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Highly Porous and Nutrients-Rich Biochar Derived from Dairy Cattle Manure and Its Potential for Removal of Cationic Compound from Water

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Abstract: The use of biochar in the horticulture and crop fields is a recent method to improve soil fertility due to its porous features and rich nutrients. In the present study, dairy manure (DM) was used as a biomass precursor in the preparation of highly porous biochar (DM-BC) produced at specific conditions. Based on N_2 adsorption-desorption isotherms and scanning electron microscopy (SEM) observations, the resulting biochar featured its microporous/mesoporous textures with a BET surface area of about 300 m^2/g and total pore volume of 0.185 cm^3/g, which could be a low-cost biosorbent for the effective removal of methylene blue (MB) from the aqueous solution. As observed by the energy dispersive X-ray spectroscopy (EDS), the primary inorganic nutrients on the surface of DM-BC included calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), silicon (Si), sulfur (S), sodium (Na) and aluminum (Al). Furthermore, the resulting biochar was investigated in duplicate for its biosorption performance of cationic compound (i.e., methylene blue, MB) from the aqueous solution with various initial MB concentrations and DM-BC dosages at 25 °C. The findings showed that the biosorption kinetic parameters fitted by the pseudo-second order rate model with high correlations were consistent with its porous features. These experimental results suggested that the porous DM-based biochar could be reused as a biosorbent, biofertilizer, or soil amendments due to the high porosity and the abundance in nutrient minerals.

Keywords: manure pyrolysis; biosorbent; pore property; nutrient mineral; biosorption kinetic model

1. Introduction

Livestock industries produced a variety of commodities like meat and milk, but they also generated large volumes of excrement and manure that could cause adverse effects on environmental quality if not well managed [1]. Due to the contents of cellulose-derived organics, nutrients (e.g., nitrogen, phosphorus) and other constituents (e.g., pathogens, heavy metals) in the livestock waste, major forms of environmental pollution associated with waste management such as eutrophication of surface water, leaching of nitrates and pathogens, excess nutrients and heavy metals built up in the soil, and release of odorants (e.g., ammonia, hydrogen sulfide) and greenhouse gas (e.g., methane, carbon dioxide) emissions. More importantly, the livestock industries, especially in beef and dairy cows, contributed a significant share (about 15%) to anthropogenic emissions of greenhouse gas (GHG), including carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) [2]. For instance, manure contains organic matters and nitrogen components that can lead to CH_4 and N_2O emissions during storage and processing, implying that the livestock sector plays an important role in global warming and climate change. In this regard, converting cattle manure into carbon-rich material (i.e., biochar) could be one of the available technologies for mitigating emissions of GHG from the livestock sector [3].

To be used effectively as an environmental biosorbent, the properties of biochar should be associated with those of activated carbon with porous structure and granular clay with negative charge. In this regard, biochars produced at higher pyrolysis temperatures and adequate residence times (10–60 min) from biomass feedstocks with high carbon contents have larger values of specific surface area [4]. Herein, specific surface area (SSA), an important index to be indicative of adsorptive capacity of biochar, is commonly obtained by nitrogen (N_2) adsorption/desorption isotherms at −196 °C using a surface area & porosity analyzer [5]. On the other hand, the oxygen-containing functional groups on the surface also play an important role in the aqueous interactions between target adsorbate and biochar adsorbent. Generally, surface oxide groups will add a polar nature to carbon materials with hydrophilicity, acidity and negative charge [5].

