IIETA International Information and Engineering Technology Association
Advancing the World of Information and Engineering

International Journal of Design & Nature and Ecodynamics
Vol. 19, No. 1, February, 2024, pp. 259-265
Journal homepage: http://iieta.org/journals/ijdne

Optimizing the Performance of Sunflower (Helianthus annuus L.) Seed Shell-Derived Biochar for Lead Ion Adsorption

Bunga Elim Somba[1*], Mery Napitupulu[2], Daud K. Walanda[2], Alam Anshary[1], Wardah Shafiyah Talo[2]

[1] Department of Agrotechnology, Faculty of Agriculture, Tadulako University, Palu 94118, Indonesia
[2] Department of Science Education, Faculty of Education, Tadulako University, Palu 94118, Indonesia

Corresponding Author Email: elimsomba1961@gmail.com

https://doi.org/10.18280/ijdne.190128

Received: 2 December 2023
Revised: 26 January 2024
Accepted: 2 February 2024
Available online: 29 February 2024

Keywords:
sunflower, biochar, lead removal, adsorption, pyrolysis, remediation

ABSTRACT

Sunflower seed shells are agricultural waste that is abundant and often underutilized. Converting these shells into biochar for lead ion adsorption not only provides a value-added use for the waste material but also addresses the issue of agricultural residue management. Sunflower seed shell biochar is produced through a pyrolysis process, transforming the agricultural waste into a carbon-rich material with a high surface area and porous structure. The study aims to determine the effect of biochar derived from sunflower seed shells (BSFL) as an adsorbent by determining the optimum pH and optimum weight in absorbing lead ions. Water content and ash content were determined using the drying and dusting method. The research results showed that the characteristics of sunflower seed shell biochar were 45%, the water content was 3.6% and the ash content was 7.2%. Determination of the optimum pH varied from 3, 4, 5, and 6 while determination of optimum weight was carried out with weight variations of 30 mg, 60 mg, 90 mg, 120 mg, and 150 mg respectively. The research results showed that the optimal pH of sunflower seed shell biochar for adsorbing lead was 5 with the percentage of adsorbed was 99.58%. Meanwhile, the optimum weight of biochar to adsorb Lead ions is 120 mg with a percentage of Lead adsorbed is 99.71%. The pH influences the surface charge of the biochar and the speciation of lead ions, while the weight determines the available surface area for adsorption. Biochar morphology pore and the content of the element characterized by SEM-EDS indicated the macropores and the carbon content of 62.65%. The finding contributes to reducing environmental pollution, addressing waste management challenges, and leveraging biochar's efficiency for the removal of lead ions from contaminated water sources, providing insights into the key factors influencing its adsorption capacity.

1. INTRODUCTION

The contamination of water bodies with heavy metals, particularly lead, has become a pressing environmental concern due to its toxic effects on human health and the ecosystem. Various industries, including mining, metallurgy, and manufacturing, contribute significantly to the release of lead ions into the environment, leading to widespread pollution [1]. Environmental pollution due to heavy metal processing waste is becoming a concern as industry develops. Pollution by heavy metal waste is caused by a lack of waste processing resulting from the production process before being discharged into the environment. The waste produced generally contains many metal elements such as lead, cadmium, cobalt, copper, and so on [2]. Most of this heavy metal waste is toxic, mutagenic, and carcinogenic and can endanger human health [3].

Conventional methods for lead ion removal from contaminated water, such as chemical precipitation and ion exchange, often exhibit limitations in terms of cost, efficiency, and environmental impact. Therefore, there is an increasing demand for the development of sustainable and cost-effective approaches for the remediation of lead-contaminated water fields [4].

Biochar, a carbon-rich material derived from the pyrolysis of biomass, has garnered considerable attention as a promising adsorbent for heavy metal removal due to its high surface area, porosity, and potential for metal ion binding. Sunflower (Helianthus annuus L.) seed shell, an agricultural waste product abundant in carbon content, presents a viable and eco-friendly precursor for the production of biochar. Biochar is a solid material that has a high carbon content produced from the pyrolysis process. When compared to activated carbon, biochar is considered cheaper, because it does not require chemicals for activation [5]. More and more research materials are modifying biochar to increase its adsorption capacity, but biochar modification can cause waste and pollution from chemical reagents and biochar modification is quite expensive. Biochar comes from materials containing lots of lignin and cellulose from plant waste such as rice husks [6], rice straw [7], and other agricultural waste [8]. Making biochar is generally very simple because the basic ingredients come from waste that is no longer used and are easy to find.

Several studies on the use of biochar as an adsorbent have been carried out previously such as biochar derived from young coconut shells [9], cacao dried leaves [10], corn stalks [11], durian bark [12], bananas' peels and stems [13], and ketapang shells [14]. The modeling and optimization of biochar-based adsorbents derived from kenaf [15], and red fruit peel (freycinetia arborea gaudich) [16] using response surface methodology regarding Cd^{2+} adsorption, the research results show that pyrolysis temperature and heating time are the main factors that influence biochar yield and have a positive effect on Cd^{2+} removal rate and adsorption capacity.

