Assessment of Pulverised Fly Ash (PFA) as an Ameliorant of Lead Contaminated Soils

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Abstract: Fly Ash (FA) is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of furnace fired with coal or lignite at 1100 to 1400°C. About 95-99% of Fly Ash consists of oxides of Si, Al, Fe and Ca, about 0.5 to 3.5% consists of Na, P, K and S and the remainder is composed of trace elements. PFA has also been used as an adsorbing material when applied in treatment effluents. The use of Fly Ash as a chemical conditioner has previously been investigated with results indicating that Fly Ash does facilitate the filtering process since it decreases both specific resistance and capillary suction time. Therefore, the aim of this paper was to assess the potential of PFA as an ameliorant for soil artificially spiked with various Lead compounds (PbSO₄, PbCO₃, PbNO₃ and PbS). Additions of quicklime and Fly Ash to the contaminated soils effectively reduced heavy metal leachability well below the regulatory limits for hazardous wastes. The results showed the effect of PFA on leaching of lead was significant for all the samples. A high interaction value depicting sampling effect over the use of the PFA as an ameliorant was observed. The order of the difference between samples treated with PFA and without PFA was PbNO₃ > PbSO₄ > PbCO₃ > PbS (17 mg L⁻¹) when compared to that of the control. The results also demonstrated that, effect of filtration and PFA as an ameliorant had a significant effect in reducing toxicity. However, it is important to consider the source of PFA, as certain sources could in essence impart certain toxic elements, defeating the primary purpose of amelioration.

Key words: Pulverised fly ash, toxicity, ameliorant, lead contamination

INTRODUCTION

Coal Combustion Products (CCP) are produced in coal-fired power stations, which burn either hard or brown coal. Due to the mineral component of coal and combustion technique, fly ash (FA), bottom ash (BA), boiler slag (BS) and fluidized bed combustion (FBC) ash as combustion products, as well as the products from dry or wet flue gas desulphurization, especially semi dry absorption (SDA), products and flue gas desulphurization (FGD) gypsum are produced.

The volume of CCP generated worldwide is reported to be on the increase due to the reliance on coal as a major source of energy[1]. For example, approximately 55% of U.S. energy is generated from coal and it is expected that coal will continue to be the leading electrical power source at least until 2010[2]. About 105 million tons of coal combustion products were produced by American power generating utilities in 1997[3]. In China, coal mining waste management is a major problem because of the huge quantities of coal produced for energy production, 75% of which comes from coal[4].

Fly Ash (FA) is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of furnace fired with coal or lignite at 1100 to 1400°C. By mid 1950’s, fly ash from coal combustion became known as Pulverised Fuel Ash (PFA) within the UK. This was to differentiate it from Fly Ashes delivered from other processes, since PFA is delivered from firing boilers with pulverised coal[5]. PFA is still produced in large quantities during the day-to-day operations of coal-fired power plants.

Economically viable ways of using CCP rather than having to dispose of, it have to be investigated. There is already a vast body of information on utilisation of Fly ash (FA) in building/construction, production of aggregates and more recently for agriculture[6]. Within the UK, PFA has been used for over 50 years for a wide range of applications[5]. Knowledge of the physical and chemical properties of Fly Ash is essential for understanding and in the future, predicting the behaviour of PFA in soil. The physical structure of Fly Ash often consists of “hollow spheres” and these particles show an increased surface area, capillary action and nutrient-holding capacity compared with sand[6]. Fly Ash also has been reported to improve the nutritional status of soils via increases in cation exchange capacity (CEC) and by provision of some essential nutrients[7-9]. However, since almost all naturally existing elements are present in PFA[10,11], the potential release of trace elements may also be an issue.
Chemically, the composition of Fly Ash varies depending on the quality of coal used and the operating conditions of the Thermal Power Stations. About 95-99% of Fly Ash consists of oxides of Si, Al, Fe and Ca, about 0.5 to 3.5% consists of Na, P, K and S and the remainder is composed of trace elements. In fact, Fly Ash consists of practically all the elements present in soil except organic carbon and nitrogen (Table 1). Thus, it was found that this material could be used as an additive/amendment material in agriculture applications. The chemistry of PFA reflects the mineral origins of the coals when formed millions of years ago. The combustion process concentrates these minerals. However, most elements are held in the glassy particles that are formed in the furnace. While the trace elements composition may indicate potential for environmental effects, the available leachable elements are minimal. With proper design, unbound PFA can be used as a fill material posing only negligible risk, even to sensitive aquifers.