Although there are many researches reusing dairy cattle manure as a feedstock for biochar production, only few studies focused on using the dairy manure-based biochar as an adsorbent or biosorbent for the removal of pollutants from the aqueous solution and soil systems [6–14]. Cao and other researchers [6,7] prepared the biochars at low temperatures (200–500 °C), indicating that the resulting biochar (SSA 2.7–13 m^2/g) can be used as an effective sorbent for removal of lead and atrazine from the aqueous solution. Uchimiya et al. [8] studied biochars, produced at two pyrolytic temperatures (350 and 700 °C), for examining their retentions of heavy metal ions (i.e., Pb, Cu, Ni, and Cd) in a specific soil. Qian and Chen [9] investigated the high adsorption of aluminum (Al) onto the biochars produced at different temperatures (400 and 700 °C) due to the organic components and silicate particles contained. Xu et al. [10] produced the biochars (SSA 1.9 and 5.6 m^2/g) at 200 and 350 °C and determined their extents for the removal of heavy metals (Cd, Cu and Zn) from the aqueous solution, showing that the Ca/Mg-containing minerals (i.e., carbonates and phosphates) contained in the biochars play a vital role in the high adsorption capacity. Ma et al. [11] conducted the aqueous sorption experiments of cadmium (Cd) removal by the biochar, suggesting that the favorable sorption could be attributed to the oxygen-containing functional groups (i.e., hydroxyl, carboxyl and carbonyl) in the biochar. Zhu et al. [12] performed the removal of methylene blue (MB) from aqueous solution by the biochars produced at 200 and 800 °C (denoted as CMB_{200} and CMB_{800}, respectively; SSA 0.3 and 3.6 m^2/g), showing a better MB sorption by CMB_{200} due to its strong interactions involving ion exchange, electrostatic attraction, hydrogen bonding and physical adsorption. Chen et al. [13] reported the removal of Cd and Pb with the biochars (including the biochar modified by NaOH treatment; SSA 9.4 and 25.9 m^2/g) produced at 300 °C, revealing that the sorption mechanisms are predominantly controlled by chemisorption and complexation with carboxyl/hydroxyl functional groups. Zhao et al. [14] prepared the biochar (SSA 74 m^2/g) obtained at 700 °C for studying its effects on adsorption of sulfate, showing that the electrostatic interaction between the biochar and sulfate ion could be the determining adsorption mechanism.

In a previous study [15], the thermochemical properties of manure-based biochars produced from dairy (Holstein) manure at moderate temperatures (400–800 °C) with holding time of 60 min were studied, showing that the DM-based biochar can be used as a solid fuel due to its high contents of carbon (60 wt%) and calorific value (22.3 MJ/kg). As mentioned above, limited researches focused on reusing DM-BC as a biosorbent for removal of cationic pollutants from aqueous solution. In order to obtain a porous biochar with a high surface area and rich nutrient minerals, a biochar product was produced at the extreme temperature (i.e., 900 °C) in this work. Subsequently, the resulting DM-BC was tested for evaluating its effectiveness in the removal of target adsorbate (i.e., MB) from the aqueous solution.

2. Materials and Methods

2.1. Materials

The dairy (Holstein) manure (DM) for the production of high-surface-area biochar was taken from the university's farm (Pingtung, Taiwan). Details on the pretreatment of DM have been described in the previous studies [15,16]. The cationic dye methylene blue (MB), which was purchased from Merck Co. (Darmstadt, Germany), was targeted as an adsorbate because it can be used as a probe molecule for determining the surface area of carbon material [17].

2.2. Biochar Preparation Experiments

Because the temperature has been shown to be the most important process parameter in the pyrolysis experiments [7,18], the DM-BC products were produced in duplicate at very high temperature (i.e., 900 °C), moderate residence time (30 min) and low heating rate (10 °C/min) under an inert nitrogen atmosphere in this work. The yields of the DM-BC products were defined as the ratio of DM-BC mass to DM mass (5 g for each experiment), showing a yield of 22.5% on average.

2.3. Physical and Chemical Characterizations of Resulting Biochar

In this work, the main purpose was to produce biochar with high pore properties (including specific surface area, pore volume and porosity). Therefore, the physical properties of DM-BC were mainly based on the N_2 adsorption-desorption isotherms by using a surface area and porosity analyzer (Model No.: ASAP 2020; Micromeritics Co., Norcross, GA, USA). Regarding the calculation of main pore properties, they were based on the Langmuir equation, Brunauer-Emmett-Teller (BET) equation and *t*-plot method [5,19]. For instance, the micropore (pore diameter or width <2.0 nm) surface area and micropore volume were obtained from the *t*-plot method. On the other hand, the single point surface area was calculated at a relative pressure of 0.30 because it is a simplified BET method. The total pore volume of resulting biochar was obtained by converting the adsorbed N_2 amount at a relative pressure of approximately 0.95 to equivalent liquid N_2 volume [19]. In order to calculate the porosity of biochar from the values of densities [5,20], a gas pycnometer (Model No.: AccuPyc 1340; Micromeritics Co., USA) was further used to measure the true density of resulting biochar. However, its particle density was estimated by the values of true density and total pore volume [20]. The average pore width of resulting biochar was roughly obtained using its BET surface area and total pore volume based on the assumption of cylindrical geometry in all pores [5,20]. Furthermore, the porous textures and elemental compositions on the surface of DM-BC were measured using a scanning electron microscopy (Model No.: S-3000N; Hitachi Co., Tokyo, Japan) and an energy dispersive X-ray spectroscopy (Swift ED3000, Oxford Instruments, Abingdon, UK), respectively.