Sunflowers are one type of agricultural plant cultivated in Indonesia. Sunflowers are plants from the Asteraceae family, the Helianthus genus, and more than seventy species known throughout the world [9]. One of the wastes produced from processing sunflower seeds is sunflower seed shells. Usually, sunflower seed shell waste is thrown away. One solution to this condition is to turn waste into a useful product by processing waste sunflower seed shells which contain the same content as peanut shells [10]. Sunflower seed shells contain lignocellulose which can produce an energy source in the form of carbohydrates. The main organic macronutrients of sunflower seed coats are lipids, carbohydrates, and proteins, with lignin 20-25% of the total weight. The total organic carbon derived from cellulose, hemicellulose, and lignin accounts for more than 40%, making the C/N ratio quite high. Lignin, a complex aromatic polymer, contributes to the structural stability and porous nature of biochar. This structural characteristic enhances the surface area available for adsorption, providing ample sites for metal ion binding. Cellulose and hemicellulose, on the other hand, undergo thermal decomposition during pyrolysis, leaving behind carbonaceous residues. These residues contribute to the overall carbon content of the biochar, influencing its adsorption properties. The lipid and protein contents are about 5% and 4% respectively, and nearly 3% of the lipids are waxes, fatty acids, and alcohol [9].

This study aims to investigate the performance of biochar derived from sunflower seed shell (BSFL) as an adsorbent for lead ion removal from aqueous solutions. The biochar's physicochemical properties, such as surface area, and pore structure will be characterized and correlated with its adsorption capacity for lead ions. Additionally, the influence of various parameters, including pH, contact time, initial concentration, and temperature, on the adsorption efficiency will be systematically evaluated. It is predicted that a greater weight of biochar will affect the adsorption capacity at a certain pH. The findings of this research endeavor hold the potential to contribute to the development of sustainable and efficient strategies for the remediation of lead-contaminated water, utilizing biochar derived from readily available agricultural residues.

2. MATERIALS AND METHODS

2.1 Preparation of biochar

Sunflower seed shells are washed using clean water to remove dirt and then dried under the sun. The dried sunflower seed shells are then burned (pyrolysis) using a furnace at a temperature of 350℃ for 2 hours. The resulting biochar was crushed using a mortar and pestle, then sifted using an 80-mesh sieve to collect the more uniform and consistent particle size distribution of biochar. Perform analysis to determine the physicochemical properties of the produced biochar, including water and ash content, surface.

2.2 Characterization of biochar

To analyze the water content in biochar, 2 grams of BSFL was placed in a porcelain cup of known weight. Next, the porcelain cup containing the sample was placed in the oven at 110°C for 1 hour. Then the sample was cooled in a desiccator for 15 minutes and weighed. Furthermore, 2 grams of BSFL were weighed and placed in the porcelain which the weight was measured. Then it was put into a furnace at a temperature of 600℃ until a constant weight was achieved, ensuring complete ashing process. After that, the sample was cooled in a desiccator for 15 minutes and then weighed it.

2.3 Determination of biochar adsorption capacity on lead ion

50 mL of 80 ppm lead solution was placed into 4 flasks, then an acetate buffer solution was added. The pH was monitored using a calibrated pH meter, and the addition of the acetate buffer was carefully controlled until the target pH 3, 4, 5, and 6 reached. After that, the lead solution was mixed by adding 0.2 grams of biochar. Next, the flask was shaken with a shaker for 10 minutes and then set aside for 24 hours. The next step is filtering by using the 0.45 μm pore size filter paper to ensure efficient separation without compromising the integrity of the biochar or the filtrate, The filtrate obtained is then analyzed using AAS to determine the effect of pH on the adsorption capacity of biochar.

To determine the effect of biochar weight, 30, 60, 90, 120, and 150 mg of biochar were mixed with 50 mL of 80 ppm lead solution and the optimum buffer solution obtained in the previous step, in a 100 mL flask. The mixture was shaken with a shaker for 10 minutes and then left for 24 hours. The filtrate was obtained through filtration followed by analysis of the Lead ion concentration using AAS.

A series of standard lead solutions with known concentrations were prepared and analyzed using AAS to construct a calibration curve. The calibration curve was used to establish a linear relationship between the absorbance and the concentration of lead ions. Calibration standards covered the expected concentration range of lead ions in the experimental samples. The AAS method was validated through the analysis of certified reference materials containing known concentrations of lead ions. The obtained results were compared with the certified values to assess the accuracy and precision of the AAS technique.

3. RESULTS AND DISCUSSION

3.1 Biochar characteristic

The product of Pyrolysis raw material and the analysis of water and ash content are presented in Table 1.

