Immobilization of Lead by Phosphated Biochar Produced from Fish Farming Sludge and Sewage Sludge in a Contaminated Urban Soil

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Abstracts: An evaluation was conducted on the application of phosphate biochar produced from Sewage Sludge (SS) of a Wastewater Treatment Plant (WWTP) for lead immobilization in contaminated soils of the Human Settlement (HS) Virgin of Guadalupe, in the district of Mi Peru. Biochar was generated by a slow pyrolysis process at 500°C. The biochar was dosed at 10% biochar/soil on lead-contaminated soil, and the factors studied were the type of biochar and time of application. A complete factorial design was performed, and the data were processed using Design Expert v11 software. The results showed that the maximum lead immobilization was 50.83% for BSS for 20 days at a dose of 10% biochar/soil. According to the factorial model, an R^2 of 0.85, an adjusted R^2 of 0.83, an *F-value* of 79.64, and p-values lower than 0.05 (95%) were obtained, indicating that the factor (F_2) of application time is significant for the treatment. It was concluded that both types of sludge have the potential for lead immobilization in contaminated soil, and the application time is significant for lead immobilization.

Keywords: Biochar, Immobilization, Heavy Metals, Slow Pyrolysis, Lead.

1. INTRODUCTION

Heavy metal contaminated soil is a growing concern due to rapid global industrialization that threatens the health of animals and humans. [1]. Lead is one of the most important heavy metals since, it is unique in their physical and chemical characteristics and its wide use in the industrial production around the world [2]. The causes of lead contamination are mainly the result of anthropogenic activities such as industrial processes, vehicular traffic, the use of fertilizers, and waste incineration [3]. Lead-containing contaminants persist in different chemical species in the soil due to the non-degrading characteristic whereas lead-containing particles emitted from anthropogenic sources can be deposited directly on the soil surface [4].

The effects of lead uptake by plants generate phytotoxicity and an adverse impact on humans due to lead transfer through the food chain [5]. Lead ingestion from lead-contaminated foods can cause learning difficulties in children, neuronal toxicity, kidney disease, and cancer [6], neuropathy, encephalopathy, peripheral, hearing loss, and impaired cognitive function [7].

In recent decades, Callao, that is a region of Peru, has presented places with critical impacts due to lead, which is why, in 2017, the Ministry of the Environment (MINAM) declared an environmental emergency for a period of 90 days, due to the fact that the Environmental Quality Standard (EQS) has been exceeded for soil, in the lead parameter [8]. The main area polluted with lead is the Human Settlement (HS) Virgen de Guadalupe of the district of Mi Peru, having as a main generating source the industrial factories dedicated to the smelting of metals and recovery of lead from residual batteries [9].

In situ heavy metal immobilization technology has been considered an effective and environmentally friendly method to decrease the availability of heavy metals from the soil [10]. When stabilizing materials are applied, the availability of heavy metals decreases, thus also preventing their entry into the food chain [11]. The effectiveness of this method is highly dependent on the performance of the additives used to immobilize the metals in the soil.

Biochar is a widely used additive due to its great capacity to adsorb heavy metals, [12]. The mechanisms of immobilization of different heavy metals by biochar are generally attributed to its physicochemical properties. Nevertheless, these mechanisms could change significantly in the environment [13]. For example, metals bound by cation exchange can be easily released into the environment and are therefore readily bioavailable. Metals bound by surface precipitation are potentially bioavailable and can dissolve due to changes in pH in the medium. [14]. Therefore, it must be ensured that biochar immobilizes metals through more stable mechanisms in the soil to ensure its efficiency and effectiveness in immobilization.

Phosphated biochars, which have been studied for immobilization in situ, are considered relatively inexpensive and easy to handle [15], this type of biochar form stable precipitates and complexes [16]. The research of [17] immobilized metals using phosphated biochar forming insoluble precipitates as minerals [Pb5(PO4)3X; X=F, Cl, B u OH] [18]. Therefore, it is important to evaluate different phosphated biochar substrates for immobilizing lead. The main objectives of this study are the following:

(1) Assess the effect of the type of phosphated biochar on the immobilization of lead; and (2) Assess the effect of biochar application time on the immobilization of lead in the soil.

2. MATERIEL AND METHODS

2.1. Characterization Of Soil Contaminated With Lead

The soil contaminated with lead is in HS Virgen de Guadalupe, in the district of “Mi Peru”. Table 1 shows five (5) locations where the contaminated soils were sampled. Figure 1 shows the sampling that was carried out according to the guide of the MINAM [19]. Lead measurement was performed using the ICP-ES analytical assay according to the Environmental Protection Agency (EPA) method (Method 3050B, Rev. 2,1996/EPA Method 200.7, Rev. 4.4,1994).

