Journal of Analytical and Applied Pyrolysis 155 (2021) 105038

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Development of fluorine-intercalated biochar material for radiation shielding

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ARTICLE INFO

Keywords:
Biochar
Shielding material
Radiation shielding
Composites

ABSTRACT

Biochar is a sustainable, carbon rich material that can be utilized for several applications including ionizing radiation protection. In this work, a high electron dense fluorine-doped biochar-based carbon material was developed by treating biochar with fluorine-based catalysts. Its application as a composite additive created several radiation protection materials was explored and compared to industry standards. It was found that the biochar composites were able to compete with the industry standards in both alpha radiation and gamma radiation, showing no significant difference between the materials and industry standards (p-value >.99), effectively performing as well as the industry standards. Lead was the most effective material at blocking beta radiation due to its high area density (about 1200 mg/cm^2), but the biochar composites were able to reduce beta radiation by over 80 % in some composites, performing exceptionally well relative to their lower area densities (less than 200 mg/cm^2). In general, the results indicated that the newly developed biochar composite materials have excellent shielding performance and can be used as an effective replacement for the industry standards ranging from lead to concrete.

1. Introduction

Radiation is admitted from a wide variety of origins ranging from natural sources such as radon to artificial sources such as X-ray machines. These sources can release damaging ionizing radiation that is capable of damaging DNA and develop different forms of cancer. Lung cancer, breast cancer, thyroid cancers, and leukemia have all be associated with exposure from different sources of radiation [1,2]. Fifteen percent of the globally emitted radiation is from artificial sources with 93 % of the artificial radiation coming from medical sources and the other 7 % from nuclear sources. Hospitals and Clinics constantly use X-rays and other ionizing radiation machines for different treatments and diagnostic tools whereas scientist also utilize various radiation emitting machines within their research to characterize materials and profile specific chemical bonds [3]. These machines often emit alpha, beta, gamma, and occasionally neutron radiation as either primary radiation or as by products. There are several safety precautions needed when operating these types of machinery such as lead aprons, safety glass and protective concrete barriers. These materials are often wasteful, heavy/bulky and can pose a threat to human health and the natural environment.

Lead-shielding products are the leading material present in most medical institutions. Lead based products provide personal protection from X-ray (gamma) radiation during medical operations [4]. Although lead is the leading material towards medical protection, it is also very toxic, can be environmentally dangerous, and is very high in mass [5]. Due to these characteristics, there is a growing demand for lightweight materials that can effectively protect individuals while maintaining a low cost and a low environmental footprint.

Polymer composites are a growing interest due to its ability to meet these requirements as well as providing mechanical strength, and good neutron attenuation [6,7]. Most commercially available thermoplastics can be blended with different forms of agricultural waste and powders creating polymer-based composites [8]. Concrete is commonly used to create storage and barriers in order to contain emitted radiation but over time concrete can become brittle and will need to be replaced with more concrete leading to additional environmental waste. Biochar when used as a concrete additive increases the strength of the concrete as well as increases the flammability resistance and mold resistance [9].

Agricultural waste is currently being transformed into various materials in order to be utilized in different ways. Biochar is emerging as a versatile, multi-purpose material used primarily for bioremediation and

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https://doi.org/10.1016/j.jaap.2021.105038
Received 25 October 2020; Received in revised form 17 January 2021; Accepted 31 January 2021
Available online 4 February 2021

nutrient retention typically derived from agricultural wastes. Biochar is a solid organic carbon rich mass that is formed through the carbonization of biomass sources creating a porous structure that leads to high surface areas. Biochar very closely resembles graphite which is the leading moderator in nuclear reactors [10]. The high porosity and high surface area of biochar allows for increased surface interactions with gases and other molecules that may attach to the surface. Using this characteristic, biochar becomes a great material that can be used as a polymer additive or loaded with various molecules to provide efficient, lightweight, low cost and environmentally friendly radiation protection.