Table 1 shows that the yield of BSFL is 45%, indicating the efficiency of the conversion process. The resulting yield depends on the type of raw material, water content, and conditions for making biochar (pyrolysis), especially regarding temperature and heating time [11]. The water content of sunflower seed shell biochar was 3.6%. This is because the raw material is completely dry so the water content contained in biochar is small. The number of water content will greatly influence the absorption capacity. Based on National Indonesia Standard (SNI) number 06-3730-1995, the permitted water content in powder form is a maximum of 15%. Meanwhile, the ash content of BSFL was 7.2%. This is caused by the content of inorganic elements oxidizing to form ash compounds at high temperatures, causing deposits of inorganic elements to stick to the surface of the biochar [12]. The obtained water content satisfies the conditions with a water content of >5% and satisfies the technical activated charcoal SNI 06-3730-1995 quality requirements. Because charcoal is hygroscopic, its moisture content and the specific gravity of the material it is made of are strongly correlated. In contrast to heavy materials like wood, materials with low specific gravity have a binding structure between carbon particles that is less compact and has spaces that are filled with water vapor from the air, which leads to more excellent water content [13]. The material's moisture content, ash content, volatile matter content, carbon content, and calorific value are all unaffected significantly by its density level. Nonetheless, the material's fuel power and compressive strength are significantly impacted by its density [14].

Table 1. Characteristics of sunflower seed shell biochar (BSFL)

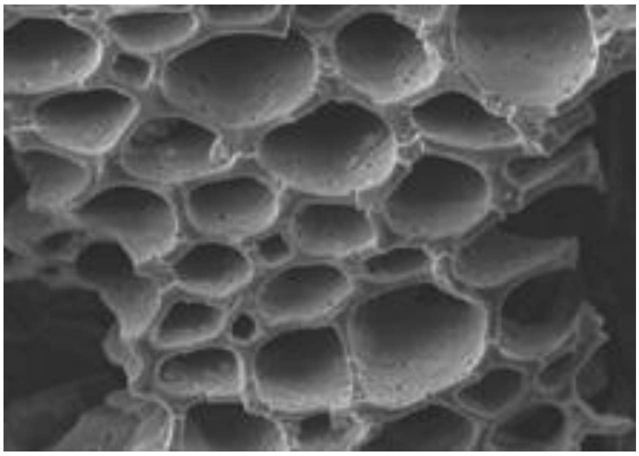
Sample	Pyrolysis Temperature	Yield (%)	Water Content (%)	Ash Content (%)
Sunflower seed shells	350	45	3.6	7.2

On the other hand, the ash content increases with increasing pyrolysis temperature. In line with the research [15]. This is because the concentration of mineral materials increases gradually as the pyrolysis temperature increases. The biochar surface area is decreased when the pores become clogged due to an excessive ash content [16]. The lower the ash content, the higher the fuel's calorific value because ash cannot burn or produce heat [15]. The amount of metal oxidation in activated carbon is determined by the ash content. Minerals and carbon compounds are present in activated carbon that is derived from natural materials. The amount of ash in the activated carbon will reveal its mineral composition [6].

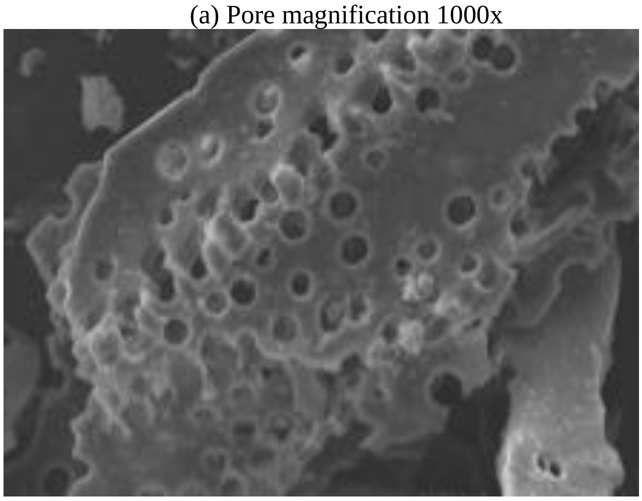
3.2 SEM-EDS of BSFL

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) aims to find out the surface morphology of the sample and the element content in the sample. The results of the Scanning Electron Microscopy (SEM) are shown in the following image (a) 1000x magnification, (b) 2000x magnification, (c) 5000x magnification, and (d) 10000x magnification.

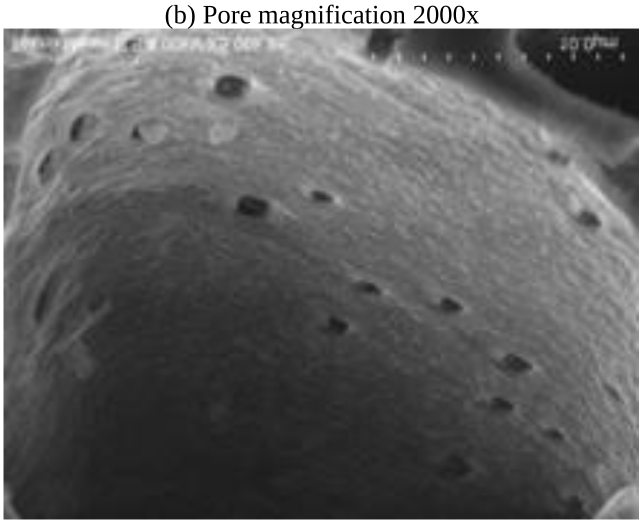
Figure 1 shows the morphology of the biochar sample. The microstructure of biochar with a magnification of 1000-10,000x shows that the morphology of the biochar sample is honeycomb-shaped and has a porous surface that is evenly distributed and the pore size is quite large, but the pore size is not uniform. A good pore structure can make it easier for electrolyte ions to diffuse on the biochar surface [16]. Based on pore size, IUPAC divides porous materials into three categories, namely micropores (< 2 nm in diameter), mesopores (2 – 50 nm in diameter), and macro pores (> 50 nm in diameter). Each of these pores has a specific function in the absorption process. Mesopores have the function of capturing absorbed material and acting as an entrance to the micropore [17]. Macro pores have the function of accelerating adsorbate molecules towards smaller pores that are located in deeper fields [18]. Meanwhile, the pores that play the most role in adsorption are micropores. Absorption will increase with the smaller the particle size. This is due to the increase in pore area in the adsorbent and more ions will be absorbed on the surface of the biosorbent [18]. The elemental composition and distribution within BSFL are shown in Figure 2.