TABLE 1: COORDINATES OF THE SAMPLING POINTS OF SOIL CONTAMINATED WITH LEAD

SAMPLE	COORDINATES (UTM)	
	NORTH	EAST
P1	268959	8688300
P2	269085	8688154
P3	268912	8688095
P4	268882	8688225
P5	268905	8688183

FIGURE 1: SAMPLING OF CONTAMINATED SOIL WITH LEAD

2.2. Sampling of Fish Farming Sludge and Sewage Sludge of a WWTP

According to the Biosolids Monitoring Protocol and Supreme Decree Number 015-2017-VIVIENDA that approves the Regulation for the Reuse of Sludge generated in Wastewater Treatment Plants. 20L of Sewage Sludge (SS) was collected from the “Sol Naciente” Wastewater Treatment Plant (WWTP) located at coordinates 8730196N; 321013E. WWTP has an aerobic treatment process by activated sludge with a flow rate of 15L/s, the sample is collected from the equalizing tank prior to entering the digesters. The sample of Fish Farming Sludge (FFS) collected was 20L from the "Pariamarca" trout farming located at coordinates 8675928N; 277343 E.

Figure 2: Sampling of (a) Sewage Sludge of WWTP (b) Fish Farming Sludge

2.3. Biochar production

The biochar production was carried out using a stainless-steel tube oven. Samples of dried SS of WWTP and FFS with a size of 1.18 mm to 2 mm were placed in the center of the oven. Figure **3** shows the configuration of the pyrolysis reactor. The pyrolysis reactor had a temperature regulator and pressure gauge for gas pressure control. The flow remained stable during all the experiments carried out. The outlet of the reactor was connected to a vessel filled with water to form a closed system and allow the leachate to settle. Synthesis gas and volatile vapors were allowed to escape through the outlet of the vessel. About 2 kg of sample was used for the pyrolysis process**.**

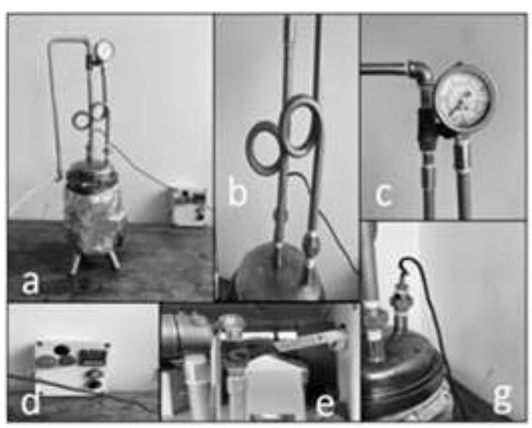

Figure 3: Temperature controlled pyrolysis reactor, (a) front view; (b) Heat diffusers; (c) manometer; (d) Temperature controller; (e) gas outlet and (f) temperature sensor.

The biochars were produced from FFS and SS of WWTP, then were listed as BFFS and BSS, respectively. As processing of the wet residual sludge, it was placed in a convective dryer at 80°C for 12 hours, then the dried sludge was pyrolyzed in a 5 L capacity tubular reactor under limited oxygen conditions at 500°C for 1.5 h at a speed heating of 25°C/min according to [20]. Then, the biochar produced was crushed and passed through a 20-mesh sieve. After production, the phosphorus content in the biochar was characterized by the atomic absorption method. For the analysis of compounds, the FTIR-ATR/ASTM E1252 Infrared Spectroscopy method was used as a qualitative analysis.

2.4. Experimental Design

A complete factorial experimental design was developed, the factors studied were: (F_1) Type of biochar (BFFS and BSS), and (F_2) Application time (10 to 20 days). The factorial design contemplated 4 treatments with 3 repetitions and 4 central points with a total of 16 treatments (Table **2**). The experiment was carried out in pots where 0.5 kg of contaminated soil was treated according to the proposed experimental design, a dose of both biochars was mixed at (10%) [21]. It was maintained at a soil moisture of 60%.