Recently, biochar has been investigated as a novel Electromagnetic Interference shielding (EMI-S) carbon material. Farhan et al. [11] showed that biochar, produced from plane tree seeds, having porous structure, rich in surface functional groups and composed with iron, is an effective EMI-S material in the X-band range. Although these materials were found to be effective, the biochar materials served as a foundation and utilized the heavy metals such as iron in order to achieve these results. Currently, space-based organizations such as NASA and the Italian Space Agency are seeking lightweight materials capable of radiation shielding. Radiation serves as the limiting constraint to long duration human exploration and discovery. Carbon shielding draws interest due to its low atomic number, low atomic weight, high temperature range and structural properties. The ratio of atomic number and atomic weight serves as a predictor of secondary neutron production. Carbon has a ratio of 0.5 which is one of the best ratios out of the elements, thus lowers the probability of neutron backscatter. Most polymers cannot tolerate the extreme temperature cycling of the day-night lunar cycles, but carbon-carbon can easily handle these extremes. By utilizing these attributes and combining with additional layering and/or composites, carbon-based radiation shielding materials are becoming a promising solution to galactic radiation [12].

The purpose of this paper is to create a fluorine-intercalated biochar and explore its application as additives creating several radiation protection materials (e.g., polymer, film composites, and concrete additives) towards radiation shielding (Fig. 1). Fluorine was chosen due to its low atomic mass, high electronegativity, high stability towards carbon atoms and high electron density. The low atomic mass of fluorine lowers the probability of neutron backscatter as well as reduce the intensity of an occurrence. By selecting a highly electronegative element, the material is more resistant to displacements and broken bonds. The higher electronegativity leads to higher material stability and increased lifetime performance. Carbon-fluorine bonds are capable at preserving stability, while maintaining a high electron density capable of dealing with the energy from the incoming radiation. Other elements are not able to minimize neutron backscatter as well as maximize stability. The carbon-fluorine bonds within graphitic materials change from ionic to covalent bonds thus creating a wide range of chemical characteristics such as metallic conductivity, high resistivity, super hydrophobicity and high electrochemical reactivity [13]. Fluorine bonding also creates the most stable pi interactions using the gauche effect thus creating a stable electron dense material [14]. Radiation protection materials come in a wide variety of form factors specializing in different characteristics such as flexibility, weight, and cost of production. In order to represent the versatility of biochar, several different composites were developed and analyzed.

2. Materials and methods

2.1. Biochar and its fluorination

The biochar was prepared by the catalytic fast pyrolysis of loblolly pine sawdust and sieved into the particle size range of 0.18−0.25 mm. To create a strong carbon-fluoride bond, liquid hydrofluoric acid was used as an impregnation medium for biochar fluorination. The biochar samples were submerged in a 20 % hydrofluoric acid solution and sonicated overnight at 25℃ in order to fluorinate the biochar. A previous experimental design was conducted and showed these parameters were efficient to produce fluorinated biochar.

2.2. Preparation of membrane composite

In order to create a material that is flexible and easy to manage, polydimethylsiloxane (PDMS) was chosen to create a membrane. PDMS was used to create a membrane coating as well as a standalone membrane. For preparation of biochar-based membrane, 1.72 g of PDMS was mixed with 1 g of biochar and 5 g of toluene. This mixture was then stirred for 30 min before being sonicated for 10 min under 40 kHz at room temperature. For preparation of standalone membrane, 17.27 g of