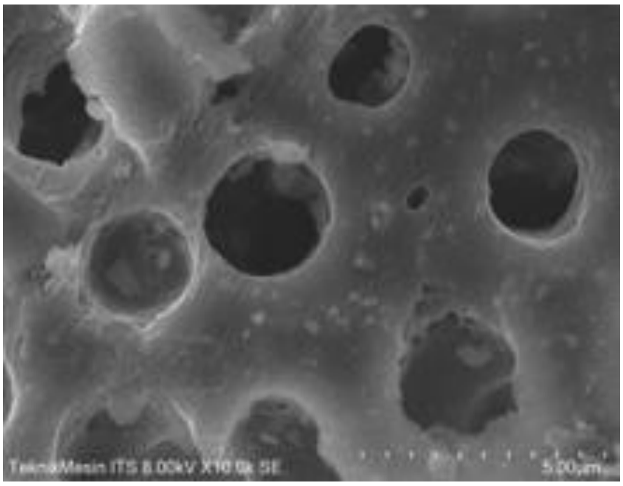
(a) Pore magnification 1000x



(b) Pore magnification 2000x



(c) Pore magnification 5000x



(d) Pore magnification 10,000x

Figure 1. Pore surface structure analysis of BSFL was performed using a scanning electron microscope (SEM) with magnification 1000x (a), 2000x (b), 5000x (c), and 10000x (d)

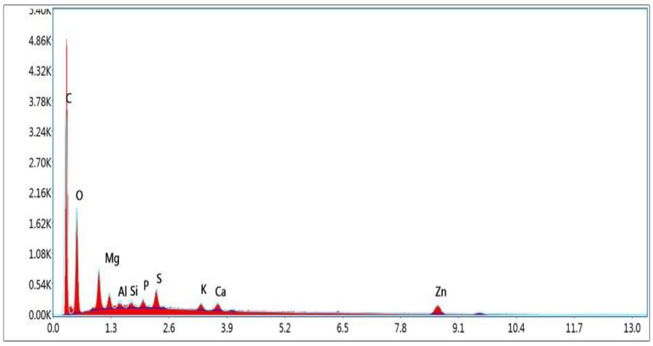


Figure 2. EDS analysis shows the distribution of carbon and other elements in BSFL

Table 2. Elemental content biochar

Element	Weight %	Atomic %
C	51.97	62.65
O	36.65	33.17
Mg	1.64	0.97
Al	0.65	0.35
Si	0.50	0.26
P	0.66	0.31
S	1.40	0.63
Ca	0.89	0.32
K	0.64	0.24
Zn	5.02	1.11

Table 2 shows BSFL contains elements including 62.65% carbon, 33.17% oxygen, 0.97% magnesium, 0.35% aluminum, 0.26% silicon, 0.31% phosphorus, 0.63% sulfur, 0.24% potassium, 0.32% calcium and 1.11% zinc. The carbon content in BSFL is relatively high, which is more than 60%. The organic C content in biochar is limited by several organic plant residues such as cellulose. The cellulose that is still contained in biochar contains 37% carbon and 43-45% inorganic minerals [19]. Carbonization is characterized by the degradation of non-carbon atoms, thereby increasing the C content [20].

3.3 Measurement of adsorption capacity of BSFL on lead ion with pH variations

One of the factors that influence the adsorption of metal ions is pH [21, 22]. The relationship between pH and lead adsorption can be seen in Figure 3. Figure 3 indicates that the higher the pH, the greater the adsorption power. Adsorption at pH 3.4 and 5 shows an increase in adsorption capacity, where at pH 3 the absorption capacity is 99.39%, at pH 4 99.49%, and at pH 5 it reaches 99.58%. This is because at low pH, the surface of the biosorbent will be surrounded by H^+ so that the surface is positively charged and this condition causes a repulsive force between metal ions and the biosorbent, and little metal is absorbed [23].