Table 2: Experimental matrix using a factorial design

Treatment	Type of biochar	Time of application (days)
1	BFFS	20
2	BSS	10
3	BSS	20
4	BFFS	20
5	BFFS	15
6	BFFS	10
7	BSS	20
8	BSS	10
9	BSS	10
10	BSS	15
11	BFFS	15
12	BSS	10
13	BFFS	10
14	BSS	15
15	BFFS	20
16	BFFS	15

2.5. Data analysis

The use of the full factorial design makes it possible to compare the effect of the factors studied on the different response parameters and obtain a statistically significant difference. The analysis of variance (ANOVA) was used for the analysis and processing of the data [22]. The coefficient of determination (R_2), (R_2predictive) and (R_2 adjusted) for factor model analysis.

The analysis of the residuals was carried out, for the validation of the complete factorial model. In this way all the assumptions were contrasted globally and, therefore, a lack of normality of the residuals can also be due to the inappropriateness of the model or to the existence of heteroskedasticity.

The *F-value* and *p-value* were analyzed to give model acceptability of each response. Statistical tests were completed with Design Expert v11 software using α=0.05.

3. RESULTS AND DISCUSSIONS

3.1. Lead concentration

Table **3** shows the concentrations in the different sampling points of the soil contaminated with lead in the HS Virgen de Guadalupe, in the district of Mi Peru. According to the EQS, the concentration of lead allowed for soil with houses is 140 mg/kg and according to Table **3**, of the 5 points sampled, point P1 exceeds the EQS. The experiment was carried out with the concentration of the sample at point P1.

Table 3: Lead concentration in the contaminated soil

Sample	Lead (mg/Kg)
P1	198.76
P2	4.69
P3	50.63
P4	136.23
P5	69.53

3.2. Biochar characterization

Table 4 shows the phosphorous concentrations of the biochar produced.

Table 4: Phosphorous content in biochar

Type of Biochar	Unit	Total Phosphorous
BSS	%	2.73
BFFS	%	1.22

Figure **4a** and Figure **4b** show the infrared Fourier spectra of BFFS and BSS produced at 500°C. BFFS and BSS showed a minimum intensity of C-H alkanes groups at 2920 cm-1, there is a significant difference of the C-O-C carboxyl groups at 1419.1 cm-1, being BSS the most intense. Finally, both biochar had ether groups C-O-C at 1000.0 cm-1. There is a greater presence of alkanes and carboxyl groups in the BSS in respect of BFFS. According to [23], the stabilization mechanisms of heavy metals by biochar is complexation with functional groups that contain oxygen.

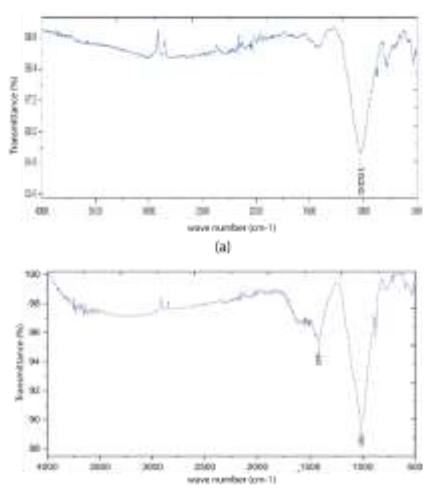

Figure 4: Infrared FT-IR spectra of biochar from BSS (a) and BFFS (b).

3.3. Experimental results

Table **5** shows the results of the 16 experimental treatments in a random combination by the type of biochar (BSS, and BFFS) and the application time and the response variable as the percentage of lead immobilization (%Pb). The maximum lead immobilization reached 50.83% with an experimental arrangement of BSS 20 days after its application.

Table 5: Results of the experimental matrix of the different treatments

Treatment	Final Lead concentration (mg/kg)	Lead Immobilization Efficiency (%)
1	118.9	40.18
2	194.35	2.22
3	97.73	50.83
4	121.19	39.03
5	166.8	16.08
6	177.73	10.58
7	120.36	39.44
8	183.38	7.74
9	194.66	2.06
10	177.3	10.8
11	173.39	12.76
12	189.06	4.88
13	180.47	9.2
14	175.03	11.94
15	109.52	44.9
16	170.94	14

Figure **5** shows the graph of the variation of the type of biochar and the time of application, both biochars decrease the lead concentration as a function of time, the greatest immobilization is generated by BSS. According to [24], the biochar yield increases significantly the higher the phosphorus content, so the biochar from BSS has a higher phosphorus content than that from BFFS. One of the important aspects that determine the yield of biochar are the dehydration and volatilization reactions that occur during the pyrolysis process, since the release of volatile matter at high temperatures will decrease the yield of biochar. This trend in the results is consistent with those reported by [25].

