applied sciences

MDPI

Article

The Various Forms of Cow Manure Waste as Adsorbents of Heavy Metals

Oviyanti Mulyani [1,*], Benny Joy [1] and Dikdik Kurnia [2]

[1] Department of Soil Science and Land Resources Management, Faculty of Agriculture, Padjadjaran University, Jatinangor 45363, Indonesia; joy@unpad.ac.id
[2] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University, Jatinangor 45363, Indonesia; dikdik.kurnia@unpad.ac.id
* Correspondence: oviyanti.mulyani@unpad.ac.id

Abstract: In recent years, the application of cow manure waste as an adsorbent of heavy metals in water and soil has increased. The analysis of the most effective adsorbents from cow manure as materials that can reduce heavy metals, while being low-cost and easy to produce, is important in the agricultural field. This study investigated adsorbents from cow manure, such as compost, biochar and humic acid, and analyzed the capability of the adsorption mechanisms of Cr, Pb and Cd. The experiments were performed as a function of pH, adsorbent dose, initial metal ion concentration, and contact time. To investigate the mechanism of the adsorption process, the Langmuir and Freundlich models were used. The results showed that the optimum conditions of Cr, Cd and Pb ions were achieved by compost, biochar and humic acid with 83–99% removal. An adsorption isotherm model for compost, biochar and humic acid generally followed the Langmuir and Freundlich models. This study ranks the different forms of cow manure waste in the following order based on their ease of production, high adsorption capacity, and low cost: biochar > compost > humic acid.

Keywords: biochar; compost; cow manure; humic acid; organic waste; pollution

Citation: Mulyani, O.; Joy, B.; Kurnia, D. The Various Forms of Cow Manure Waste as Adsorbents of Heavy Metals. *Appl. Sci.* **2022**, *12*, 5763. https://doi.org/10.3390/app12115763

Academic Editors: Rafael López Núñez and Francisca Suárez Estrella

Received: 20 April 2022
Accepted: 1 June 2022
Published: 6 June 2022

1. Introduction

Livestock is essential for rural livelihoods and the economic sector in developing countries [1]. More than 40–70% of beef, milk, lamb, pork and poultry are produced in developing countries, such as Indonesia. In 2019, Indonesia's agriculture sector had 115 big and small active farms, and the number of livestock, primarily beef cattle, was approximately 183,152 head [2,3]. This enormous number of beef cattle produces a large amount of waste on a daily basis. Manure can thus constitute a valuable supply of nutrients for crops, but it can contaminate water sources when animals are present in high quantities [1]. A large amount of research has been undertaken to investigate how to decrease the negative impact of manure on the environment, with studies looking at the mechanism of adsorption, specific metal ion binding, cation exchange, precipitation, and complexation [4–8]. There are many forms of manure that can have a positive impact on the environment, such as biochar, compost and humic acid [9–13]. Biochar has great potential for increasing heavy metal immobilization in contaminated agricultural regions [14].Compost has many benefits for soil as a result of its thermophilic aerobic microorganism activity, which converts organic material into a hygienic and biodegradable product [15]. Additionally, the decomposition of organic matter, such as humic acid, is an important study area in the adsorption process, increasing mineral nutrient levels and enhancing soil characteristics, such as chemical and microorganism aspects [16–18]. Handling animal manure is the most effective approach to mitigate the effects of global warming on agricultural land, as well as a potential solution to agricultural and plantation management. This material has the potential to improve soil conditions and agricultural yields, especially in less fertile soils. The decomposition of animal waste can keep water and nutrients in the soil. This study aims to provide important information regarding the effectiveness of cow manure as a cheap and easy to produce adsorbent that can effectively decrease the heavy metals in the environment. This is in line with [19], which focused on the study of available and low-cost adsorbents that could remove heavy metal ions in the environment. The purpose of this research was to examine the capability of different types of adsorbents to reduce heavy metal content. This study provides fundamental information on the different types of cow manure adsorbents, such as compost, biochar and humic acid, and their impact on pollutant reduction.

2. Materials and Methods

2.1. Field of Study

Lembang District, West Bandung Regency, West Java, Indonesia, was chosen as the cow manure collection area (Figure 1). This study applied a survey, a comparison and descriptive approaches to find suitable locations. The locations of animal husbandry facilities were mapped using field surveys. The results of the field survey are mapped on the base map with a 1:50,000 scale Topographical Map of Indonesia (RBI) and the 1:50,000 scale administrative map of the Lembang District. The coordinates of each location were captured using a GPS (Garmin 585, Taipei, Taiwan), and mapped using ArcGIS desktop 10.2.