Table 1: Physical and chemical characteristics of Indian fly ash and soil

| Properties | Fly Ash |
|------------|---------|
| BD (g cm⁻¹) | <1.0    |
| W.H.C. (%)  | 35-40   |
| Porosity (%)| 50-60   |
| P (%)       | 0.004-0.8|
| K (%)       | 0.19-3.0|
| S (%)       | 0.1-1.5 |
| Fe (%)      | 36-1333 |
| Zn (ppm)    | 14-1000 |
| Cu (ppm)    | 1-26    |
| Mn (ppm)    | 100-3000|
| B (ppm)     | 46-618  |

Modified from http://www.tifac.org.in/news/flyagr.htm

PFA has also been used as an adsorbing material when applied as an ameliorant in treatment effluents. The idea of using coal fly ash to synthesize artificial zeolite for water treatment is based on the fact that both materials have a similar chemical composition, namely a high content of aluminisilicate glass and high surface areas. Another example for using PFA, is to remove metal ions and phenols from water. In addition PFA has always been used for sludge conditioning for sludge originating from wastewater treatment containing high amounts of water (up to wt. 95%) and that needed to be dewatered in order to reduce its volume and disposal costs. The use of Fly Ash as a chemical conditioner has been investigated with results indicating that Fly Ash does facilitate the filtering process since it decreases both specific resistance and capillary suction time. Fly Ash has been found to have great potential for agriculture. For example, some of the advantages relate to modification of soil texture and bulk density, improvement of water holding capacity of soil, optimisation of soil pH, increase crop yield, as a micronutrient supplement to soil, creation of conducive conditions for better plant growth and reduction of soil crusting. The addition of appropriate quantities of Fly Ash can alter the soil texture. Fly Ash addition at 70 t ha⁻¹ for example, was reported to alter the texture of sandy and clayey soil to loamy.

However, despite positive uses of PFA, the rate of its production clearly far outweighs utility as a by product. This is because the remaining PFA material and its disposal practices involve holding ponds, lagoons, landfills and slag heaps, all of which can be regarded as unsightly, environmentally undesirable and/or a non-productive use of land resources, as well as posing an on-going financial burden through their long-term maintenance. Although as mentioned earlier, Fly Ash has immense potential in agriculture, there are some possible concerns, which need to be attended to or kept under control, such as the release of toxic elements into ground water, decreased germination rates of some crops due to high levels of Fly Ash application including uptake of heavy metals toxic elements by the plants. The uptake of heavy metals, toxic elements by plants was demonstrated when Fly Ash was applied to the soil. These elements were found to be absorbed by plants grown on such soils (treated with Fly Ash) and could enter into the food chain. However, the data on trace element uptake and accumulation by plants are limiting. Boron in Fly Ash is reportedly readily available to plants and investigators consider it to be a limiting factor in utilisation of unweathered Fly Ash. Regional Research (RRL), Bhopal conducted a study regarding the uptake of heavy and trace metals from Fly Ash by some vegetable crops and it was observed that the uptake was quite low and remained within the normal range.

Some studies have shown possible negative effects of Fly Ash application. For example, Fly Ashes contain a small amount of trace and heavy metals, which may percolate down the soil profiles and pollute ground water. However related studies have shown that the solubility of these elements is less than 10%. Moreover Natusch reported that leaching potential between 5 to 30% of toxic elements (especially Cd, Cu and Pb) in Fly Ash was observed in a related laboratory experiment. On the other hand Galloway et al. observed that at least 10% of total Cd would be solubilized in the acidic pH range of 3 to 5. It is unlikely, however that these will have a major effect on the quality of ground water. Furthermore, recent research has shown that the quality of ground water did not change with the application of Fly Ash and that all the parameters including the trace and toxic metal contents were within permissible limits.