2.4. Biosorption Kinetic Tests

The adsorption kinetic experiments were also described in the previous study [21]. The batch adsorption kinetics of DM-BC was performed in a 3 L mixing tank with a 2 L solution. The data on the adsorbed uptake of methylene blue (MB) from aqueous solution (2 L) were obtained at the temperature of 25 °C and agitation speed of 200 rpm. The adsorption parameters included initial MB concentrations (i.e., 5, 10, and 15 mg/L) and DM-BC dosages (i.e., 0.15, 0.3 and 0.5 g). During the adsorption tests, an aliquot solution (about 13 cm^3) was taken out at specified intervals (i.e., 5, 10, 20, 30, 40, 50, and 60 min). After filtrating with a nylon membrane filter (pore size of 0.45 μm) with a filter size of 25 mm (Chrom Tech Inc., Apple Valley, MN, USA), the determination of MB concentration in the filtrate solution was obtained by the U-2900 spectrophotometer (Hitachi Co., Tokyo, Japan) at 664 nm. The adsorbed amount of MB (q_t, mg/g) at the sampling time (i.e., contact time) of t was thus calculated by the solution volume, adsorbent (DM-BC) mass, and the difference between remaining MB concentration at t (C_t) and initial MB concentration (C_0). Herein, the solution volume was assumed to be 2 L without significant change for each biosorption experiment, because total sampling volume was only about 0.09 L. On the other hand, the sampling solution taken at each specific time in the biosorption experiments was analyzed in duplicate using separate samples, showing that the reproducibility of the measurements is within 3%.

3. Results and Discussion

3.1. Pore Properties of Resulting Biochar

Although the chemical properties of biochar may affect the use as an adsorbent in the environmental applications, its effectiveness mainly depends on its pore properties. Table 1 listed the pore properties of resulting biochar (DM-BC), which include surface area, pore volume, density and porosity. In this work, the DM-BC was produced at the same pyrolysis conditions in duplicate, showing that their pore properties were close to each other. Obviously, the DM-BC possessed favorable pore properties by comparison with other biochars produced from different feedstocks [22]. For instance, the BET surface area of DM-BC (ca. 300 m^2/g) was significantly higher than those (<186.5 m^2/g) by other similar studies using dairy manure for the preparation of biochars [6–14]. Based on the microporosity (i.e., the ratio of micropore surface area to BET surface area), listed in Table 1, it was close to 0.70, giving an indication of a mesoporosity of about 30%. Therefore, the average pore diameter (or width) was about 25.2 Å (or 2.52 nm), which can be estimated by the values of BET surface area and total pore volume if the pores are cylindrical geometry without interconnection [20]. The physical characterization of DM-BC with high surface area and mesoporosity would prefer to remove adsorbates with large molecular size from the aqueous system due to the steric effect [23].

Table 1. Pore properties of resulting biochar (DM-BC).

Property	DM-BC [a]
Single point surface area (m^2/g) [b]	288 ± 200
BET surface area (m^2/g) [c]	294 ± 21
Langmuir surface area (m^2/g)	420 ± 29
Micropore surface area (m^2/g) [d]	204 ± 16
External surface area (m^2/g) [e]	90.2 ± 4.5
Total pore volume (cm^3/g) [f]	0.185 ± 0.012
Micropore volume (cm^3/g) [d]	0.102 ± 0.008
Average pore diameter or width (Å) [g]	25.2 ± 0.2
Particle density [h]	1.66 ± 0.03
True density [i]	2.39 ± 0.01
Porosity (-) [j]	0.306 ± 0.014

[a] Based on two measurements for DM-BC samples produced at the same pyrolysis conditions; [b] obtained at relative pressure (P/P_0) of about 0.30; [c] based on the relative pressure (P/P_0) ranging from 0.05 to 0.30; [d] estimated by *t*-plot method; [e] obtained by subtracting micropore surface area from BET surface area; [f] total pore volume obtained at relative pressure (P/P_0) of about 0.95; [g] estimated by the values of BET surface area (S_{BET}) and total pore volume (V_t) (i.e., average pore width = $4 \times V_t/S_{BET}$) [20]; [h] estimated by the values of total pore volume (V_t) and true density (ρ_s) (i.e., $\rho_p = 1/[V_t + (1/\rho_s)]$) [20]; [i] measured by a pycnometer; [j] estimated by the values of particle density (ρ_p) and true density (ρ_s) (i.e., $\varepsilon_p = 1 - (\rho_p/\rho_s)$) [20].