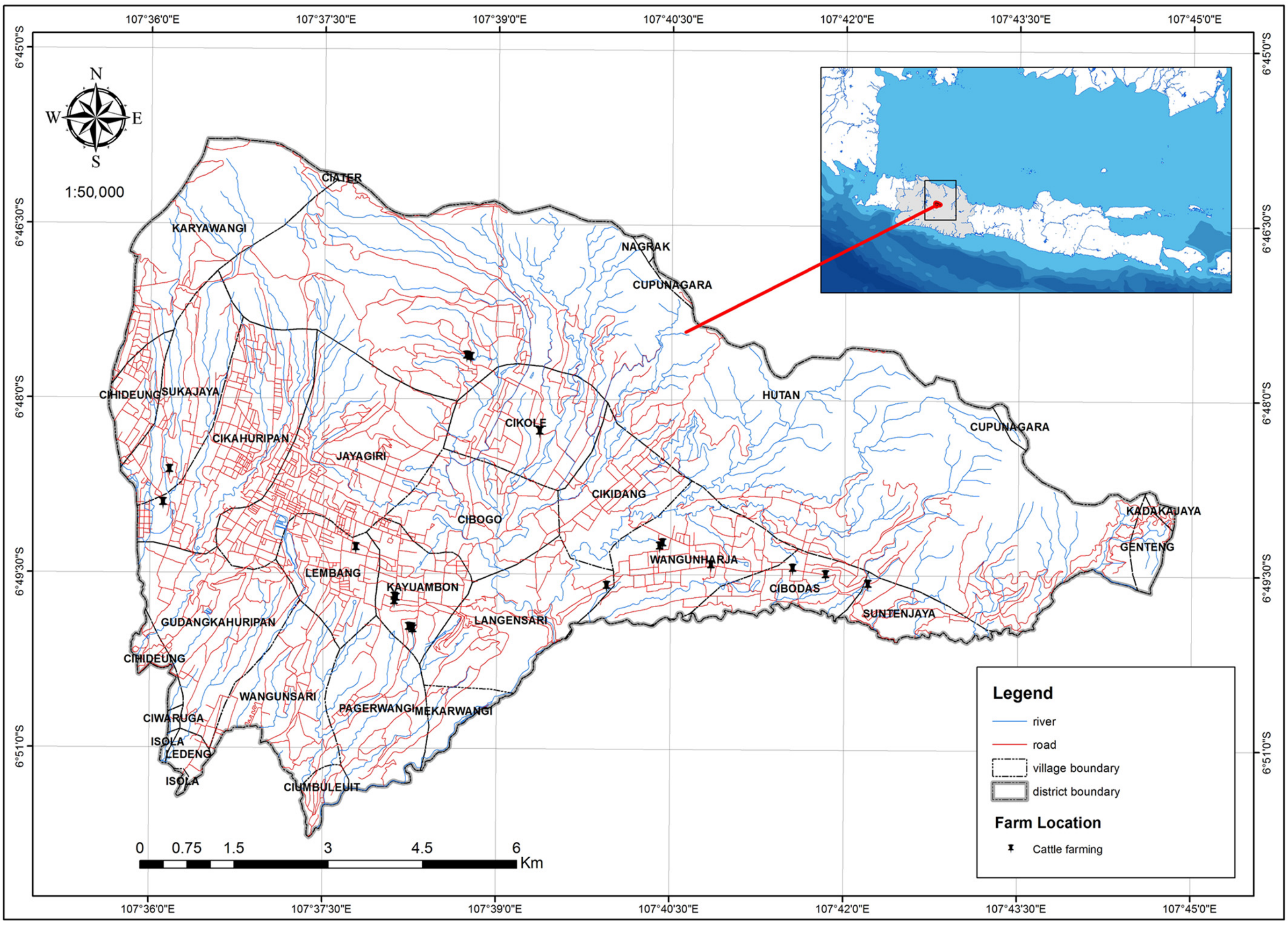


Figure 1. Map of cow manure sampling locations.

2.2. Sample Collection

A sample was obtained at each point (Figure 1). For laboratory analysis, 2 kg of samples were collected and stored in either a plastic container or a polythene bag, all of which were labeled appropriately. The cow manure was dried in a 60 °C oven, crushed until it passed through a 0.4 mm filter, and finally sealed in plastic containers that were labeled with a code. The samples were ready then for testing.

2.3. Production of Compost

The production of compost from cow manure was carried out naturally through incubating cow manure for 2 weeks. The purpose of this was to reduce the water content and to decompose the cow manure material.

2.4. Production of Humic Acid

The extraction of humic acids (HAs) from a dry sample of cow manure is the first step in humic acid synthesis. NaOH extraction with a 10:1 comparison was used to remove HA from this substance. For the analysis of HA, the same approach was used in this study as in [20]. The purification of HA from HA extract was conducted in the same way as in [21]. Equation (1) in [22] contains the formula for estimating the Humification Rate (HR) by calculating the HA (% content of humic acid) and FA (% content of fulvic acid) and comparing it to the percentage of organic C content.

$$\frac{\text{HA} + \text{FA}}{\text{Organic C}} \times 100\% \tag{1}$$

2.5. Biochar Production from Cow Manure

The first step of producing biochar from the cow manure was to weigh the air-dried biomass samples. They were then pyrolyzed at 400 °C for 90 min in an electrical muffle furnace. Proximate analysis techniques, such as volatile matter, ash content and fixed carbon, as well as the chemical characteristics of biochar, can be seen in the procedures described in [23]. The size of the biochar was 0.4 mm.

2.6. Heavy Metal Adsorption by Compost, Biochar and HA

The adsorption of heavy metals (Cr, Pb and Cd) from compost, biochar and HA was analyzed by adjusting the following variables: pH (1-9), contact time (20, 40, 60, 80 and 100 min), weight of adsorbent, by increasing the ratio of the adsorbent (0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g) in the same volume of metal solution, and metal concentrations (Pb: 6, 8, 10, 12 and 14 mg/L; Cd: 1, 3, 5, 7 and 9 mg/L; and Cr: 1, 3, 5, 7 and 9 mg/L). For each treatment, 0.5 g of each adsorbent was dissolved in 50 mL heavy metal solution (Pb 10 mg/L, Cd 5 mg/L and Cr 15 mg/L), shook for 120 min, left overnight and filtered. The heavy metals were analyzed using AAS.

2.7. Percent Removal

The percentage removal of heavy metal from the solution was calculated using the equation below [24]:

$$\%\ \text{Removal} = \frac{C_0 - C_i}{C_0} \times 100 \tag{2}$$

where C_0 and C_i are the initial and equilibrium concentration (mg/L) of metal ions in solution, respectively.

2.8. Isotherm of Adsorption

The adsorption mechanism plays a critical role in decreasing pollution levels in the environment. To determine the equilibrium adsorptive behavior, we used the Langmuir and

Freundlich equations (Equations (3) and (4) below) [24] to measure the adsorption isotherm.

$$\text{Langmuir Equation}: \frac{C_e}{q_e} = \frac{1}{b.\theta} + \frac{C_e}{\theta} \quad (3)$$

$$\text{Freundlich Equation}: \ln q_e = \ln K + \frac{1}{n}\ln C_e \quad (4)$$

where q_e is the equilibrium amount adsorbed (mg/g) and C_e is the equilibrium concentration of metal ions in solution (mg/L). In the Langmuir equation, (mg/g) is the measure of the adsorption capacity under experimental conditions, and b is a constant related to adsorption energy. Freundlich treatment yielded the n parameters, which represent the bond energies between the metal ion and the adsorbent, and K, which represents bond strength.

3. Results and Discussion

3.1. Morphological Surface of Compost, Biochar and Humic Acid

The analysis of morphological surfaces using SEM-EDX showed that the size and form of the constituent particles of adsorbents varied (Figure 2). Compost, biochar and humic acids from cow manure exhibited a morphologically irregular form. Most forms in the compost gave a more platy shape than biochar and humic acid. This variation is caused by the difference in processing level in the formation of compost, biochar and humic acids.