The pH of the solution affects the surface charge of the BSFL. At different pH levels, the functional groups present on the biochar's surface (such as -COOH, -OH, etc.) may become protonated or deprotonated, altering the overall charge of the biochar surface [24]. This, in turn, can influence the attraction or repulsion between the lead ions and the biochar surface. As the pH increases, the hydrogen ion concentration will decrease, so that the surface of the biosorbent becomes negatively charged, and the interaction between metal ions and the bio adsorbent results in a high adsorption capacity [25]. Lead ions exist in solution in different forms depending on the pH. At higher pH levels, lead ions may form hydroxide precipitates or complexes, altering their availability for adsorption onto the BSFL surface. Changes in pH can affect the speciation and solubility of lead ions, thereby influencing their adsorption onto the biochar.

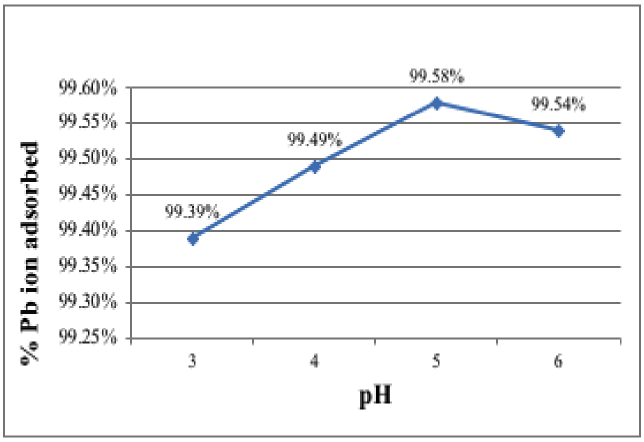


Figure 3. The curve of the relationship between BSFL solution pH and % lead adsorbed

Furthermore, there was a less significant decrease at pH 6 where the absorption capacity was decreased to 99.54%. The optimum pH for the adsorption of lead ions is pH 5 and equilibrium is achieved for lead with a contact time of 20 minutes [26]. The optimal pH for lead ion adsorption onto BSFL is 5. In some cases, certain pH ranges might enhance the adsorption capacity due to favorable surface charge characteristics of the biochar or the lead ion speciation [27]. However, at extreme pH values, the surface charge of the biochar or the solubility of lead ions might hinder effective adsorption. Variations in pH can impact the presence of other ions or compounds in the solution, potentially competing with lead ions for adsorption sites on the biochar [28]. The presence of other ions might hinder or enhance the adsorption capacity of BSFL for lead ions depending on their chemical properties.

Studying the adsorption capacity of BSFL on lead ions across a range of pH values allows the determination of the optimum pH conditions for maximum adsorption. This information is crucial for practical applications and for designing efficient adsorption systems.

3.4 Measurement of adsorption capacity of BSFL on lead ion with weight variations

Another factor that influences adsorption is the weight of the adsorbent. The relationship between adsorbent weight and lead adsorption can be seen in Figure 4.

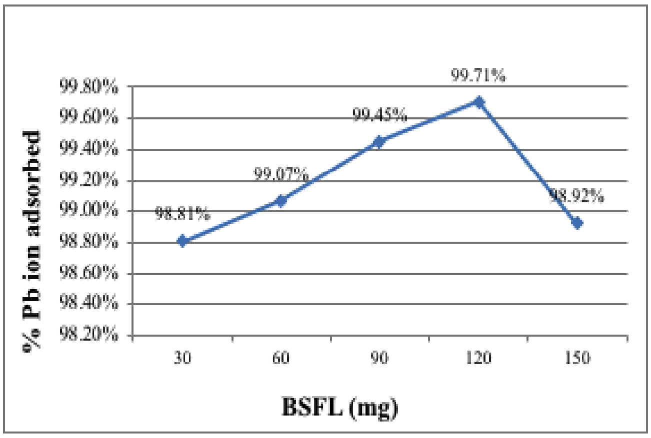


Figure 4. The curve of the relationship between adsorbent weight and % lead ion adsorbed

Figure 4 shows the percentage of lead ion adsorbed with variations in carbon weight. The lead ion adsorption process occurred as the mass of BSFL increased from a weight of 30 mg to a weight of 120 mg with a percentage of 98.81% to 99.71%.

The graph shows that the weight of the adsorbent affects the adsorption capacity because as the weight of the adsorbent increases, the amount of lead ion adsorbed increases and reaches equilibrium up to 120 mg BSFL. The increase can be attributed to the availability of more adsorption sites on the biochar surface. At a weight of 150 mg, the adsorption process is declared to have stopped because based on the value of the percentage of lead ion adsorbed it has approached equilibrium. This is because the number of adsorbate molecules that bind to the adsorbent was decreased [29]. The amount of adsorbent affects the adsorption process where increasing mass causes the adsorbent to reach a saturation point if the surface is filled with adsorbate. This saturation phenomenon may be attributed to the saturation of available adsorption sites. So, the mass BSFL of 120 mg was determined as the optimum mass. The increase in adsorption is related to the amount of adsorbent, an increase in efficiency, and a decrease in adsorption [30].