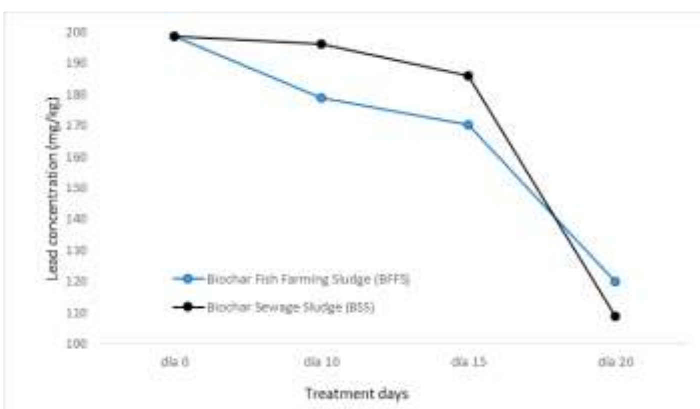

Figure 5: Lead concentration and variation with biochar type and application time.

3.4. Effects of process parameters on lead immobilization

Figure **6** shows the semi-normal probability that makes it possible to analyze the main effects of the study factors in the first instance. Color-coded squares provide details on whether the effects are positive. Figure **6** shows that the B-application time presents a high magnitude of the significant effect while the type of biochar or its interactions do not.

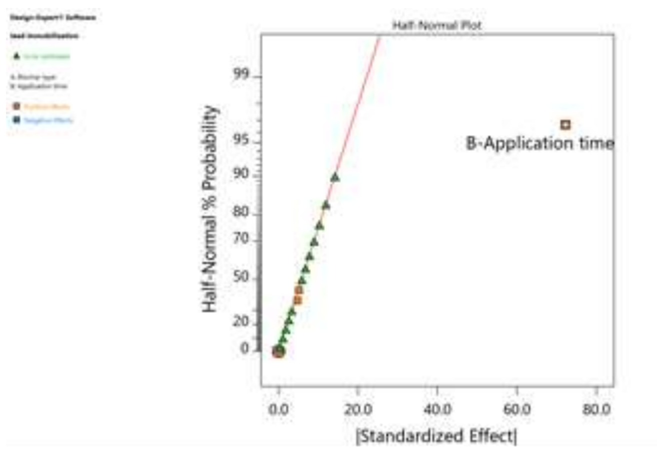

Figure 6: Seminormal probability of the effects of the study parameters.

Figure **7** shows the Pareto chart. This diagram shows that 20% of the factors would explain 80% of the immobilization of metals. According to this analysis, factor B: Application time is the factor that explains the immobilization of lead in contaminated soil.

Research report 47% lead immobilization [26], 88.22% cadmium % [27], 81.89% lead [28] with this study having a maximum efficiency of 50.83% in Lead immobilization, the studies mentioned report application time greater than 30 days, which coincides with the significant effect of the time reported in this study, the longer the biochar application time improves the immobilization of metals.

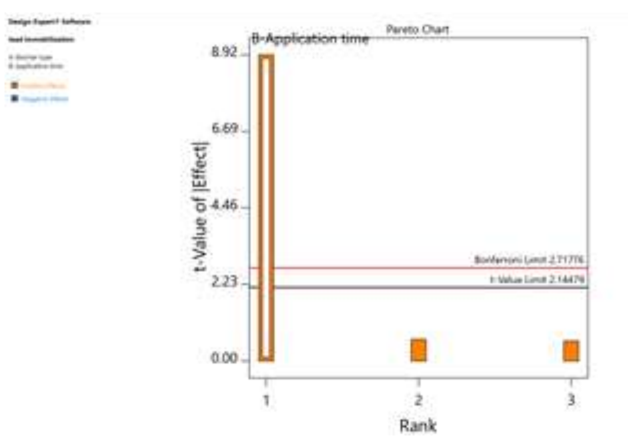

Figure 7: Pareto diagram of the effects.

3.5. Prediction of lead immobilization

In the statistical model used, the equation was calculated in terms of coded factors, this equation could be used to make predictions about the response for given levels of each significant factor. The regression equation for the value of lead removed (%) was obtained as follows:

lead removed (%) = +73.27 + 35.13 (Application time) (1)

The regression equation is observed to fit the experimental data well, with the regression coefficients and the results of the test of significance (ANOVA) listed in Table **5**, the negative and positive signs of the equation means the effect of the synergies and antagonistic of variables [29].