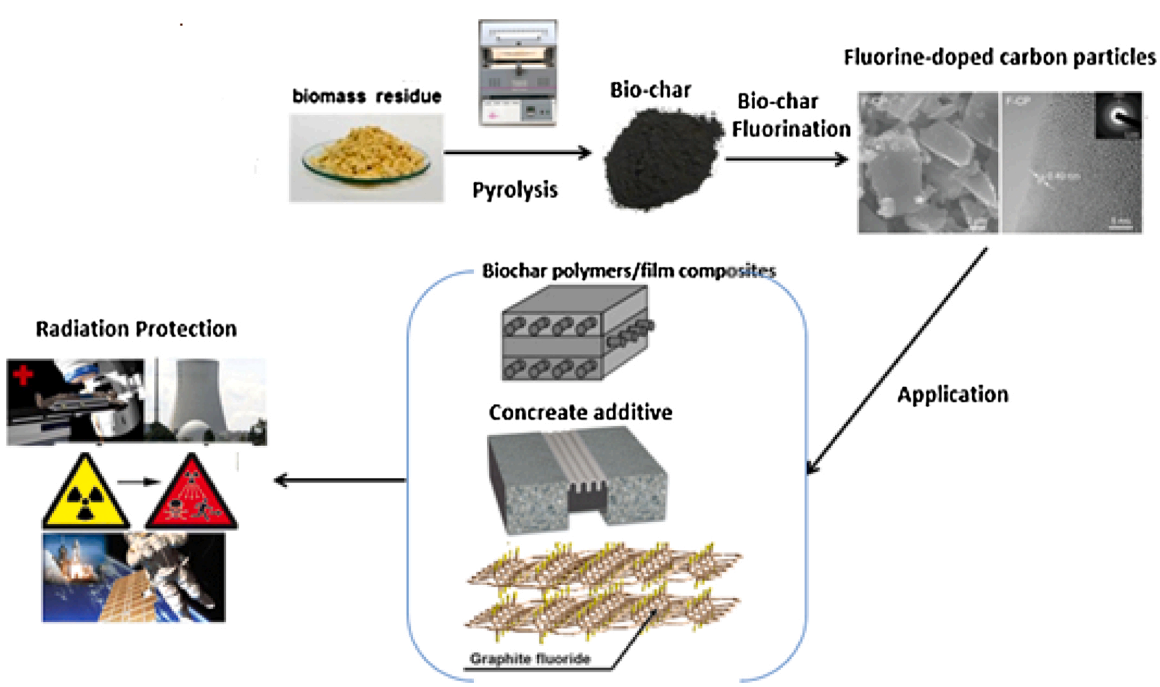

Fig. 1. Schematic of development of fluorine-intercalated biochar and explore its application towards radiation shielding.

PDMS was added and the mixture was mixed for 90 min and sonicated for an additional 10 min. The resulting mixtures were spin coated on aluminum dishes overnight resulting in the membranes labeled as Star (aluminum coating) and Membrane (standalone membrane).

2.3. Preparation of pressed polymer composite

To produce a thin, sturdy, and yet flexible biochar polymer matrix, biochar was added to a solution of *N-N*-Dimethylformamide and PVDF (Polyvinylidene fluoride). PVDF was the polymer of choice due to its chemical composition as well as its low density (1.78 g/cm^3). PVDF is chemically comprised of carbon chains with hydrogen and fluorine functional groups thus maintaining the chemical composition of the fluorinated biochar. Through experimentation, the best ratio to produce biochar polymer matrixes was 1-part biochar to 5 parts PVDF. N-N-Dimethylformamide was added as a binder in order to bind all the materials together and allow the polymer to be pressed. The following was found to be the optimal procedure to create the biochar polymer matrix denoted as Pressed in the results: 2 g of biochar was added to 1 g of PVDF. The mixture was then stirred in order to disperse the powder evenly. 2.5 mL of *N-N*-Dimethylformamide was added in total at increments of 0.5 mL. Between the increments, the mixture was folded over and turned in order to maximize the coverage of the binder. Once all the *N-N*-Dimethylformamide was added, the polymer was rolled into a ball and slightly indented before placing into the mechanical press. The polymer was pressed at about 1000 lbs. of pressure using a Carver 4350 pellet press in order to reduce the thickness yet keep the polymer intact. The polymer was dried under this pressure and the resulting biochar matrix is labeled as Pressed.

2.4. Preparation of concrete composite

To produce a biochar infused concrete the following procedure was used: 0.5 g of biochar was added to 10 g of quikrete concrete and mixed well. 0.75 mL of distilled water was then added to the mixture creating a slurry. The slurry was then placed in a mold under a press and dried overnight to create the composite.