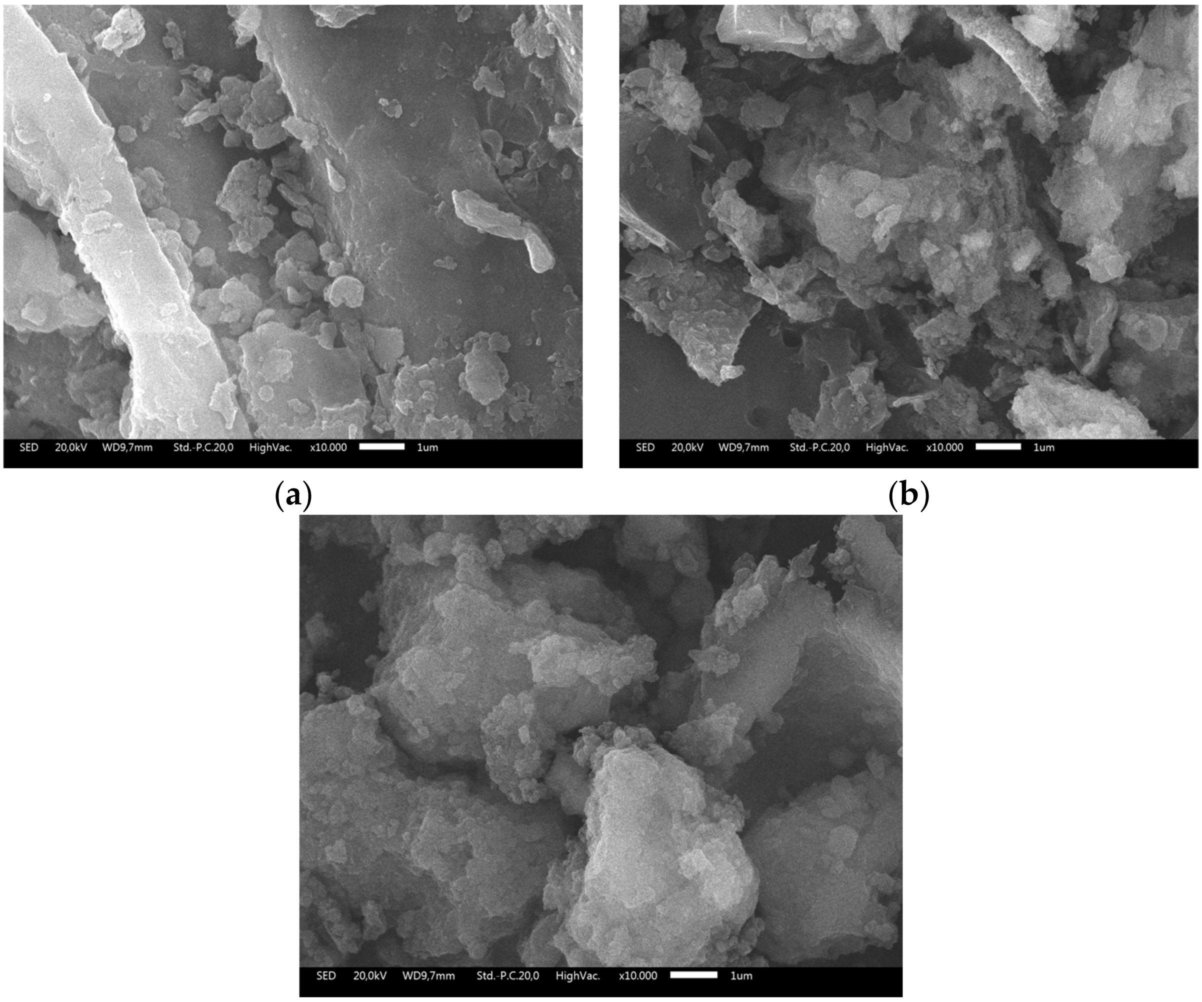


Figure 2. SEM-EDX analysis of compost (**a**), biochar (**b**) and humic acid (**c**) (10.000× magnification).

In general, the decomposition process can make a solid material's surface more porous [25]. In this case, the adsorbents of cow manure had a C:N ratio of 27 after two weeks of incubation (Section 3.2), which means that the material needed more time to fully decompose. Based on biochar morphology, the SEM-EDX analysis showed that the biochar had more pores than compost and humic acid, which was caused by an increase in the growth of pores in the biochar samples with the increase in temperature. The increase in temperature in process production could allow a significant improvement in biochar pore characteristics [26]. The morphological form of humic acid was irregular, but mostly of granular and crumb type. This is in line with the results of Rupiasih and Vidyasagar [27], where the humic acid from cow manure, vermicompost, sludge, and sediment showed granular structure (crystal-like forms aggregate in various shapes).

Table 1 shows that the major components adsorbed from the three adsorbent materials were C and O. This is in line with the work of Masruhin et al. [28], where the presence of C and O in all materials indicated that there are constituents of polyelectrolyte macromolecules that have functional groups, such as carboxyl (-COOH).

Table 1. Material composition based on SEM-EDX analysis.

Component	Content (wt%)		
	Compost	Biochar	Humic Acid
C	54.21	57.24	65.00
O	35.57	33.18	26.90
Si	3.97	4.69	0.41
Ca	2.02	1.93	0.46
Mg	0.91	0.85	-
Al	0.82	0.79	0.58
K	0.86	0.76	-
Cl	1.07	-	0.48
S	-	-	0.16
Fe	-	0.31	-
Na	-	0.24	-

3.2. Heavy Metal Adsorption of Cr, Pb and Cd

The chemical analysis results gave the compost material a pH of 6.73, water content of 10.79%, total N of 1.72%, organic C of 46%, K of 0.45%, P_2O_5 of 0.04%, a C:N ratio of 27, 0.06 mg/L of Cr, 0.10 mg/L of Pb, and 0.003 mg/L of Cd. The results of the proximate analysis of compost showed volatile matter of 82.23% and ash content of 82.34%. Humic and fulvic acid contents derived from compost were 1.84% and 6.63%, respectively. Biochar had a pH of 9, water content of 3.29%, Cr levels of 0.11 mg/L, a Pb level of 0.13 mg/L, and Cd levels of 0.008 mg/L. The nitrogen level was 2.07%, with 0.09% P and Organic C of 30.12%. The ash content was 54.93%, and the volatile matter was 49.98%, according to the proximate analysis. Humic acids had 14.38% water content, 4.04% nitrogen content and 55.06% organic C content. The Humification Rate (HR) from compost was 18.41%. The humification process can be understood as a process of synthesis or resynthesis of organic compounds, which is influenced by various factors, such as the climate, quantity and quality of plant material, and soil management [29]. The HR value shows the ratio of the organic acid content in the material. For the HR analysis, a higher HR value indicates that the formation of humic and fulvic acid content in the soil is greater than the input of fresh organic matter in the soil [22]. The general features of compost, biochar and humic acids at various pH levels in relation to heavy metal adsorption are shown above (Figure 3).

Humic acid, compost and biochar exhibited various adsorption behaviors at each acidity level. Figure 3 shows that humic acid a lower adsorption capacity than both compost and biochar. This was related to humic acid's adsorption mechanism, which was affected by pH. This can also be shown in [30], which suggested that the acidity of the solution altered the mechanism of metal adsorption. As a result of the extraction with NaOH or KOH, the negative charge of humic acids might be saturated by Na or K ions. The acids achieved optimum solubility and stability in suspension as the pH increased [31]. This mechanism is consistent with humic acid's behavior, which was dissolved in base circumstances and separated in acidic conditions [31]. Figure 3 shows that the biochar had a relatively constant adsorption capacity compared with other adsorbents. The morphological characteristics of the adsorbent material (Figure 2) could also affect the adsorption capacity of heavy metals, where materials with more pores had a greater capability of adsorbing the heavy metals than others. This is in line with [32], which showed that carbonization and calcination produced a more porous adsorbent material. This condition was different from that of humic acid, which produced the same path. In general, the mechanism of the adsorption process was influenced by the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate [24]. In general, the behavior of heavy metal Pb in relation to adsorbent humic acid produced a consistent path. The rate of heavy metal adsorption increased when the pH of the solution rose, with the optimum adsorption at a pH of 8. This is in line with [30], which showed that the adsorption behavior of lignin at various pH levels provides a consistent pattern of Pb adsorption.