In order to describe the pore structures of DM-BC studied, Figure 1 showed its N_2 adsorption-desorption isotherms. Obviously, the biochar was highly porous because Type I isotherms were obtained on microporous materials with the pore width less than 2 nm [19]. Due to the very high adsorption potential, a very high uptake occurred at relatively relative pressures (P/P_0) of less than 0.05. However, DM-BC contained pores over a range of sizes or widths, including micropores (<2.0 nm) and mesopores (2.0–50.0 nm). Therefore, the observed isotherms revealed the feature with both Type I and Type VI. Also shown in Figure 1, the hysteresis loop occurred at the isotherms as the relative pressure increased in the adsorption process and then decreased in the desorption process. This progress led to the multilayer adsorption and pore (capillary) condensation, which commonly occurs in the mesoporous materials. According to the classification of hysteresis loops by the International Union of

Pure and Applied Chemistry (IUPAC), the loop of DM-BC should belong to type H4, which could be associated with narrow slit-shaped pores [19]. Furthermore, the pore size distribution of the resulting biochar showed two peaks depicted in Figure 1, indicating that the micropores and mesopores were present in the DM-BC. On the other hand, its SEM images, seen in Figure 2, showed a porous texture on the surface, thus resulting in its high pore properties as indicated in Table 1 and Figure 1.

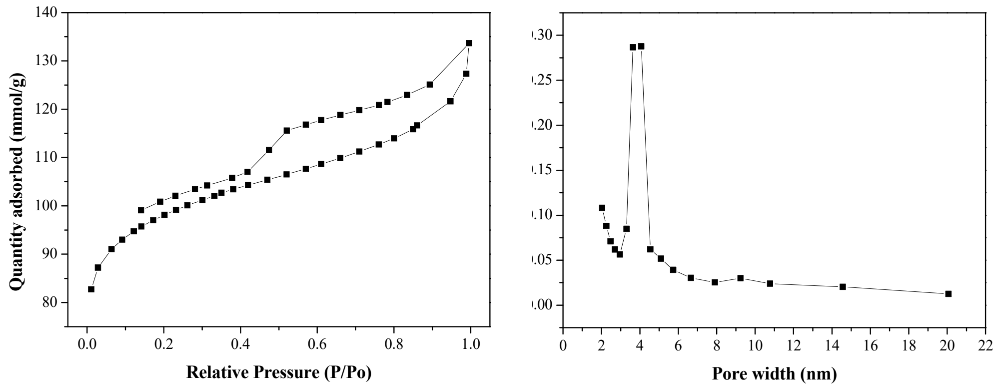


Figure 1. N_2 adsorption-desorption isotherms (**left**) and pore size distribution (**right**) of DM-BC.