2.5. Preparation of biochar carbon nanofibers

The biochar carbon nanofiber was prepared using the procedure outlined in our previous study [15]. A 10 wt.% bicomponent solution was prepared by dissolving Polyacrylonitrile (PAN) and biochar in the mass ratio of 30:70 in DMF. Biochar was first dispersed in DMF and sonicated for 30 min., and then added to PAN solution under constant stirring. A 30 mL syringe was next filled with the spinning solution and fitted with a blunt end 15-gauge stainless steel needle. As shown in Fig. 2, The electrospinning setup comprised of a high voltage power supply (Series FX, Glassman High Voltage Inc., New Jersey, USA) and a flat movable stainless-steel collector plate. The collector setup was fabricated in house and made up of two slides, a computer with a software that controls the motion, and a 30 inch by 30-inch stainless steel plate. The solution was electrospun at a flow rate of 1 mL/h and 15 kV and collected on a grounded aluminum foil that was placed at 20 cm from the tip of the syringe. The resulting electrospun fiber mats were detached from the collector and dried at room temperature in a fume hood for at least 24 h before further use. The collected electrospun fiber mats were then cut and stacked between 6 × 6 in. graphite plates (graphite store), and placed in a furnace (Carbolite HTF 18/8, Sheffield, UK) for further heat treatment. All the samples were stabilized in air from room temperature to 280 °C at a heating rate of 1 °C/min and the temperature was held at 280 °C for 6 h to allow complete stabilization. After the stabilized fibers were cooled down to room temperature, they are carbonized in nitrogen at 1200 °C with a heating rate of 5 °C/min and held for 1 h before cooled down to room temperature.

2.6. Radiation testing of fluorine-doped biochar based materials

In order to test the effectiveness of the radiation blocking materials, a simple Geiger tube setup was utilized. The radiation sources, and the standard materials were from Spectrum Techniques in Oak Ridge TN, and the Geiger Tube (SN-7927A) and Interface (850 Universal Interface) were both from PASCO provided by the Physics department at Wake Forest University. The radiation sources were placed on top of 2 metal weights in order to raise the source closer to the Geiger tube, effectively drowning out any background radiation. Background radiation was recorded for reference, although it had very minimal effect of the readings. Each material was measured for one minute with 15 s intervals in order to test the effectiveness of the material. The counts were recorded for 3 replications in order to record an average count per minute.

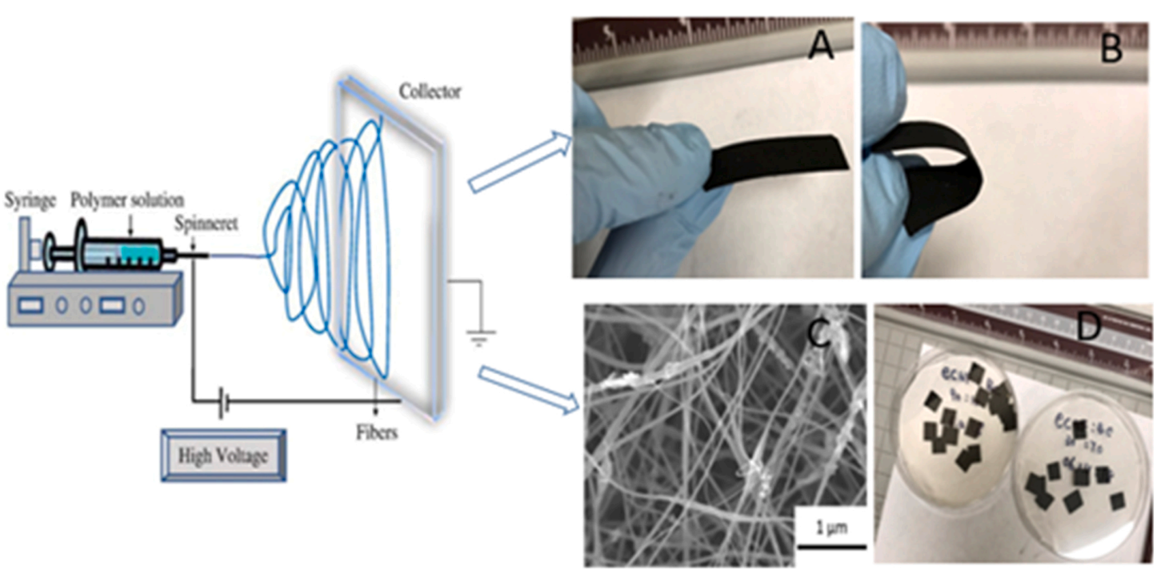

Fig. 2. Schematic illustration for obtaining porous ECNF electrodes using electrospinning method. A) and B) Photo of the ECNF; C) SEM of the ECNF; D) Photo of the electrode.