An increase in the weight or dosage of BSFL tends to enhance the adsorption capacity for lead ions. Higher amounts of biochar provide more available surface area and active sites for lead ions to bind, leading to increased adsorption [31]. This increase in adsorption capacity is often proportional to the amount of biochar used, up to a certain point where saturation or equilibrium may occur [32]. More weight of BSFL typically means a higher surface area and pore volume available for lead ions to adhere to. This increased surface area provides more active sites and interaction sites for the lead ions to attach and be adsorbed [33]. The optimal weight or dosage of BSFL for achieving maximum adsorption capacity is 120 mg. At this point adding more biochar shows there is no significant increase in the adsorption capacity further, indicating saturation or reaching the maximum adsorption capacity of the available surface area [34]. After reaching the optimal dosage, the relationship between the weight of BSFL and adsorption capacity might display diminishing returns. This means that adding additional biochar might not proportionally increase the adsorption capacity and could lead to the wastage of resources [35]. Conducting adsorption experiments with varying weights of BSFL allows the determination of the optimal dosage for achieving maximum adsorption efficiency. This information is vital for designing effective adsorption systems or remediation techniques.

The saturation point in lead ion adsorption on sunflower seed shell biochar provides valuable insights for optimizing biochar utilization in practical applications. This understanding contributes to the development of efficient and cost-effective water treatment strategies, aligning with the broader goals of sustainability and environmental stewardship.

4. CONCLUSION

The pyrolysis of sunflower seed shells at 350°C resulted in the production of biochar with promising characteristics. The yield of biochar was found to be 45%, exhibiting a notable conversion efficiency from the precursor material. Furthermore, the biochar demonstrated a low water content of 3.6% and an ash content of 7.2%, indicating its suitability for adsorption applications. Adsorption studies revealed that variations in pH significantly influenced the adsorption capacity of BSFL for lead ions. The surface charge properties of BSFL and the speciation of lead ions at different pH levels played a crucial role in determining the adsorption efficiency. Optimal adsorption was observed at a specific pH range, highlighting the pH-dependent behavior of the adsorption process. Optimum adsorption of lead ion by BSFL based on pH variations occurs at pH 5 with a percentage of lead metal absorbed of 99.58%. The results were obtained from an initial lead ion concentration of 4 mg/L. The variations in the weight or dosage of BSFL showed a direct correlation with its adsorption capacity. Higher weights of BSFL generally resulted in increased adsorption due to the greater availability of active sites and surface area for lead ion binding. However, beyond an optimal dosage, a plateau effect or diminishing returns were observed, suggesting a saturation point in adsorption capacity. The optimum adsorption of lead ion by BSF based on variations in adsorbent weight occurred at 120 mg with a percentage of lead metal absorbed of 99.71%.

The findings of this study signify the potential of sunflower seed shell biochar (BSFL) as a viable and eco-friendly adsorbent for lead ion removal from aqueous solutions. Understanding the pH-dependent behavior and dosage optimization is crucial for practical applications in water remediation and purification processes. The study's findings can be more effectively translated into actionable insights for water treatment practitioners and decision-makers. Moving forward, further research into the kinetics, thermodynamics, and real-world applications of BSFL as a lead ion adsorbent is warranted. Addressing factors such as scale-up feasibility, cost-effectiveness, and long-term efficacy will contribute to the practical implementation of BSFL in environmental remediation strategies.

Future work endeavors could focus on investigating the structural integrity, functional stability, and overall performance of sunflower seed shell biochar under continuous use and various regeneration cycles. Such insights would contribute to the development of robust and durable water treatment systems that can withstand the challenges posed by extended operational periods and repeated use in practical applications. This emphasis on biochar stability ensures a more complete picture of its long-term effectiveness and guides its potential integration into sustainable and resilient water treatment strategies.

ACKNOWLEDGMENT

The author is grateful to the Chemistry Education study program students for collecting the sample, including the Lab Assistants at the Faculty of Animal Husbandry Laboratory and the Teacher Training and Education Faculty Laboratory, who have helped a lot. The research grant from the Graduate studies is highly appreciated.

REFERENCES

[1] Liu, Z., Lu, B., Xiao, H., Liu, D., Li, X., Wang, L.A., Urbanovich, O., Nagorskaya, L. (2019). Effect of mixed solutions of heavy metal eluents on soil fertility and microorganisms. Environmental Pollution, 254: 112968. https://doi.org/10.1016/j.envpol.2019.112968

[2] Yu, S., Du, B., Baheiduola, A., Geng, C., Liu, J. (2020). HCB dechlorination combined with heavy metals immobilization in MSWI fly ash by using n-Al/CaO dispersion mixture. Journal of Hazardous Materials, 392: 122510. https://doi.org/10.1016/j.jhazmat.2020.122510

[3] Zhang, X., Gao, B., Creamer, A.E., Cao, C., Li, Y. (2017). Adsorption of VOCs onto engineered carbon materials: A review. Journal of Hazardous Materials, 338: 102-123. https://doi.org/10.1016/j.jhazmat.2017.05.013

[4] Neolaka, Y.A., Riwu, A.A., Aigbe, U.O., Ukhurebor, K.E., Onyancha, R.B., Darmokoesoemo, H., Kusuma, H.S. (2023). Potential of activated carbon from various sources as a low-cost adsorbent to remove heavy metals and synthetic dyes. Results in Chemistry, 5: 100711. https://doi.org/10.1016/j.rechem.2022.100711