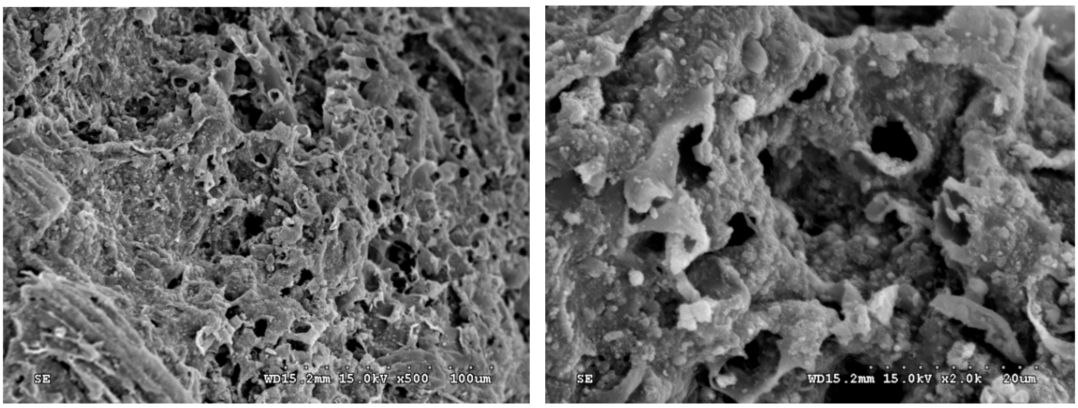
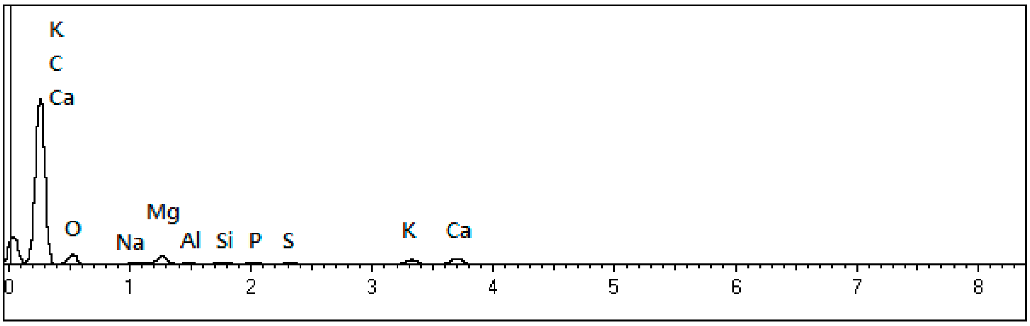


Figure 2. SEM images (**left**: ×500; **right**: ×2000) of DM-BC.

3.2. Chemical Characterization on the Surface of Resulting Biochar

During the SEM observations, the elemental compositions on the surface of resulting biochar were further analyzed by using the energy dispersive X-ray spectroscopy (EDS). As revealed in Figure 3, it showed that the main elements, including carbon (41.95 wt%) and oxygen (36.27 wt%), were present in the DM-BC. The high content of oxygen in the resulting biochar was significantly high, implying that its surface contained some oxygen-containing functional groups (e.g., carbonyl and hydroxyl) and minerals (e.g., K_2O and CaO) for probable connection with the polar nature (i.e., hydrophilicity) [24]. Also, the resulting biochar contained some soil nutrient elements, including calcium (Ca, 7.06 wt%), magnesium (Mg, 4.96 wt%), potassium (K, 4.80 wt%), phosphorus (P, 1.56 wt%), sulfur (S, 1.25 wt%), silicon (Si, 1.06 wt%), sodium (Na, 0.63 wt%) and aluminum (Al, 0.48 wt%). These results were consistent with the previous study [16]. These mineral elements in the resulting biochar could be composed by the forms of oxides, silicates, and/or phosphates. Therefore, this manure-based biochar can be reused as an excellent biofertilizer or soil amendment because it can enhance soil fertility based on the following benefits [25]: recovery of P and other nutrients from manure, increased cationic mineral released (cation-exchange capacity), moderating of soil acidity due to the alkalinity of the cationic oxides (e.g., K_2O), increased water retention and number of beneficial microbes in soils, and reduced leaching of nitrogen-containing compounds (cations like ammonium) into water bodies.



Element	Weight %	Atomic %
Carbon	41.95	54.28
Oxygen	36.27	35.24
Calcium	7.06	2.74
Magnesium	4.96	3.17
Potassium	4.80	1.91
Phosphorus	1.56	0.78
Sulfur	1.25	0.61
Silicon	1.06	0.59
Sodium	0.63	0.42
Aluminum	0.48	0.27

Figure 3. EDS analysis of DM-BC.

3.3. Biosorption Kinetic Performances of Resulting Biochar

Adsorption or biosorption process is a common method in the water and wastewater treatment and soil remediation. For better performance and cost-effective operation, biosorption capacity and process time required for equilibrium are important parameters in the system. Therefore, several biosorption kinetic equations or models have been used to predict the biosorption behaviors in the aqueous systems [26]. Among them, a pseudo-second order rate equation was commonly used to fit the biosorption kinetic data for explaining the physicochemical aspects, including physical biosorption, chemical attraction and ion-exchange. Its linear form was given below [27]