3. Results and discussion

3.1. Physical characterization of biochar-based materials

The morphology and microstructure of the different biochar composite samples were carried out by SEM. Fig. 2 depicts the surface morphologies of the biochar composites. The star membrane secured very tightly to the aluminum pan. It maintained a rubber like consistency, with very strong adherence to the pan. The pressed membrane has a stiff leather like consistency, able to bend multiple times without any observable damage, but not extremely resilient to creasing or tight folds. The standalone membrane was identical to the star membrane except, the membrane was unattached and thus able to bend freely adding to its flexibility. The biochar carbon nanofiber was very light and the most fragile out of all the composites. The biochar carbon nanofiber began to crumble in the heat but was the thinnest of all the materials. The biochar concrete and regular concrete were almost identical in appearance except for the darker appearance the biochar added to the concrete mixture. The added biochar concrete also required more water than the regular the concrete, but the biochar concrete was more physical stable and durable.

The density and thickness of the comparable materials are shown in Figs. 3 and 4, respectively. As shown in Fig. 4, lead has the highest density among all the materials. The stacked biochar membrane is the 2nd densest materials. The biochar carbon nanofiber (CK12) is the thinnest materials among all the comparable materials (Fig. 5).

3.2. Radiation shielding performance

In order to test the effectiveness of the biochar-based materials against radiation, three forms of radiation were tested - alpha, beta, gamma. The shielding performance of developed biochar-based material for alpha, beta and gamma ray were compared with the commonly used industry standard shielding materials (Aluminum Foil, Polyethylene, Plastic, Lead, and Concrete) and the experimental results are shown in Figs. 6–8.

Based on the results, the biochar-based materials were comparable to the industry standards at blocking ionizing radiation (Figs. 6–8). Overall, the pressed polymer biochar (pressed) seemed to perform the most efficiently with every type of radiation given its density and thickness. Alpha radiation was greatly reduced by every form of radiation protection, mainly due to the relative thickness of the materials. Alpha particles are large, consisting of two protons and two neutrons bound together in a single molecule, thus having low penetration depth. Typically, alpha particles are some of the easiest forms to shield against due its size. Sufficient thickness and close particle dispersion greatly shield against alpha radiation. As shown in Fig. 6, Other than the biochar membrane coating (star) and biochar carbon nanofibers (CK12), all the biochar materials were able to provide a buffering against alpha radiation. There was no evidence of a difference between any of the materials (p values $>.85$) thus all the materials produced similar results. Due to the distance between the alpha emitter source and the material, the ambient air served as an initial buffer to the radiation particles resulting in lower counts. Previous data showed higher buffering capabilities at a distance of a few millimeters but was excluded due to the lack of samples. The pressed polymer biochar was the thinness of the biochars and allowed the least number of alpha particles through the material.

Beta radiation buffering is highly linked to the density of the buffering material. Lead as a blocking material performed the best in terms of beta radiation due to its high density (Fig. 7). Beta particles consist of high energy electrons and occasionally positrons that are emitted through the radioactive decay of a nucleus. Beta particles commonly have lower ionizing energy than alpha particles, but deeper penetration. In order to combat these particles, materials such as heavy metals are used to absorb the electrons as the particles pass through the materials electron fields. Although materials with more electrons perform better against beta radiation, as the beta particles decelerate, x rays are given off (bremsstrahlung X-rays). The higher the atomic mass of a material, the more damaging the bremsstrahlung X-rays making fluorinated biochars desirable. Excluding lead, the biochar materials again performed adequately compared to the other industry standards. Beta radiation counts seem to be lower in materials with higher densities, thus the denser materials were able to perform better. Although Lead performed the best at blocking beta radiation, it is also the densest of all the

