutes at constant temperature (25°C). The mixtures were filtered with 0.45 µm syringe filter, and the concentration of ammonia-N in the supernatant was analysed using Nessler's reagent calorimetric method.

RESULTS AND DISCUSSION

Ash content for SMS (27.8% w/w) is slightly higher than that of rubber wood sawdust (22.7% w/w) (Ghani et al., 2013), due to the fact that SMS was added with 5% lime ($CaCO_3$). For SMSB, the weight percentage (% w/w) for moisture, fixed carbon, ash, and volatile matter are 5.0%, 37.0%, 6.5%, and 51.5% respectively.

Table 2 shows elemental compositions for SMS, and SMSB. Pyrolysis process has increased percentage of C and H contents, and decreased O and N. The H/C_{org} molar ratio for SMSB (0.4) was lower than that of SMS (1.6), indicating that SMSB is more stable than SMS (Budai et al. 2013). Soluble fraction from the ash in SMSB was removed during the leaching process with HCl solution, involving the loss of Ca (by 10% w/w) and K (by 0.4% w/w). However, presence of heavy metals such as Cr, Pb and Zn remain unchanged.

Table 2

Elemental composition (% w/w dry basis) for SMS and SMSB

Elements	SMS	SMSB
C	44.0	72.8
O	21.4	18.6
H	5.8	2.0
N	1.0	0.1
S	0.1	0
Ca	12.8	2.8
Cr	0.1	0.1
K	0.5	0.1
Mg	0.8	0.8
Pb	0.2	0.2
Zn	0.1	0.1

The acidic functional groups on the surface of SMSB consists of primarily carboxylic (0.3 mmol/g) and phenolic groups (0.5 mmol/g). The amount for basic functional groups for SMSB was 0.2 mmol/g.

Figure 1 shows the percentage removal (%) of ammonia-N from the aqueous solution containing different dosages of SMSB. The percentage removal (%) for ammonia-N increased with increasing SMSB dosage by up to 1.0 g/L. Then, the percentage removal (%) began to concave slightly towards 5.0 g/L sorbent dosage, reaching 23% or ammonia removal. Based on this result, sorbent dosage of 1.0 g/L was adopted for all sorption experiments.
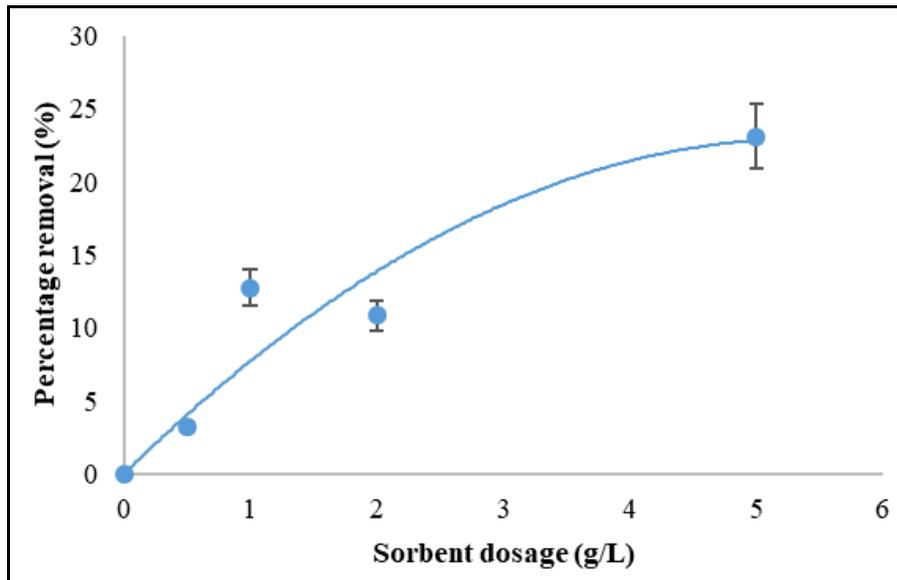
Figure 1. Percentage removal of ammonia-N as a function of SMSB sorbent dosage (g/L) (Initial ammonia-N concentration = 50 mg/L; solution pH = 6.2; agitation speed = 150 rpm; contact time = 120 minutes)

Figure 2 shows SMSB q_e values for sorption of ammonia-N as a function of contact time (minutes). A rapid initial sorption stage occurred till the 10th minute, then proceeded with at a lower sorption rate, and reached equilibrium at the 60th minute with an equilibrium sorption capacity, q_e of 3.0 mg/g. The ammonia-N sorption kinetic data for SMSB was better described by the pseudo-second-order kinetic model (R^2= 0.942) compared with the pseudo-first-order model (R^2 = 0.644), showing that the rate limiting step may be controlled using chemical process (Yong, Bolan, Lombi, & Skinner, 2013).