$$t/q_t = 1/(k \times q_e^2) + (1/q_e) \times t \tag{1}$$

where q_t is the biosorbed amount of adsorbate (i.e., MB) at the contact time t (mg/g), q_e is the amount of MB biosorbed at equilibrium (mg/g), k is the pseudo-second-order rate constant (g/(mg·min)), and t is the contact time (min). Figures 4 and 5 showed the biosorption behaviors of DM-BC for removal of MB from aqueous solution under various conditions at temperature of 25 °C and agitation speed of 200 rpm. In the early period, the residual MB concentration (C_t/C_0) rapidly decreased as contact time increased, implying that the interaction (biosorption potential) between adsorbate (MB) and biosorbent (DM-BC) was strong. Herein, MB was used as a model compound because some pesticides (e.g., paraquat) are cationic in the aqueous solution or soils. Therefore, the pseudo-second order rate equation was adopted in this work. The fitted values of biosorption rate parameters for describing the system have been listed in Tables 2 and 3, indicating that the correlations between the experimental data and fitting results was highly consistent.

The fitted biosorption capacity (i.e., q_e) increased as the initial adsorbate (MB) concentration (i.e., C_0) increased from 5 to 15 mg/L, as seen in Table 2. This result was reasonable because more MB molecules were adsorbed at equilibrium onto the biochar (DM-BC) without exhausting its adsorption sites. On the other hand, the decrease of q_e with increasing biochar dosage was indicative of exhausting adsorption onto excessive biochar by the limited MB molecules. Furthermore, the rate constant values (*k*) indicated an increasing trend at higher biochar dosages due to the increase in more biosorption sites provided. These results agreed with those by the previous study [21] and other studies [12,28,29]. It is well known that carbon adsorption is an advanced wastewater treatment process. Based on the data in Table 2, the wastewater volume completely biosorbed by 1 kg DM-BC at 25 °C is equal to about 5 m^3 if it contains the MC concentration of 5 mg/L.

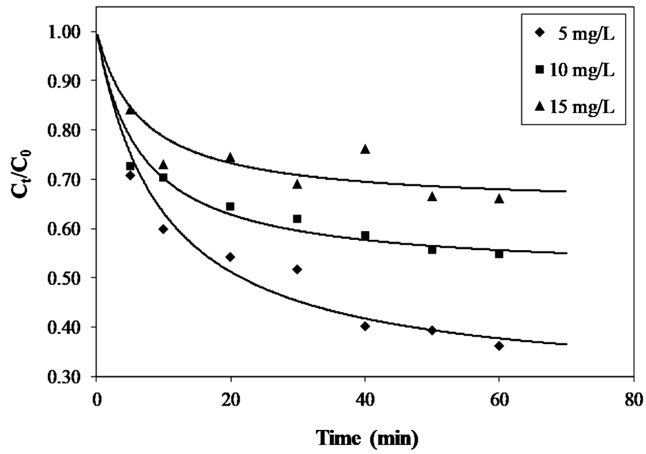


Figure 4. Plots of dimensionless concentration vs. time at different initial MB concentrations. Biosorption conditions: DM-BC dosage of 0.3 g/2 L, temperature of 25 °C, and agitation speed of 200 rpm. Symbols: C_t = residual MB concentration at time *t*, C_0 = initial MB concentration. Full lines: calculated from Equation (1) and Table 2.

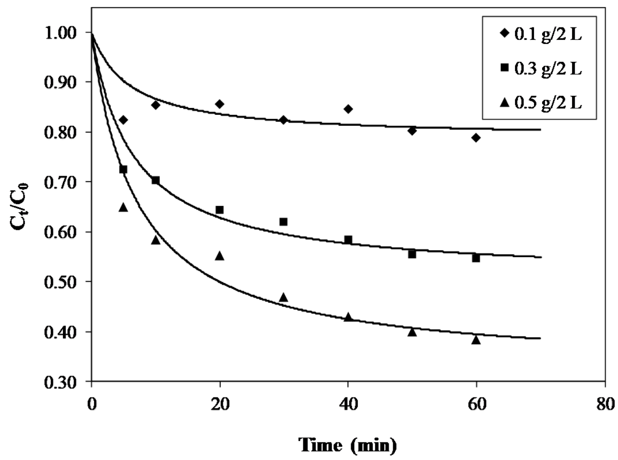


Figure 5. Plots of dimensionless concentration vs. time at different DM-BC dosages. Biosorption conditions: initial MB concentration of 10 mg/L, temperature of 25 °C, and agitation speed of 200 rpm. Symbols: C_t = residual MB concentration at time *t*, C_0 = initial MB concentration. Full lines: calculated from Equation (1) and Table 3.

Table 2. Kinetic parameters for methylene blue (MB) biosorption onto DM-BC at initial MB concentrations based on the pseudo-second-order model [a].