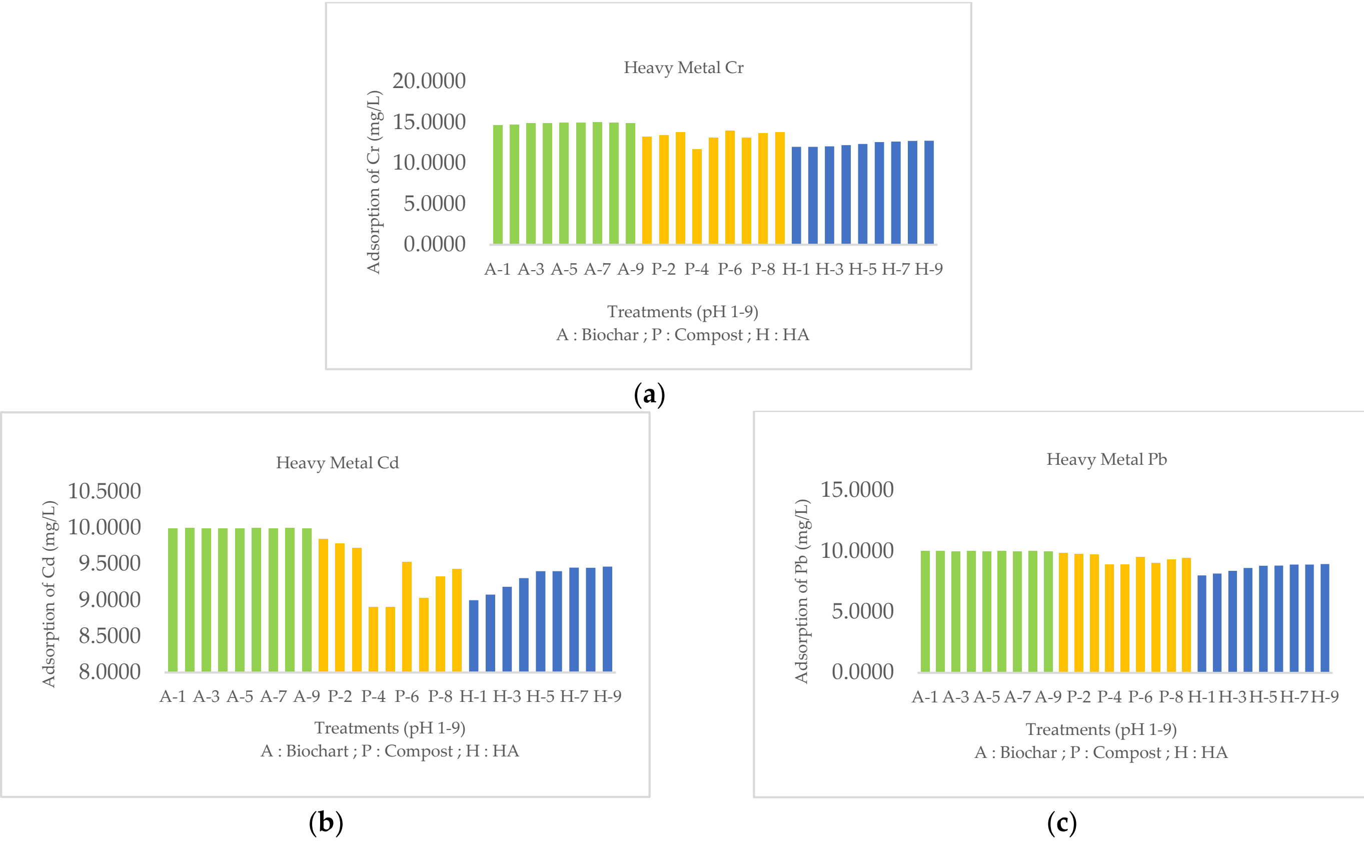
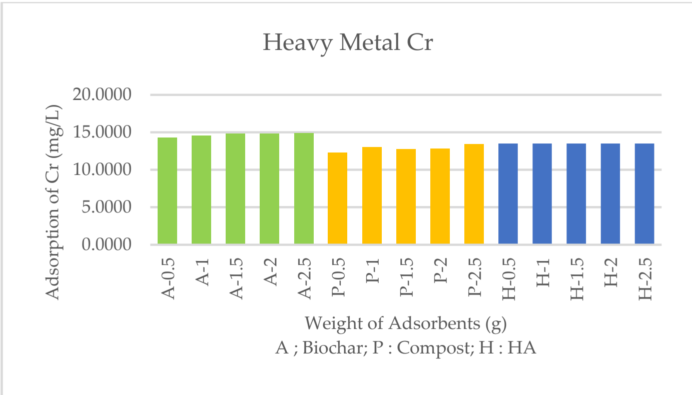
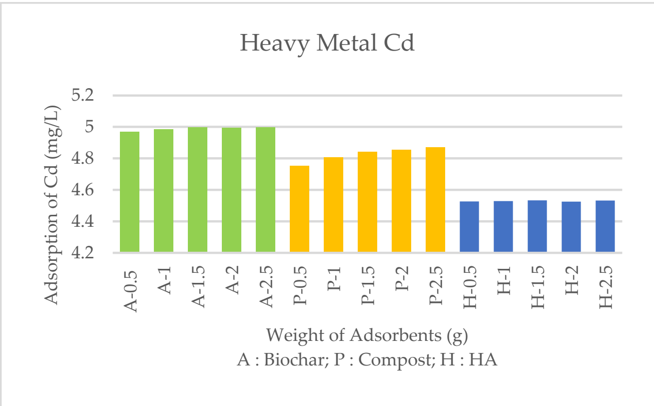


Figure 3. The adsorption of heavy metals Cr (**a**), Cd (**b**) and Pb (**c**) at various pH levels.

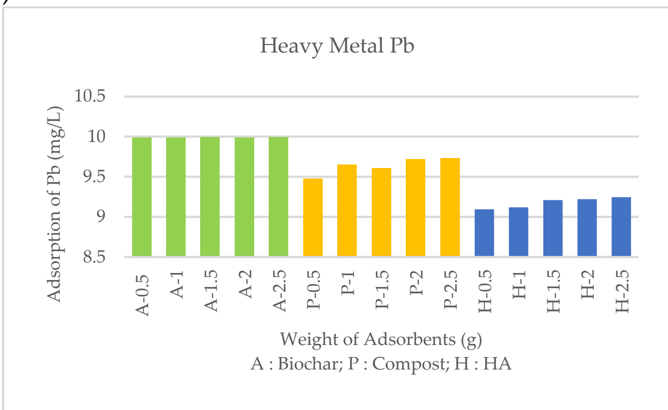
The adsorption of all heavy metals rose with an increase of the adsorbent material, as shown in Figure 4. The adsorption of Cr in solution gave a constant path with higher adsorption for three type of adsorbents than other heavy metals, and biochar was gave the higher adsorption that compost and humic acid. According to [33], biochar has a negative charge on the surface that can bind the heavy metal, which increases the adsorption process. The increase in the adsorbate in solution to be adsorbed by materials was responsible for the rise in adsorption metals [34].