[5] Wang, Y., Jin, X., Pan, Y., Li, J., Guo, N., Wang, R. (2018). Facile conversion of radish to nitrogen ‐ doped mesoporous carbon as effective metal ‐ Free oxygen reduction electrocatalysts. ChemNanoMat, 4: 954-963. https://doi.org/10.1002/cnma.201800231

[6] Dunnigan, L., Ashman, P.J., Zhang, X., Kwong, C.W. (2018). Production of biochar from rice husk: Particulate emissions from the combustion of raw pyrolysis volatiles. Journal of Cleaner Production, 172: 1639-1645. https://doi.org/10.1016/j.jclepro.2016.11.107

[7] Motlagh, E.K., Asasian-Kolur, N., Sharifian, S., Pirbazari, A.E. (2021). Sustainable rice straw conversion into activated carbon and nano-silica using carbonization-extraction process. Biomass and Bioenergy, 144: 105917. https://doi.org/10.1016/j.biombioe.2020.105917

[8] Zeidabadi, Z.A., Bakhtiari, S., Abbaslou, H., Ghanizadeh, A.R. (2018). Synthesis, characterization and evaluation of biochar from agricultural waste biomass for use in building materials. Construction and Building Materials, 181: 301-308. https://doi.org/10.1016/j.conbuildmat.2018.05.271

[9] Anshary, A., Napitupulu, M. (2022). Surface performance of biochar from young coconut shells (cocos nucifera) for Cd^{2+} ion adsorption. International Journal on Advanced Science, Engineering and Information Technology, 12(2): 774. https://doi.org/10.18517/ijaseit.12.2.14621

[10] Malik, A., Napitupulu, M., Napitupulu, N.D., Walanda, D. K., Anshary, A. (2023). Utilization of tropical forest cacao dried leaves for environment improvement. International Journal of Design & Nature and Ecodynamics 18(2): 457-463. https://doi.org/10.18280/ijdne.180225

[11] Walanda, D.K., Anshary, A., Napitupulu, M., Walanda, R.M. (2022). The utilization of corn stalks as biochar to adsorb BOD and COD in hospital wastewater. International Journal of Design & Nature and Ecodynamics, 17(1): 113-118. https://doi.org/10.18280/ijdne.170114

[12] Napitupulu, M., Walanda, D.K., Natakusuma, Y., Basir, M., Mahfudz. (2018). Capacity of adsorption of cadmium (II) ion by bio-charcoal from durian barks. Journal of Surface Science and Technology, 34(1-2): 30-36. https://doi.org/10.18311/jsst/2018/11055

[13] Napitupulu, M., Al-Gifary, M., Walanda, D.K. (2019). Adsorption of Cd(II) by carbon prepared from peels and stems of kepok banana (musa paradisiaca formatypica). Cellulose Chemistry and Technology, 53(3-4): 387-394.

[14] Napitupulu, M., Walanda, D.K., Napitupulu, N.D., Riskiantari, E. (2023). Preparation of biochar from ketapang shells (Terminalia Catappa l.) for dyes adsorbent to support environmental principles. AIP Conference Proceedings, 2719: 030033. https://doi.org/10.1063/5.0133320

[15] Yang, X., Kang, K., Qiu, L., Zhao, L., Sun, R. (2020). Effects of carbonization conditions on the yield and fixed carbon content of biochar from pruned apple tree branches. Renewable Energy, 146: 1691-1699. https://doi.org/10.1016/j.renene.2019.07.148

[16] Wang, S., Zhang, H., Huang, H., Xiao, R., Li, R., Zhang, Z. (2020). Influence of temperature and residence time on characteristics of biochar derived from agricultural residues: A comprehensive evaluation. Process Safety and Environmental Protection, 139: 218-229. https://doi.org/10.1016/j.psep.2020.03.028

[17] Legnaioli, S., Campanella, B., Pagnotta, S., Poggialini, F., Palleschi, V. (2019). Determination of ash content of coal by laser-induced breakdown spectroscopy. Spectrochimica Acta Part B: Atomic Spectroscopy, 155: 123-126. https://doi.org/10.1016/j.sab.2019.03.012

[18] Zhao, L., Zheng, W., Cao, X. (2014). Distribution and evolution of organic matter phases during biochar formation and their importance in carbon loss and pore structure. Chemical Engineering Journal, 250: 240-247. https://doi.org/10.1016/j.cej.2014.04.053

[19] Rawal, S., Joshi, B., Kumar, Y. (2018). Synthesis and characterization of activated carbon from the biomass of Saccharum bengalense for electrochemical supercapacitors. Journal of Energy Storage, 20: 418-426. https://doi.org/10.1016/j.est.2018.10.009

[20] Choma, J., Jagiello, J., Jaroniec, M. (2021). Assessing the contribution of micropores and mesopores from

nitrogen adsorption on nanoporous carbons: Application to pore size analysis. Carbon, 183: 150-157. https://doi.org/10.1016/j.carbon.2021.07.020