The results obtained were then analyzed using ANOVA to assess the significance and adequacy of the model. To evaluate the significance of the model the results obtained were analyzed by using ANOVA. The F-value and p-value indicated the importance of the differences of the study factors. Table **6** shows that the factorial model has an *F-value* of 79.64, this implies that the model is significant. There is only a 0.01% chance that such a large F-value will occur due to errors.

P-values less than 0.05 indicate that the model terms are significant. In this study, the B-Time of application is the only term of the model that presents a high degree of significance. Studies such as the elaboration of fishbone biochar as an absorbent [30] show an *F-value* equal to 23.25 and the P value less than 0.0001 in their second degree statistical model. Study on the use of Kernel palm shell biochar to be used as a partial substitute for the cement composition [31] show that the pyrolysis temperature and the residence time are more significant with F-value of 141.71 in a quadratic model. [32] studied the residues of palm oil sludge, as a potential adsorbent, for the removal of sulfur dioxide, obtaining an *F-value* of 43.93, all of its study parameters of the quadratic model being significant.

Table 6: ANOVA matrix of lead immobilization (% removed)

Resources	Sum of squares	GL	Sum of means	F-value	p-value
Model	3375.37	1	3565.8	79.64	< 0.0001
B-Application time	3375.37	1	3565.8	79.64	< 0.0001
Residual	588.38	14	44.78		
Lack of Fit	494.16	4	128.5	11.39	0.001
Pure Error	94.22	10	11.29		
Cor Total	3963.75	15			

In addition, it was necessary to validate the model, so it was verified through the correlation of the coefficient of determination (R^2value, R^2adjusted y R^2predictive), coefficient of variation (CV%), Precision Adequate and PRESS. The value of R^2 for equation (1) was 0.8505. This means that around 85.05% of the regression model was attributed to the experimental variables analyzed. Furthermore, the R^2 predictive was 0.8103, it was consistent with the R^2 adjusted of 0.8398. All R^2 for the equation (1) was considered relatively high and comparable, which means that the factorial model was satisfactorily defined based on the experimental data within the range of operational variables.

Table 7: Adjustment indicators of the factorial design of the experiment

Indicators	% Immobilized lead
R^2	0.8505
R^2 adjusted	0.8398
R^2 predictive	0.8103
Precision Adeq	15.264
%C.V	33.81
PRESS	795.26

In addition, adequate precision (Adeq. Precision) was used to measure the noise/signal ratio. the signal is adequate and the model can be used to navigate the design space if a ratio has more than 4. The Adeq. Precision of this study was favorable, that is, 15.26, with a CV% value (33.81) and PRESS (795.25).

Figure **8** shows the predicted values and the actual values for lead immobilization (%). The results obtained were quite close to the experimental values that successfully demonstrated the correlation between factor B-Application time.

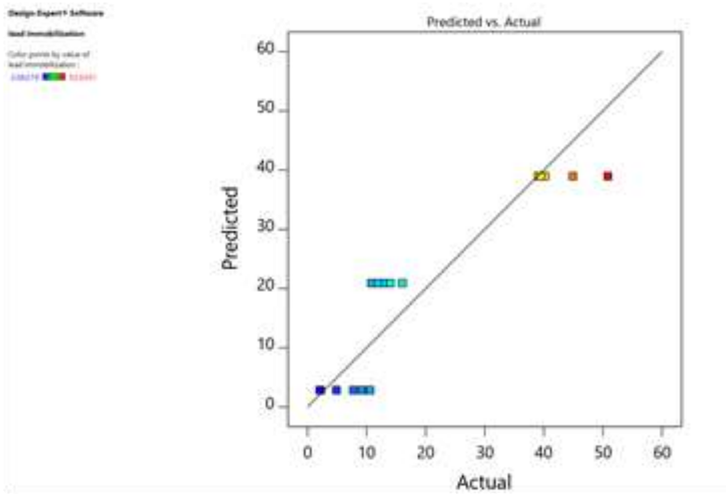

Figure 8: Predicted graph values and the actual values.

CONCLUSIONS

The application of biochar based on phosphate-rich sewage sludge is a promising way to immobilize lead in contaminated soils. FFS and SS of a WWTP have shown that they can be used, which have an accessible economic value, allowing their use to recover soil. The BSS showed a higher efficiency (50.83%) in the immobilization of lead in the soil with an application of 20 days and a dose of 10%. It was possible determining that the effect of the application time on the immobilization of lead from contaminated soil was the most significant ($p<0.05$).

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