(**a**)



(**b**)

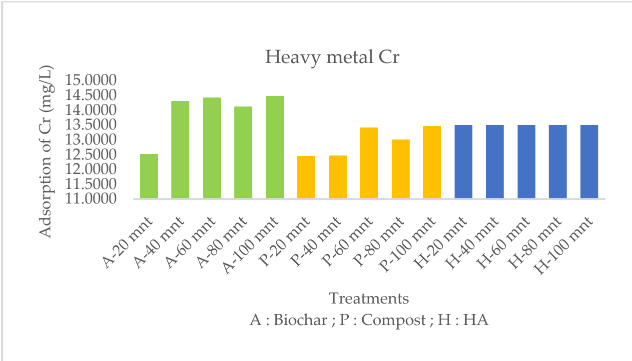


(**c**)

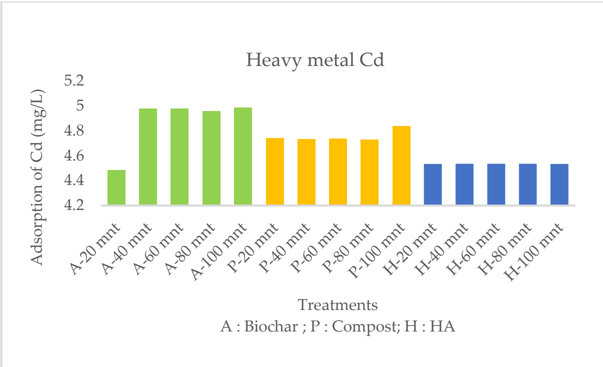
Figure 4. The adsorption of heavy metals Cr (**a**), Cd (**b**) and Pb (**c**) at various weights of adsorbent.

The adsorption of heavy metals at varied contact times during each 120 min treatment is depicted in Figure 5 (biochar, composts and humic acids).

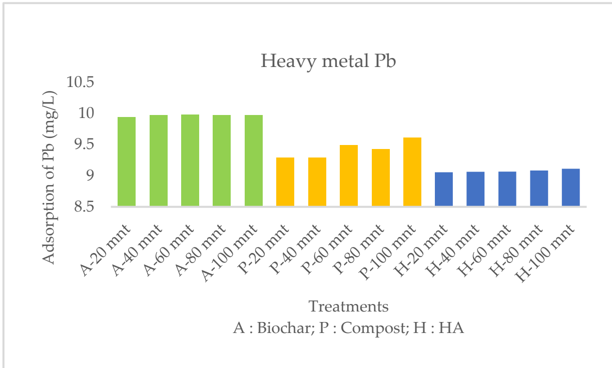
Figure 5 shows that the metal content in the solution decreased as the contact time increased. This is because the active surface of the adsorbent decreased as the contact time rose, which could decrease the adsorption rate and eventually achieve the equilibrium phase. All adsorbents followed the same path in the adsorption of Cr, Cd and Pb. The adsorption process of biochar and compost was fast in the first 20 min, but gradually slowed down from 40 to 100 min (Figure 5). The condition caused by the adsorption analytes reached the equilibrium phase between 60 and 100 min of the contact time. This is in contrast with the humic acid adsorption process, which was 1:100 (adsorbent to ml of heavy metals) in the comparison adsorbent, and showed a slowly increasing rate adsorption at different contact times. The contact time of adsorption Pb by lignin got maximum adsorption at half and hour with an adsorption efficiency of 88.77% at pH 5 [30]. On the other hand, in some studies, Pb took approximately 2 h to reach saturation until equilibrium was attained [24]. In terms of material adsorption capacity, the mechanism of increasing the adsorption showed that the analytes were still adsorbed. In general, the adsorption process was influenced by contact time, because the longer contact time can make a higher of adsorption of heavy metals in solution until saturation was reached. This effect was comparable for all of the heavy metals (Cr, Pb and Cd) and was linked to the materials' maximal adsorption, which decreased during the desorption process [30]. The qualities of the adsorbent were one of the most significant factors in the adsorption process. The adsorbent purity, adsorbent surface area (pore volume) and temperature were variables to consider [35].



(**a**)



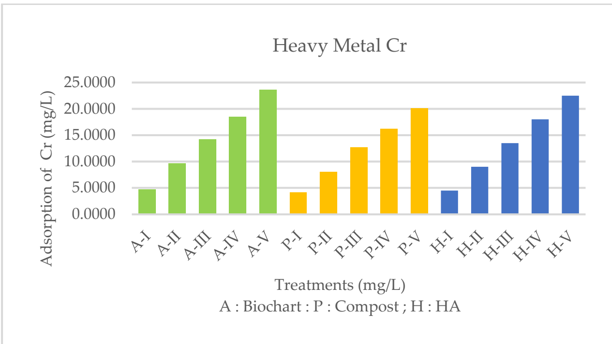
(**b**)



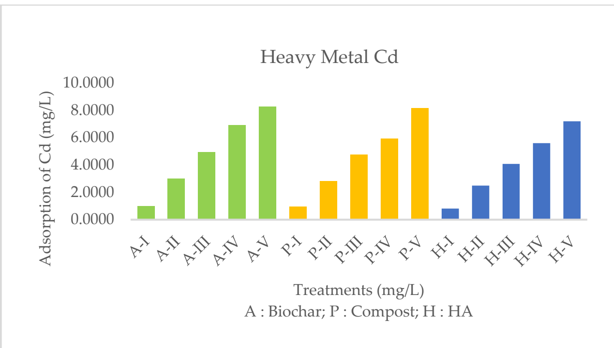
(**c**)

Figure 5. The adsorption of heavy metals Cr (**a**), Cd (**b**) and Pb (**c**) at various contact times.

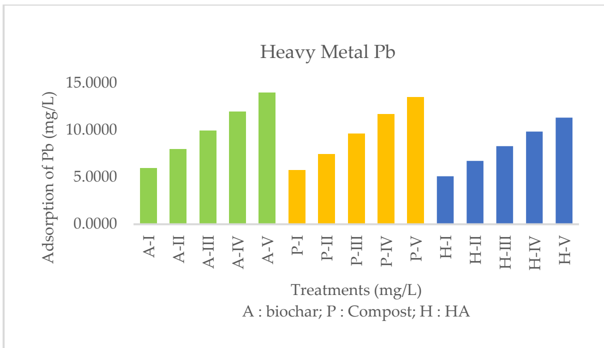
The adsorption of heavy metals at various metal concentrations is depicted in Figure 6 (biochar, compost and humic acids).



(**a**)



(**b**)



(**c**)

Figure 6. The adsorption of heavy metals Cr (**a**), Cd (**b**) and Pb (**c**) at various concentrations of metals.

The equilibrium phase was the ideal period for maximum adsorption capacity. This condition occurred when the analyte was adsorbed by the whole surface of the adsorbent, and the adsorption remained constant, since the active side of the adsorbent was covered with analyte. The analysis of the percent removal based on the mass of the adsorbent showed that the adsorption process of Cr by biochar produced 95.43 to 99.34% removal, by compost ranged from 82.05 to 83.43%, and by humic acid was 90% on average. This condition was similar to the percent removal of Pb by biochar, where the average variable was 99%, compost ranged from 94.75 to 97.32% and humic acid ranged from 90.94 to 92.46%. For heavy metal Cd removal by biochar, the average variable was 99%, compost was between 95.03 and 97.41% and humic acid was 90%. The percent removal for all the treatments can be seen in Figure 7.