[21] Denis, M., Jeanneau, L., Pierson-Wickman, A.C., Humbert, G., Petitjean, P., Jaffrézic, A., Gruau, G. (2017). A comparative study on the pore-size and filter type effect on the molecular composition of soil and stream dissolved organic matter. Organic Geochemistry, 110: 36-44. https://doi.org/10.1016/j.orggeochem.2017.05.002

[22] Yang, H., Yi, N., Zhao, S., Xiang, Z., Qaseem, M.F., Zheng, B., Li, H., Feng, J.X., Wu, A.M. (2021). Characterization of hemicellulose in Cassava (Manihot esculenta Crantz) stem during xylogenesis. Carbohydrate Polymers, 264: 118038. https://doi.org/10.1016/j.carbpol.2021.118038

[23] Biochar application to soils: A critical scientific review of effects on soil properties, processes and functions. https://data.europa.eu/doi/10.2788/472, accessed on Feb. 22, 2024.

[24] He, Y., Yao, T., Tan, S., Yu, B., Liu, K., Hu, L., Luo, K., Liu, M., Liu, X., Bai, L. (2019). Effects of pH and gallic acid on the adsorption of two ionizable organic contaminants to rice straw-derived biochar-amended soils. Ecotoxicology and Environmental Safety, 184: 109656. https://doi.org/10.1016/j.ecoenv.2019.109656

[25] Fan, Y., Zheng, C., Liu, H., He, C., Shen, Z., Zhang, T.C. (2020). Effect of pH on the adsorption of arsenic(V) and antimony(V) by the black soil in three systems: Performance and mechanism. Ecotoxicology and Environmental Safety, 191: 110145. https://doi.org/10.1016/j.ecoenv.2019.110145

[26] Titma, T. (2018). The effect of surface charge and pH on the physiological behaviour of cobalt, copper, manganese, antimony, zinc and titanium oxide nanoparticles in vitro. Toxicology in Vitro, 50: 11-21. https://doi.org/10.1016/j.tiv.2018.02.010

[27] Kurniawati, D., Puja, Bahrizal, Nasra, E., Salmariza, S. (2019). Reduction of lead (II) from aqueous solution by biosorbent derivated from lengkeng (euphoria logan lour) shell with batch method. Journal of Physics: Conference Series, 1317: 012026. https://doi.org/10.1088/1742-6596/1317/1/012026

[28] Fatimah, N.M. (2021). Lead(II) adsorption by biochar prepared from tanduk banana peels (Musa X Paradisiaca). Journal of Physics: Conference Series, 1763: 012024. https://doi.org/10.1088/1742-6596/1763/1/012024

[29] Godymchuk, A., Papina, I., Karepina, E., Kuznetsov, D. (2020). Behavior of ZnO nanoparticles in glycine solution: pH and size effect on aggregation and adsorption. Colloid and Interface Science Communications, 39: 100318. https://doi.org/10.1016/j.colcom.2020.100318

[30] Zhang, H., Lu, T., Wang, M., Jin, R., Song, Y., Zhou, Y., Qi, Z., Chen, W. (2020). Inhibitory role of citric acid in the adsorption of tetracycline onto biochar: Effects of solution pH and Cu^{2+}. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 595: 124731. https://doi.org/10.1016/j.colsurfa.2020.124731

[31] Liu, J., Huang, Z., Chen, Z., Sun, J., Gao, Y., Wu, E. (2020). Resource utilization of swine sludge to prepare modified biochar adsorbent for the efficient removal of Pb(II) from water. Journal of Cleaner Production, 257: 120322. https://doi.org/10.1016/j.jclepro.2020.120322

[32] Yi, M., Cheng, Y., Wang, Z., Wang, C., Hu, B., He, X. (2020). Effect of particle size and adsorption equilibrium time on pore structure characterization in low pressure N_2 adsorption of coal: An experimental study. Advanced Powder Technology, 31: 4275-4281. https://doi.org/10.1016/j.apt.2020.09.004

[33] Barroso-Bogeat, A., Alexandre-Franco, M., Fernandez-Gonzalez, C., Gomez-Serrano, V. (2019). Activated carbon surface chemistry: Changes upon impregnation with Al(III), Fe(III) and Zn(II)-metal oxide catalyst precursors from NO_3^- aqueous solutions. Arabian Journal of Chemistry, S1878535216300132. https://doi.org/10.1016/j.arabjc.2016.02.018

[34] Luo, P., Zhong, N., Khan, I., Wang, X., Wang, H., Luo, Q., Guo, Z. (2019). Effects of pore structure and wettability on methane adsorption capacity of mud rock: Insights from mixture of organic matter and clay minerals. Fuel, 251: 551-561. https://doi.org/10.1016/j.fuel.2019.04.072

[35] Viglašová, E., Galamboš, M., Danková, Z., Krivosudský, L., Lengauer, C.L., Hood-Nowotny, R., Soja, G., Rompel, A., Matík, M., Briančin, J. (2018). Production, characterization and adsorption studies of bamboo-based biochar/montmorillonite composite for nitrate removal. Waste Management, 79: 385-394. https://doi.org/10.1016/j.wasman.2018.08.005