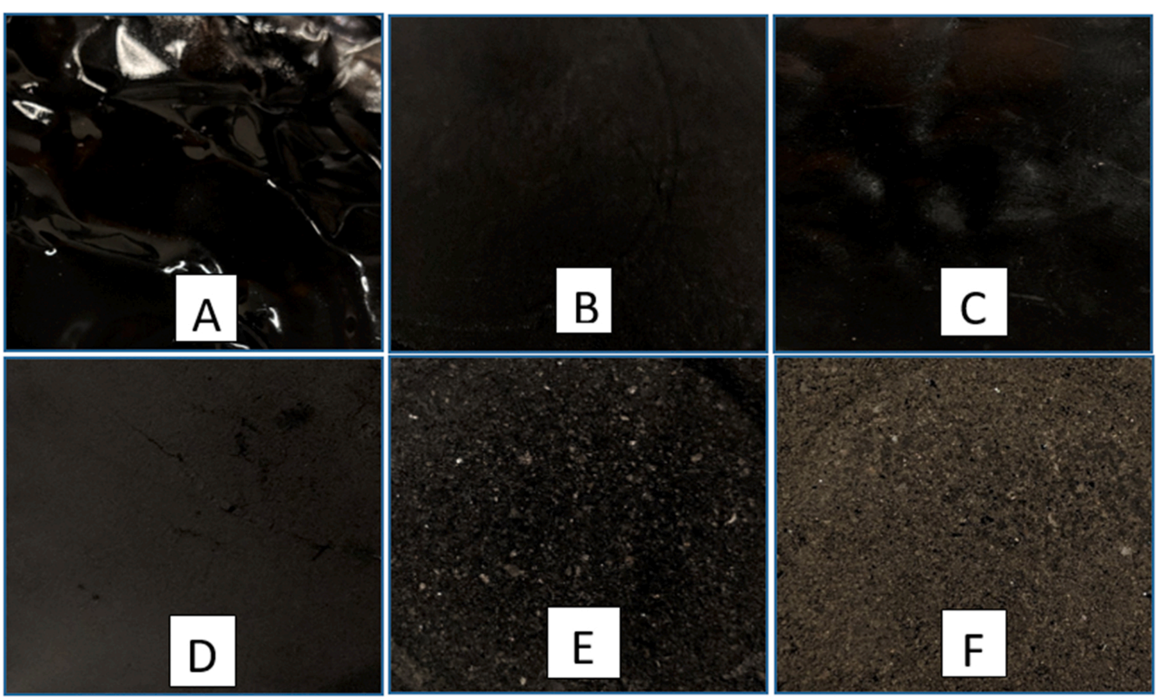

Fig. 3. SEM of the morphology of different biochar composites (A) Star membrane, (B)Pressed Membrane, (C) Standalone Membrane, (D) Biochar Carbon Nanofiber, (E) Biochar Concrete, (F) Regular Concreate.

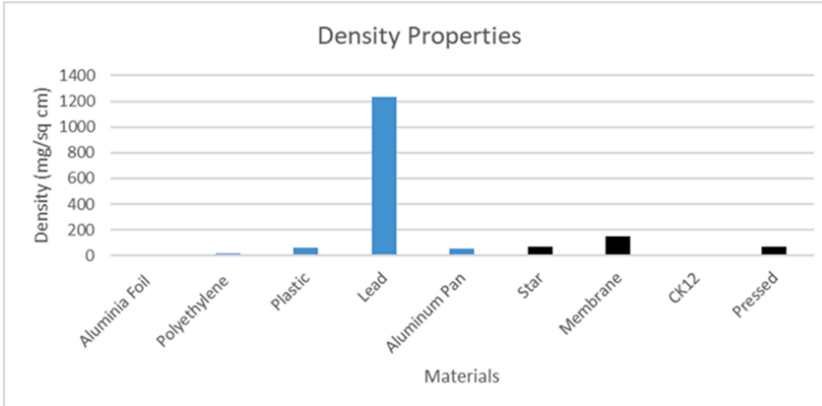

Fig. 4. Displays the mass density of the comparable materials.