Table 3
Kinetic models parameters for adsorption of ammonia-N by SMSB

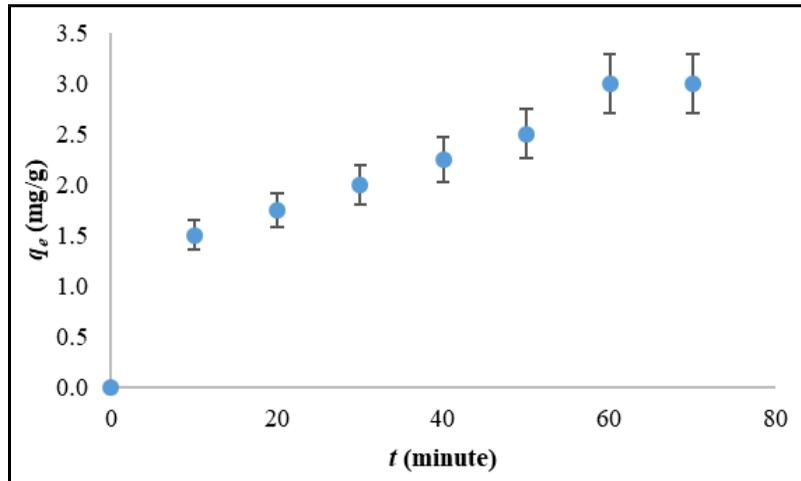| Kinetic models	R^2	q_e [mg/g]	k
Pseudo-first-order	0.644	2.73×10^{15}	-1.47
Pseudo-second-order	0.942	3.88	0.011

Figure 2. Ammonia-N sorption capacity for SMSB, q_e as a function of contact time, t (minutes) (Sorbent dosage = 1.0g/L; Initial ammonia-N concentration = 50 mg/L; solution pH = 6.2; Agitation speed = 150 rpm)

Figure 3 shows the ammonia-N sorption capacity for SMSB, q_e (mg/g) as a function of equilibrium ammonia-N concentration, C_e (mg/L). The ammonia-N adsorption by SMSB increased with increasing initial ammonia-N concentration, whereby, the q_e value increased from 0.05 to 4.41 mg/g. High initial ammonia-N concentration may overcome mass transfer resistance between aqueous and solid phase. The sorption isotherm parameters for SMSB is shown in Table 4. The ammonia-N sorption data for SMSB was best described by D-R isotherm model ($R^2 = 0.996$). Even though sorption data also fits well with Langmuir model ($R^2 = 0.987$), the q_{max} value could not be calculated due to the negative intercept value in the $1/q_e$ versus $1/C_e$ plot. In fact, the q_{max} value for Langmuir and D-R models are similar (Shi, Wang, & Zheng, 2013) and may be used to elucidate SMSB sorption capacity. The q_{max} value for the D-R model (12.6 mg/g) translates to 0.7 mmol NH_4 per unit gram of SMSB. This correlates well with the result from Boehm titration, whereby, the total acid functional groups was 0.8 mmol/g. Carboxylic and phenolic groups become negative-charge upon deprotonation, and may act as binding sites for retaining the positive-charged-ammonia-N (Shaaban et al., 2014). The E value was 4.4 kJ/mol, indicating physical nature of the adsorption process between ammonia-N and SMSB (Yunnen, Changshi, & Jinxia, 2016). The low n value from the Freundlich model (0.754) suggested less favourable sorption process and corroborates the weak physical interactions between ammonia-N and SMSB surface.