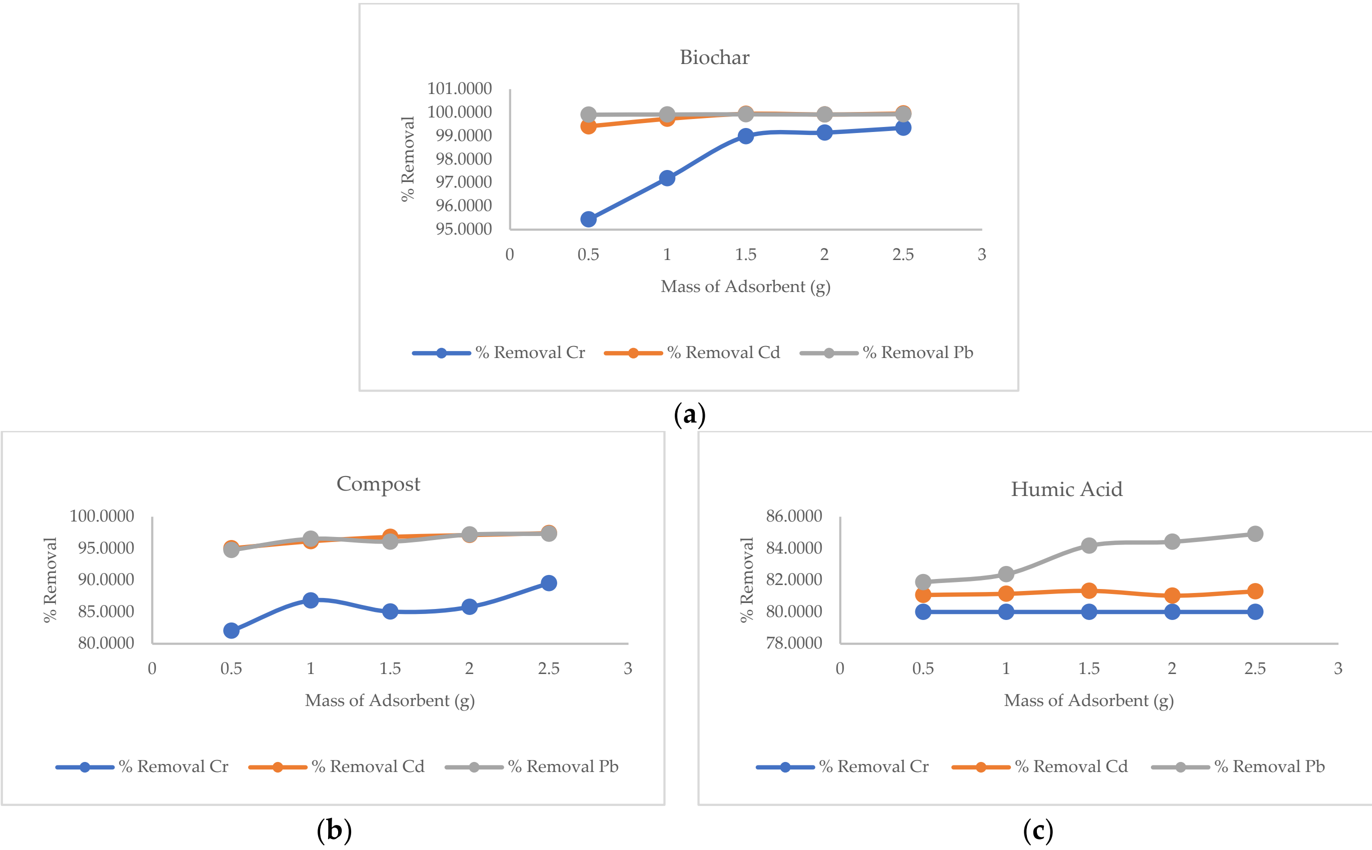


Figure 7. Percent removal of biochar (**a**), compost (**b**) and humic acid (**c**).

The percent removal of three types of adsorbents from cow manure followed a varied path, as shown in Figure 7, although in general, the percent removal of heavy metals rose with the addition of adsorbent. The percent removal was a significant indicator in determining an adsorbent's success in decreasing pollutants, as it refers to a material's maximal ability to reduce the existing pollutant content. Heavy metals were among the chemicals most commonly found in industrial waste that are harmful to humans. Heavy metals were found in the soil naturally and could not be degraded; they can stay in the soil and water for long periods of time, and rise over time [36]. Heavy metals enter animals and humans through intravascular or extravascular systems (systemic circulation) and disperse throughout the body. Minerals and heavy metals that are not essential for the body's physiological functioning accumulate in the body as toxins that are hazardous to health [37].

The results of the isotherm model study are shown in Tables 2 and 3. The three varieties of cow manure used for the adsorption of heavy metals Cr, Cd and Pb showed R^2 values ranging from 0.60 to 0.96, according to the Langmuir model study (Table 2).

Table 2. The result of the isotherm Langmuir model.

Type	Criteria	Cr	Cd	Pb
Biochar	a	0.0002	0.0012	0.0052
	b	0.0001	0.00008	0.00006
	R^2	0.9604	0.7747	0.4350
Compost	a	0.0011	0.0035	0.0013
	b	0.0046	0.0011	0.0010
	R^2	0.6016	0.9866	0.8327
Humic Acid	a	7.6264	0.1003	0.0093
	b	22.877	0.0979	0.0182
	R^2	0.8424	0.1502	0.9258

The relationship pattern for each material can be described using the calculation from Tables 2 and 3. This equation was based on R^2 and was derived from the calculation of both equations. For the biochar Cr adsorption, the model fit the Langmuir model (0.96) rather than the Freundlich model (0.62). This was different for the adsorption of Cd and Pb, which fit the Freundlich model better than the Langmuir model. The adsorption model for Cr in compost fit better with the Langmuir model (0.60) than the Freundlich model (0.55). However, the Freundlich model (0.99) outperformed the Langmuir model for Cd (0.98); similarly, the Freundlich model (0.84) exceeded the Langmuir model for Pb (0.83). Furthermore, the Langmuir model (0.84) fit the data better than the Freundlich model in the case of Cr adsorption by the humic acid adsorbent (0.81). The Langmuir model (0.92) fit better than the Freundlich model in the case of humic acid and Pb (0.91). Despite the fact that both models were extremely far from 1, the Freundlich model (0.18) matched Cd in humic acid better than the Langmuir model (0.15), necessitating another study that was more precise in predicting adsorption.

Table 3. The result of the isotherm Freundlich model.