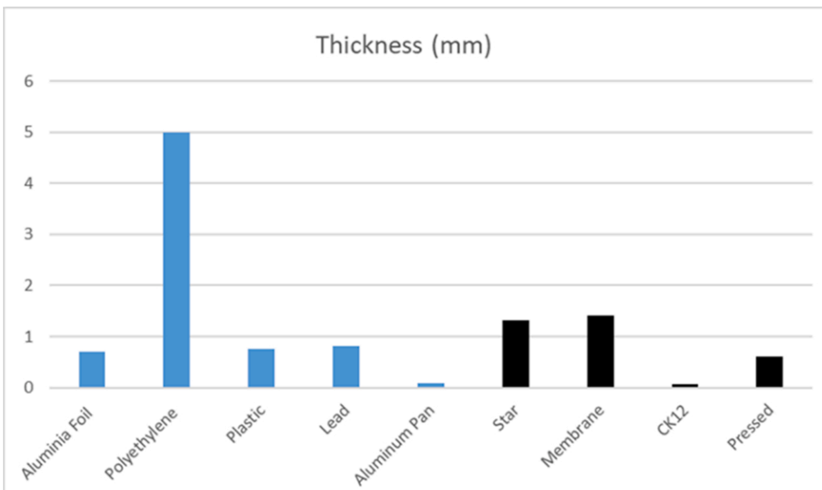

Fig. 5. Displays the thickness of the comparable materials.

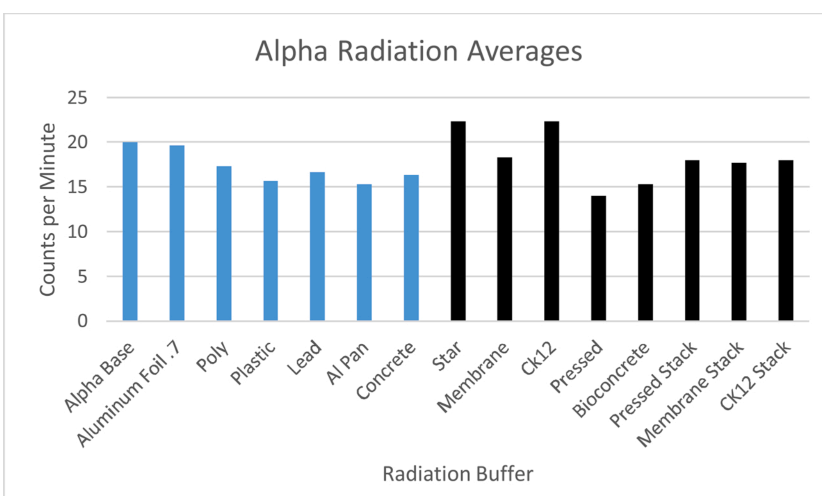

Fig. 6. Results of the amount of Alpha radiation that passes through comparable materials.

materials making it heavier and may be more susceptible at producing Bremsstrahlung radiation. The stacked biochar membrane was able to reduce the beta radiation by over 80 % while maintaining its high flexibility and lower density compared to lead. The stacked biochar membrane significantly outperformed the industry standards (p-value <.00001) excluding lead and concrete. Biochar based concrete was also able perform very well against beta radiation yet lacking the same flexibility. The biochar-based materials can be an adequate replacement for lead if multiple layers are utilized or if combined with additional materials (Fig. 7). Stacking additional layers of biochar can perform just

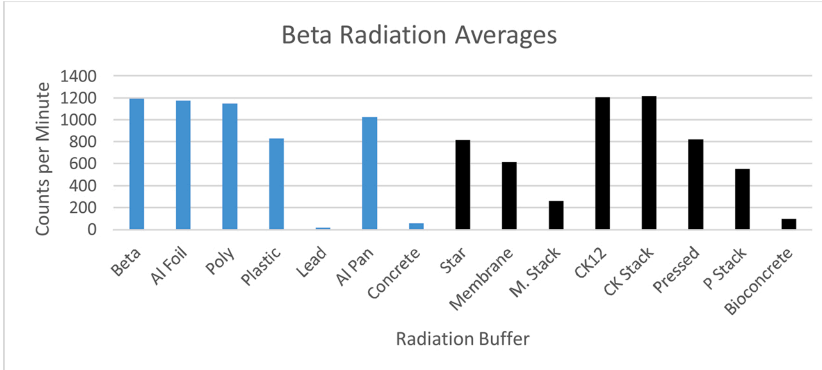

Fig. 7. Results of the amount of Beta radiation that passes through comparable materials.