Table 4

Isotherm models parameters for adsorption of ammonia-N by SMSB

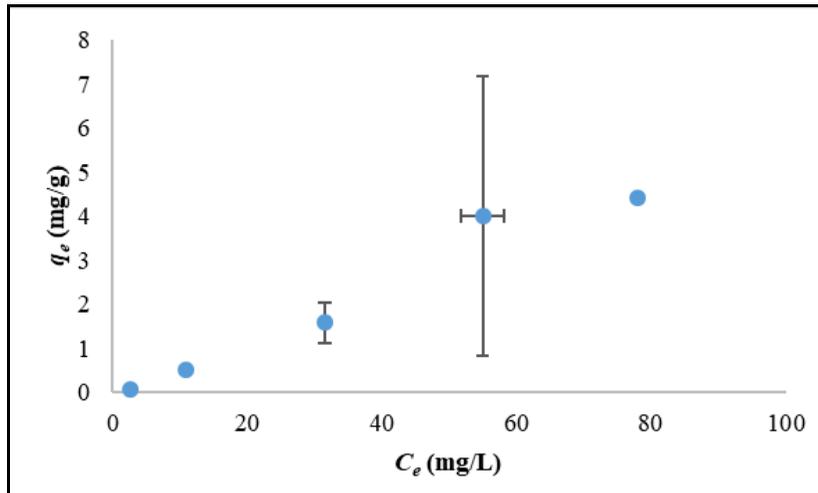| Isotherm models	R^2	q_{max} [mg/g]	K_L [mg/L]	K_f [mg/g]	K	n
Langmuir	0.987	-0.83	-0.0223	-	-	-
Freundlich	0.990	-	-	0.0163	-	0.754
D-R	0.996	12.6	-	-	0.0257	-

Figure 3. Ammonia-N sorption capacity for SMSB, q_e (mg/g) as a function of equilibrium ammonia-N concentration, C_e (mg/L) (Sorbent dosage = 1.0 g/L; Contact time = 60 minutes; solution pH = 6.2; Agitation speed = 150 rpm)

Table 5 shows the comparison of Langmuir and D-R q_{max} value for SMSB and various selected clay-based and carbon-based sorbents for sorption of ammonia-N. The q_{max} value for SMSB is comparable with those of zeolite and corn straw biochar, and is higher than commercial activated carbon (AC), and AC derivatives. This shows the great potential of SMSB as sorbent for ammonia-N from wastewater.

Table 5

Ammonia-N sorption capacity, qmax (mg/g) for various sorbents and SMSB

Sorbent	Isotherm model	q_{max} [mg/g]	Reference
Zeolite (Z3)	Langmuir	15.2	(Bernal & Lopez-Real, 1993)
Sepiolite	Langmuir	1.5	
Corn straw biochar	Langmuir	14.46	(Gai et al., 2014)
Rice husk biochar	Langmuir	3.2	(Zhu et al., 2012)
	D-R	6.8	
AC	D-R	0.48	(Shi, Wang, & Zheng, 2013)
HNO$_3$-treated AC	D-R	1.39	
HCl-treated AC	D-R	0.45	
SMSB	D-R	12.6	This study

Table 6 shows the parameters for sewage wastewater. The percentage removal of ammonia-N for SMSB at 1.0 g/L and 2.0 g/L were similar (5.3 %), with a sorption capacity of 0.80 mg/g. It indicates that the different dosage of SMSB did not affect the percentage removal of ammonia-N in real sewage wastewater.

Table 6
Parameters for sewage wastewater collected from Nilai, Negeri Sembilan

Water parameter	Average values
Ammonia-N	15.7 ± 2.01
Temperature (°C)	28.21 ± 0.01
DO (mg/L)	6.223 ± 0.161
DO (%)	79.87 ± 2.079
pH	8.037 ± 0.006
Salinity (ppt)	0.16 ± 0
TDS (g/L)	0.219 ± 0
Conductivity (mS/cm)	0.337 ± 0

CONCLUSION

In this study, batch studies were conducted for adsorption of ammonia-N from aqueous solution using SMSB as absorbent. The results from ash content, elemental analyses, and Boehm titration indicate that the dynamic behaviour and adsorption capacities of SMSB can be attributed to its surface properties. The optimum conditions for ammonia-N removal was at a dosage of 1.0 g/L and contact time of 60 minutes. Kinetic data was well described by the pseudo-second-order model. Sorption isotherm was best fitted with D-R model, where the maximum adsorption capacity was 12.6 mg/g. The sorption capacity for SMSB is comparable to establish sorbent such as zeolite, and is also greater than commercial activated carbon. Despite that, interaction between ammonia-N and SMSB surface is physical. This study shows that SMSB can be applied for recycling ammonia-N from sewage wastewater for fertilising agricultural soils.

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