Type	Criteria	Cr	Cd	Pb
Biochar	a	7.1446	3.7857	2.3304
	b	4.9084	0.5500	0.0861
	R^2	0.6246	0.8893	0.4952
Compost	a	2.2260	4.4303	1.6024
	b	19.0700	2.4192	0.4002
	R^2	0.5473	0.9976	0.8438
Humic acid	a	27,558	3.4677	0.1340
	b	57,782	36.93	0.1234
	R^2	0.8126	0.1773	0.9135

More than one surface was assumed for systems of adsorption that fit the Freundlich model. This refers to the several surface layers (multilayers) and the fact that the sides were heterogeneous for mechanisms that suited the Freundlich model. When the adsorption process followed the Langmuir isotherm, there was a different behavior in binding energy on each side. Adsorption processes that fit the Langmuir model suggest one-layer adsorption (monolayer). In general, the mobility of heavy metals varied depending on the metal type and the adsorption mechanism that occurred [38]. The adsorption process was influenced by the organic chemical functional groups and surface structures of materials that were altered during the raw material process. In terms of metal adsorption, raw material following the sequence Cu > Zn > Cd > Ni had the potential to be a good material for reducing metals in the environment [39].

Table 4 shows the analysis factors that produced adsorbent from cow manure with different types of forms.

Table 4. Analysis factors to produce adsorbent material.

Raw Material	Time	Estimation Cost of Process (USD)		Product of Adsorbent Result (g)	References	Range of % Removal Cd, Pb, Cr
100 g of cow manure	1 day	Laboratory cost (rent of laboratory tools)	USD 10 *	Biochar 75–80	[30]	95–99% **
100 g of cow manure	14 days	Fee of field worker	USD 15 ***	Compost 50–60	Naturally	82–97% **
100 g of cow manure	2–3 days	Laboratory cost (rent of laboratory tools and chemical materials)	USD 20 *	Humic acid 10–15	[23]	90–92% **

Description: * Price forecast of laboratory cost refers to price of chemical material from Alpha Chemika. ** Treatment variation analysis of heavy metals shown in Figure 7. *** Fee of field worker in Indonesia (two working days).

Despite the fact that all types of cow manure have the potential to adsorb heavy metals in solution, Table 4 reveals that the analysis cost from three types of adsorbents was varied. When the process of converting cow manure into other forms that could be used as adsorbents was viewed from an economic perspective (processing time, cost of analysis and adsorbent efficiency) it can be seen that biochar performed the best in terms of time. On the other hand, compost had a longer processing time than biochar and humic acid, but had the lowest production costs. This condition is different for humic acid, which requires 2–3 days to produce but in a small quantity and at a high cost, as a result of its production process being more complex than the other adsorbents. This is in line with [28], in which it was reported that the purification of humic substances might take two days to a week based on time and processing. The cost analysis of producing the three types of adsorbents should be considered in their utilization as adsorbent agents of heavy metals. On the other hand, the range of percent removal for Cd, Cr and Pb as effective adsorbent parameters in the adsorption process showed that biochar was the best material with average of percent removal higher than others (Figure 7).

4. Conclusions

Compost, biochar and humic acid derived from cow manure are potential adsorbents of the heavy metals Cd, Cr and Pb. The optimum condition was achieved for the time incubation, pH level, weight of adsorbent, and heavy metal solution (Cr, Cd and Pb). Compost, biochar and humic acid followed the adsorption isotherms of Langmuir and Freundlich models. This indicated that the adsorption rates was specific for each heavy metals. In general, the biochar > compost > humic acid adsorption pathway has a high potential for heavy metal removal. Additionally, from an economic aspect, biochar is more useful as an efficient and effective form of cow manure to adsorb of heavy metals. This material has many more pores than the other materials studied (compost and humic acid), and its morphology can increase the adsorption process of heavy metals in solution. The morphology of biochar is different to that of compost and humic acid derived from cow manure, which contain smaller pores, and thus achieve lower rates of adsorption of heavy metals.

Author Contributions: Conceptualization, O.M. and B.J.; methodology, O.M.; software, O.M.; validation, O.M., B.J. and D.K.; formal analysis, O.M.; investigation, B.J. and D.K.; resources, O.M.; data curation, O.M.; writing—original draft preparation, O.M.; writing—review and editing, O.M.; visualization, O.M.; supervision, B.J. and D.K.; project administration, O.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Education Fund Management Agency (LPDP), Indonesia, for the 2017 fiscal year.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All of the data supporting this article are included in the main text.

Acknowledgments: The authors are grateful to all lab members for their useful suggestions, support, and encouragement.

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

References

1. Herrero, M.; Thornton, P.K.; Gerner, P.; Reid, R.S. The roles of livestock in developing countries. *Animal* **2013**, *7*, 3–18. [CrossRef] [PubMed]
2. BPS. *Large and Small Livestock Establishment Statistics*; Badan Pusat Statistik: Jakarta, Indonesia, 2018; pp. 1–78.
3. BPS. *Large and Small Livestock Establishment Statistics*; Badan Pusat Statistik: Jakarta, Indonesia, 2019; pp. 1–76.
4. Weng, L.P.; Koopal, L.K.; Hiemstra, T.J.; Meeussen, C.L.; Van Riemsdijk, W.H. Interactions of calcium and fulvic acid at the goethite-water interface. *Geochim. Cosmochim. Acta* **2005**, *69*, 325–339. [CrossRef]
5. Benedetti, M.F.; Riemsdijk, W.H.; VA, N.; Koopal, L.K.; Kinniburgh, D.G. Metal ion binding by natural organic matter: From the model to the field. *Geochem. Cosmohim. Acta* **1996**, *60*, 2503–2513. [CrossRef]
6. Barakat, M.A. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* **2011**, *4*, 361–377. [CrossRef]
7. Saraswat, S.K.; Demir, M.; Gosu, V. Adsorptive removal of heavy metals from industrial effluents using cow dung as the biosorbent: Kinetic and isotherm modeling. *Environ. Qual. Manag.* **2020**, *30*, 51–60. [CrossRef]
8. Zhang, M.; Chen, X.; Xu, X.; Fu, Z.; Zhao, X. Applied sciences Evaluation of Non-Biodegradable Organic Matter and Microbial Community's Effects on Achievement of Partial Nitrification Coupled with ANAMMOX for Treating. No. I. *Appl. Sci.* **2022**, *12*, 3626. [CrossRef]
9. Gunamantha, I.M.; Widana, G.A.B. Characterization the potential of biochar from cow and pig manure for geoecology application. *IOP Conf. Ser. Earth Environ. Sci.* **2018**, *131*, 012055. [CrossRef]
10. Amanullah, M.M.; Sekar, S.; Muthukrishnan, P. Prospect and Potentially of Poultry Manure. *Asian J. Plant Sci.* **2010**, *9*, 172–182. [CrossRef]
11. Chang, Y.; Zhao, Z.; Sun, L.; Cui, J.; Liu, X.; Yao, D. Resource Utilization of Biogas Waste as Fertilizer in China Needs More Inspections Due to the Risk of Heavy Metals. *Agriculture* **2022**, *12*, 72. [CrossRef]
12. Angelova, V.R.; Akova, V.I.; Artinova, N.S.; Ivanov, K.I. The effect of organic amendments on soil chemical characteristics. *Bulg. J. Agric. Sci.* **2013**, *19*, 958–971.
13. Mulyani, O.; Machfud, Y.; Setiawan, A.; Joy, B. Potential of local organic matters in Jatinangor West Java Indonesia as raw materials for organic fertilizer. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *393*, 1–10. [CrossRef]
14. Woldetsadik, D.P.; Keraita, B.; Marschner, B.; Itanna, F.; Gebrekidan, H. Effects of biochar and alkaline amendments on cadmium immobilization, selected nutrient and cadmium concentrations of lettuce (*Lactuca sativa*) in two contrasting soils. *Springerplus* **2016**, *5*, 1–16. [CrossRef] [PubMed]
15. Agnew, J.M.; Leonard, J.J. The physical properties of compost. *Compost Sci. Util.* **2003**, *11*, 238–264. [CrossRef]
16. Arancon, N.Q.; Edwards, C.A.; Lee, S.; Byrne, R. Effects of humic acids from vermicomposts on plant growth. *Eur. J. Soil Biol.* **2006**, *42*, 65–69. [CrossRef]
17. Mulyani, O.; Joy, B.; Kurnia, D. A Case Study in Cianjur West Java, Indonesia: A Correlation Humic and Fulvic Acids with Mineralogical Composition and Physico-Chemical Analysis Using Partial Least Square. *J. Ecol. Eng.* **2021**, *22*, 191–204.
18. Mulyani, O.; Sudirja, R.; Joy, B.; Hanandiva, R.A. The Effect of Organomineral on pH, Nitrogen Content, Organic-C Content and Yield of Upland Rice (*Oryza sativa* L.) on Inceptisols, West Java Indonesia. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, *334*, 012071. [CrossRef]
19. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* **2011**, *92*, 407–418. [CrossRef] [PubMed]
20. Haddad, G.; El-ali, F.; Mouneimne, A.H. Humic Matter of Compost: Determination of Humic Spectroscopic Ratio (E4/E6). *Curr. Sci. Int.* **2015**, *4*, 56–72.
21. Oliveira, L.D.S.; Cristina, M.; Costa, G.; De Souza, H.A.; Blum, J. Characterization of Organic Wastes and Effects of Their Application on the Soil. *J. Agric. Sci.* **2018**, *10*, 291–298. [CrossRef]