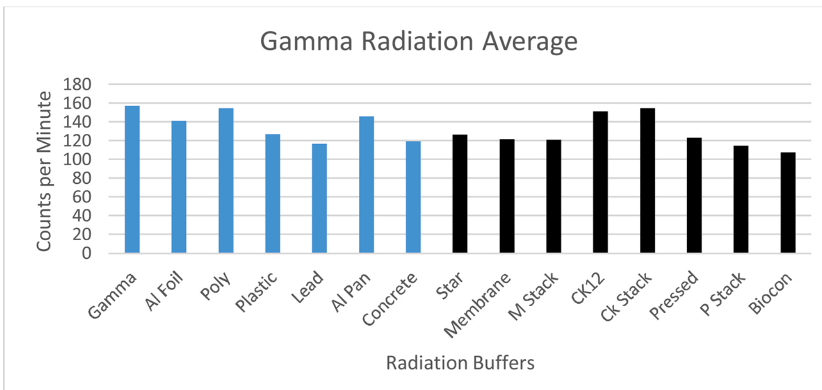

Fig. 8. Results of the amount of Gamma radiation that passes through comparable material.

as well as lead while maintaining less mass and providing better flexibility.

In terms of Gamma radiation, the biochar-based concrete performed the best but not far off from the other biochar materials (Fig. 8). Gamma rays are high energy photons resulting from the radioactive decay of an atomic nuclei. Gamma rays contain high penetrating energy, and are absorbed by materials with high atomic mass numbers and high electron density. These properties allow gamma rays to be absorbed by the interactions within these materials. The fluorine intercalated biochar is able to achieve similar characteristics through the multiple bonds and interactions created by the fluorine atoms. The interactions provide a higher electron density and stability while maintaining lower atomic masses than heavy metals. The biochar materials were all very comparable to the leading standards, providing great resistance to the gamma particles while again maintaining lower density and minimum thickness. The pressed biochar membrane stacked performed the second best, blocking more gamma radiation compared to lead and the other industry standards. Statistically there showed little evidence of a difference between the performance of the pressed biochar stacked and lead (p-value $>.99$). The biochar-based materials were able to provide adequate protection against gamma radiation compared to the industry standards.

Although the biochar composites performed significantly well when compared to the industry standards, there showed room for improvement. Beta radiation performance particularly showed the greatest opportunity. The tradeoff between mass/environmental footprint and beta radiation performance creates a subjective dilemma. Many studies sacrifice higher mass, and bigger environmental footprints for the increased performance. Traditionally, other composites may add higher dense materials such as heavy metals in order to better handle the beta radiation while sacrificing the weight, but the produced biochar composites seemed to produce adequate results even under these lightweight conditions. Other ways of increasing the biochar composites performance in beta radiation, while maintaining their mass and environmental footprint may be further researched, but outside the scope of this paper.

4. Conclusions

A high electron dense fluorine-doped biochar-based carbon material was developed. Its application as additives to creating several radiation protection materials was also investigated. Overall, by developing a high electron dense biochar, the electron density and stability were able to absorb and buffer ionizing radiation exceeding and/or meeting the level of industry standards. The strength of the carbon-fluorine bond in addition to the fluorine intercalation within the pores makes biochar a suitable candidate against ionizing radiation. The intercalated fluorine biochar was able to replace several radiation protection materials thus providing environmentally friendly and more manageable options. The flexibility to create different membranes and composites leads to versatility of the material and multiple functionalities. Overall, this biochar is a physical, environmentally, and financially effective material for dealing with radiation and can be implemented within protective equipment and materials.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgments

The authors thank USDA-CSREES-Evans-Allen Project (NC.×331-5-21-130-1) for the financial support.

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