There have been several reports in the literature of the presence of radionuclides in Fly Ash, but studies on their impact have been few. Radiochemical pollution with Uranium and Thorium series is always associated with Fly Ash.
The concentration of natural Uranium varies from 14 to 100 ppm although in exceptional cases, it could be as high as 1500 ppm, with Thorium less than 10 ppm\[34\]. Fly Ash, show to contain radioactive contaminants such as \(222\text{Ru}\) and \(220\text{Ru}\)[35]. Bhaba Atomic Research Centre, Bombay was of the opinion that most of the Indian coals and hence Fly Ash, had very low levels of radioactivity, which were well below hazardous limits\[46\]. Hence, radioactivity of Fly Ash may well not be a limiting factor for its application in agriculture. Recent research has shown that there is no significant uptake of radioactive elements by plants and that there is negligible cumulative build-up of these contaminants in soil when Fly Ash is applied for agriculture purposes.

Coal power plants are mostly located in urban areas and therefore finding disposal sites for Fly Ash is becoming increasingly difficult\[23\]. As a consequence, Ciccu\[37\] carried out an investigation to assess the potential use of Fly Ash from coal-fired power stations for immobilising the heavy metals in soils at a severely contaminated Italian mine site. The results obtained showed that heavy metal content of percolating water could be drastically diminished when the soils were mixed with Fly Ash. Gupta and Imran\[38\] successfully removed lead and chromium from wastewater using bagasse Fly Ash, a waste by-product of the sugar industry. Chien-Jung Lin et al.\[39\] looked at the effect of applying Fly Ashes to remove metal ions from wastewater and concluded that the cation exchange capacity and specific surface area of Fly Ashes increased with increasing carbon content and consequently, residual carbon in the Fly Ashes played a much more important role than the mineral content in the removal of metal by the Fly Ashes.

Dermatas and Meng\[40\] utilised Fly Ash waste material along with quicklime (CaO) to immobilise lead, Cr(III) and Cr(VI) present in artificially contaminated clayey sand soils. The experimental results suggested that the controlling mechanism for both lead and hexavalent chromium immobilisation was through surface adsorption, whereas for trivalent chromium it was the hydroxide precipitation. Additions of quicklime and Fly Ash to the contaminated soils effectively reduced heavy metal leachability well below the regulatory limits for hazardous wastes\[40\]. The aim of this paper is to investigate the effect of PFA on soils artificially spiked with various Lead compounds (\(\text{PbSO}_4\), \(\text{PbCO}_3\), \(\text{PbNO}_3\) and \(\text{PbS}\)).

MATERIALS AND METHODS

The topsoil used in these experiments was collected from the top 25 cm of an agricultural field on the Craibstone estate, which is approximately 9 km North West of Aberdeen, at an elevation of 100 m. The pots had a diameter of 150 mm and a surface area of 17,600 mm\(^2\). A Whatman 42 filter paper was placed on the base of each pot to prevent coarse material from passing through. Leaching pots were arranged on a leaching bench with holes wide enough to hold them. Funnels with aligned filter paper (Whatman 42) inside were placed under each pot placed on the leaching bench to collect leachate in a conical flask placed on the bottom of the shelf. The controls used are soils spiked with lead compounds but not treated with PFA.

Preparation of experimental pots: Thirty pots were packed with either a mixture of soil, lead compounds and Red earth, or soil with lead compound only.

Control: 3 pots of soil only
3 pots of soil+PFA

Samples: 3 pots of soil+Pb compound
3 pots of soil+Pb compound+PFA

Since 4 Pb compounds were considered (\(\text{PbS}\), \(\text{PbSO}_4\), \(\text{PbNO}_3\), \(\text{PbCO}_3\)), the total number of samples were 24. This translates to thirty pots together with 6 pots of control. The mixture of soil, Pb compound and PFA under study was thoroughly shaken together in plastic bags of 1 kg capacity to allow for homogeneity prior to packing the pots. The amount of PFA required per experimental pot was 20 g L\(^{-1}\). \(42 = 14.08\) g of PFA per pot.