Initial MB Concentration (mg/L)	k (g/mg·min)	q_e (mg/g)	Correlation Coefficient
5	0.0043	24.10	0.983
10	0.0047	32.79	0.993
15	0.0042	35.59	0.922

[a] Biosorption conditions: DM-BC dosage of 0.3 g/2 L, agitation speed of 200 rpm, and temperature of 25 °C. Symbols: k = pseudo-second-order rate constant, q_e = amount of MB biosorbed at equilibrium.

Table 3. Kinetic parameters for MB biosorption onto DM-BC at various DM-BC dosages based on the pseudo-second-order model [a].

Adsorbent Dosage (g/2 L)	k (g/mg·min)	q_e (mg/g)	Correlation Coefficient
0.1	0.0040	42.55	0.939
0.3	0.0047	32.79	0.993
0.5	0.0053	27.03	0.992

[a] Biosorption conditions: initial MB concentration of 10 mg/L, agitation speed of 200 rpm, and temperature of 25 °C. Symbols: k = pseudo-second-order rate constant, q_e = amount of MB biosorbed at equilibrium.

4. Conclusions

In this work, the resulting biochar product (DM-BC) showed its microporous and mesoporous features with the BET surface area of about 300 m^2/g and total pore volume of 0.185 cm^3/g. The porous texture can be observed by the N_2 adsorption-desorption isotherms and scanning electron microscopy (SEM). As also revealed by the energy dispersive X-ray spectroscopy (EDS), the surface of DM-BC was rich in soil nutrient elements, such as calcium (Ca), magnesium (Mg%) and potassium (K). Furthermore, it showed a rapid removal of cationic compound (i.e., MC) from aqueous solutions due to the strong interaction between the dye and the negatively-charged biochar surface and the high fitting results of pseudo-second order rate model ($R^2 > 0.94$). These experimental results suggested that the manure-based biochar could be reused as a biosorbent, biofertilizer, or soil amendments due to the high porosity and the abundant in nutrient minerals.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Tahsee, Q. Manure: Its impacts on environment quality and on soil biota with special reference to nematodes. In *Manure: Management, Uses and Environmental Impacts*; Dellaguardia, C.S., Ed.; Nova: London, UK, 2010; pp. 49–81.
2. Food and Agriculture Organization of United States (FAO). *Tackling Climate Change through Livestock*; FAO: Rome, Italy, 2013.
3. Lehmann, J.; Joseph, S. Biochar for environmental management: An introduction. In *Biochar for Environmental Management*, 2nd ed.; Lehmann, J., Joseph, S., Eds.; Routledge: New York, NY, USA, 2015; pp. 1–13.
4. Miles, T.R.; Rasmussen, E.M.; Gray, M. Aqueous contaminant removal and stormwater treatment using biochar. In *Agricultural and Environmental Applications of Biochar: Advances and Barriers*; Guo, M., He, Z., Uchimiya, S.M., Eds.; Soil Science Society of America: Madison, WI, USA, 2016; pp. 341–376.
5. Suzuki, M. *Adsorption Engineering*; Elsevier: Amsterdam, The Netherlands, 1990.
6. Cao, X.; Ma, L.; Gao, B.; Harris, W. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* **2009**, *43*, 3285–3291. [CrossRef] [PubMed]
7. Cao, X.; Harris, W. Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. *Bioresour. Technol.* **2010**, *101*, 5222–5228. [CrossRef] [PubMed]
8. Uchimiya, M.; Cantrell, K.B.; Hunt, P.G.; Novak, J.M.; Chang, S. Retention of heavy metals in a Typic Kandiudult amended with different manure-based biochars. *J. Environ. Qual.* **2012**, *41*, 1138–1149. [CrossRef] [PubMed]
9. Qian, L.B.; Chen, B.L. Duel role of biochars as adsorbents for aluminum: The effects of oxygen-containing organic components and the scattering of silicate particles. *Environ. Sci. Technol.* **2013**, *47*, 8759–8768. [PubMed]