22. Putra MJ NF, I.A.; Soemarno, S.; Suntari, R. Humification degree and its relationship with some soil physical characteristics on robusta coffee (*Coffea canephora*) plantation. *J. Degrad. Min. Lands Manag.* **2016**, *3*, 649–658. [CrossRef]
23. Ronsse, F.; Van Hecke, S.; Dickinson, D.; Prins, W. Production and characterization of slow pyrolysis biochar: Influence of feedstock type and pyrolysis conditions. *GCB Bioenergy* **2013**, *5*, 104–115. [CrossRef]
24. El-Ashtoukhy, E.S.Z.; Amin, N.K.; Abdelwahab, O. Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. *Desalination* **2008**, *223*, 162–173. [CrossRef]
25. Manohara, B.; Belagali, S.L. Evaluation of energy dispersive scanning electron microscopy and X-ray fluorescence techniques for analysis of compost quality. *Anal. Methods* **2017**, *9*, 253–258. [CrossRef]
26. Ma, X.; Zhou, B.; Budai, A.; Jeng, A.; Hao, X.; Wei, D.; Zhang, Y.; Rasse, D. Study of Biochar Properties by Scanning Electron Microscope–Energy Dispersive X-ray Spectroscopy (SEM-EDX). *Commun. Soil Sci. Plant Anal.* **2016**, *47*, 593–601. [CrossRef]
27. Rupiasih, N.N.; Vidyasagar, P.B. Analytical study of humic acid from various sources commonly used as fertilizer: Emphasis on heavy metal content. *Int. J. Des. Nat. Ecodyn.* **2009**, *4*, 32–46. [CrossRef]
28. Yang, K.; Miao, G.; Wu, W.; Lin, D.; Pan, B.; Wu, F.; Xing, B. Sorption of Cu^{2+} on humic acids sequentially extracted from a sediment. *Chemosphere* **2015**, *138*, 657–663. [CrossRef] [PubMed]
29. Tavares, R.L.M.; Nahas, E.E. Humic fractions of forest, pasture and maize crop soils resulting from microbial activity. *Brazilian J. Microbiol.* **2014**, *45*, 963–969. [CrossRef] [PubMed]
30. Masruhin, M.; Rasyid, R.; Yani, S. Penjerapan Logam Berat Timbal (Pb) dengan Menggunakan Lignin Hasil Isolasi Jerami Padi. *J. Chem. Process Eng.* **2018**, *3*, 6. [CrossRef]
31. Mindari, W.; Aini, N.; Kusuma, Z. Effects of humic acid-based buffer + cation on chemical characteristics of saline soils and maize growth. *J. Degrad. Min. Lands Manag.* **2014**, *2*, 259–268. [CrossRef]
32. Ighalo, J.O.; Adeniyi, A.G. A mini-review of the morphological properties of biosorbents derived from plant leaves. *SN Appl. Sci.* **2020**, *2*, 1–16. [CrossRef]
33. Wu, Q.; Xian, Y.; He, Z.; Zhang, Q.; Wu, J.; Yang, G.; Zhang, X.; Qi, H.; Ma, J.; Xiao, Y.; et al. Adsorption characteristics of Pb(II) using biochar derived from spent mushroom substrate. *Sci. Rep.* **2019**, *9*, 1–11. [CrossRef] [PubMed]
34. Elaigwu, S.E.; Usman, L.A.; Awolola, G.V.; Adebayo, G.B.; Ajayi, R.M.K. Adsorption of Pb (II) from Aqueous Solution by Activated Carbon Prepared from Cow Dung. *Environ. Res. J.* **2009**, *3*, 442–446. [CrossRef]
35. Adam, M.R.; Othman, M.; Kadir, S.H.S.A.; Sokri, M.Z.S.; Iwamoto, Y.; Tanemura, M.; Honda, S.; Rahman, M.A.; Jaafar, J. Influence of the natural zeolite particle size toward the ammonia adsorption activity in ceramic hollow fiber membrane. *Membranes* **2020**, *10*, 63. [CrossRef]
36. Kannan, R.; Ganesan, M.; Govindasamy, C.; Rajendran, K.; Sampathkumar, P.; Kannan, L. Tissue concentration of heavy metals in seagrasses of the Palk Bay, Bay of Bengal. *Int. J. Ecol. Environ. Sci.* **1992**, *18*, 29–34. [CrossRef]
37. Raikwar, M.K.; Kumar, P.; Singh, M.; Singh, A. Toxic effect of heavy metals in livestock health. *Vet. World* **2008**, *1*, 28–30. [CrossRef]
38. McLaren, R.G.; Clucas, L.M.; Taylor, M.D.; Hendry, T. Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 2. Leaching of metals. *Aust. J. Soil Res.* **2004**, *42*, 459–471. [CrossRef]
39. Liu, L.; Guo, X.; Zhang, C.; Luo, C.; Xiao, C.; Li, R. Adsorption behaviours and mechanisms of heavy metal ions' impact on municipal waste composts with different degree of maturity. *Environ. Technol.* **2019**, *40*, 2962–2976. [CrossRef]