10. Xu, X.; Cao, X.; Zhao, L.; Wang, H.; Yu, H.; Gao, B. Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar. *Environ. Sci. Pollut. Res.* **2013**, *20*, 358–368. [CrossRef] [PubMed]
11. Ma, F.; Zhao, B.; Diao, J.; Qiao, H.; Zhong, J. Sorption of cadmium by biochar produced from pyrolysis of cattle manure in aqueous solution. *Fresenius Environ. Bull.* **2016**, *25*, 5226–5236.
12. Zhu, Y.; Yi, B.; Yuan, Q.; Wang, M.; Yan, S. Removal of methylene blue from aqueous solution by cattle manure-derived low temperature biochar. *RSC Adv.* **2018**, *8*, 19917–19929. [CrossRef]
13. Chen, Z.L.; Zhang, J.Q.; Huang, L.; Yuan, Z.H.; Li, Z.J.; Liu, M.C. Removal of Cd and Pb with biochar made from dairy manure at low temperature. *J. Integr. Agric.* **2019**, *18*, 201–210. [CrossRef]
14. Zhao, B.; Xu, H.; Ma, F.; Zhang, T.; Nan, X. Effects of dairy manure biochar on adsorption of sulfate onto light sierozem and its mechanisms. *RSC Adv.* **2019**, *9*, 5218–5223. [CrossRef]
15. Liu, S.C.; Tsai, W.T. Thermochemical characteristics of dairy manure and its derived biochars from a fixed-bed pyrolysis. *Int. J. Green Energy* **2016**, *13*, 963–968. [CrossRef]
16. Tsai, W.T.; Liu, S.C. Thermochemical characterization of cattle manure relevant to its energy conversion and environmental implications. *Biomass Convers. Biorefin.* **2016**, *6*, 71–77. [CrossRef]
17. Marsh, H.; Rodriguez-Reinoso, F. *Activated Carbon*; Elsevier: Amsterdam, The Netherlands, 2006.
18. Steiner, C. Considerations in biochar characterization. In *Agricultural and Environmental Applications of Biochar: Advances and Barriers*; Guo, M., He, Z., Uchimiya, S.M., Eds.; Soil Science Society of America: Madison, WI, USA, 2016; pp. 87–100.
19. Lowell, S.; Shields, J.E.; Thomas, M.A.; Thommes, M. *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*; Springer: Dordrecht, The Netherlands, 2006.
20. Smith, J.M. *Chemical Engineering Kinetics*, 3rd ed.; McGraw-Hill: New York, NY, USA, 1981.
21. Tsai, W.T.; Hsu, H.C.; Su, T.Y.; Lin, K.Y.; Lin, C.M.; Dai, T.H. The adsorption of cationic dye from aqueous solution onto acid-activated andesite. *J. Hazard. Mater.* **2007**, *147*, 1056–1062. [CrossRef] [PubMed]
22. Guo, M. Application of biochar for soil physical improvement. In *Agricultural and Environmental Applications of Biochar: Advances and Barriers*; Guo, M., He, Z., Uchimiya, S.M., Eds.; Soil Science Society of America: Madison, WI, USA, 2016; pp. 101–122.
23. Tamai, H.; Yoshida, T.; Sasaki, M.; Yasuda, H. Dye adsorption on mesoporous activated carbon fiber obtained from pitch containing yttrium complex. *Carbon* **1999**, *37*, 983–989. [CrossRef]
24. Yang, R.T. *Adsorbents: Fundamentals and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2003.
25. Bergfeldt, B.; Morgano, M.T.; Leibold, H.; Richter, F.; Stapf, D. Recovery of Phosphorus and other Nutrients during Pyrolysis of Chicken Manure. *Agriculture* **2018**, *8*, 187. [CrossRef]
26. Ho, Y.S.; Ng, J.C.Y.; McKay, G. Kinetics of pollutant sorption by biosorbents: Review. *Sep. Purif. Meth.* **2000**, *29*, 189–232. [CrossRef]
27. Ho, Y.S.; Chiang, C.C.; Hsu, Y.C. Sorption kinetics for dye removal from aqueous solution using activated clay. *Sep. Sci. Technol.* **2001**, *36*, 2473–2488. [CrossRef]
28. Demirbas, A. Agricultural based activated carbons for the removal of dyes from aqueous solutions: A review. *J. Hazard. Mater.* **2009**, *167*, 1–9. [CrossRef] [PubMed]
29. Ghaedi, M.; Golestani Nasab, A.; Khodadoust, S.; Rajabi, M.; Azizian, S. Application of activated carbon as adsorbents for efficient removal of methylene blue: Kinetics and equilibrium study. *J. Ind. Eng. Chem.* **2014**, *20*, 2317–2324. [CrossRef]