The area where the bottles were placed was protected with black, plastic material to minimise the effect of light on leachate chemical properties. All the experimental treatments were carried out in triplicate.

Bioassay: Lux-marked bacterial biosensors were used during the study and the preparation of the biosensor and luminometer measurements were carried out as described. One hundred \(\mu\)L of the resuscitated biosensor suspension was added to the samples at 15 s intervals, accurately timed for measurement in the Bio Orbit 1253 luminometer (Labtech International, Uckfield, U.K). Each sample was exposed to the sensor for exactly the same time. Samples were incubated for 15 min before light output measurements were carried out at 15 s intervals. This ensured the same exposure time to the potentially toxic elements for cells in each of the cuvettes.

Chemical analysis: A 1.599 g of lead nitrate, \(\text{Pb(NO}_3\)\(_2\) (analytical grade) was carefully weighed and dissolved in deionized distilled water. When dissolution was complete, it was acidified with 1 ml of 1M \(\text{HNO}_3\) and diluted to 1 L with deionized water. Standard Lead Solution was prepared by diluting the stock (lead) solution. Concentration ranges starting from 0.1, 0.5, 100, 200, 400, to a maximum of 800 g L\(^{-1}\) which were used as calibration standards. Standard solutions of lead were prepared fresh for use from a stock solution of lead nitrate (0.1 mol L\(^{-1}\) in \(\text{HNO}_3\)). All standard and sample soil solutions were prepared to approximately 0.1 mol L\(^{-1}\) in \(\text{HNO}_3\). Care was taken to use specially...
purified water (deionized water) when diluting samples to final volume for quality control purposes.

Deionized water was also used during the final rinsing of all the plastic and glassware. This was after rinsing them first, in solution (with diluted nitric acid) in order to remove any possible traces of lead on them. During the determination of concentration two replicate determinations of absorbance were made for each sample. A blank of deionized water was used to zero the instrument.

A 10 µL sample was injected very carefully with the help of an auto sampler into the cold graphite furnace and by means of an automatic temperature programmer, dried at 120 °C for 35 s and at 140 °C for another 35 s, then heated to 200 °C and allowed to cool for 15 s. These steps were performed, automatically, to remove solvent and any removable volatile matrix. Actual atomization of the sample followed and was performed at 1800 °C, very rapidly, for 5 s. During this time the signal from the chamber (absorbance) was recorded and displayed on the screen as a function of time. Finally the furnace was heated for 5 s at 2600°C. The purpose was to remove any residues and prepare the instrument for next sampling phase. During the atomization step, the absorbance was monitored at 283.3 nm, using a slit width of 0.7 nm, set at "low" level. Purging with argon was interrupted automatically during the absorbance scan. Background correction was provided by means of the deuterium background corrector, which automatically compensated for broadband absorption interferences.

Data analysis: Two-way analyses of (ANOVA-Analysis of Variance) (except for biosensor experimental data which is One-way ANOVA) were carried out using the statistical package Minitab for windows, release 12.1 (State College, PA, USA). Mean differences were determined using t-test (paired two samples for means) and Pearson Correlations using Excel program (Microsoft® Office 2000). Significant differences between treatments were elucidated using least significance difference (LSD) values. Graphs were generated using Sigma Plot for Windows version 9.0 (Jandel Corporation, CA and USA).

RESULTS

Effect of PFA on lead concentration of leachate: The highest leachate concentration of Pb was observed with PbNO₃ (64±2.03 mg L⁻¹) while PbSO₄ (29.4±3.0 mg L⁻¹), PbS (28.7±2.973.0 mg L⁻¹) and PbCO₃ (23.37±3.37 mg L⁻¹) showed similar concentrations (Table 1). The lowest leachate Pb concentration was demonstrated with the unspiked samples (control, 4.4±0.4). The results showed that the effect of PFA on leaching of lead was significant for all the samples (Fig. 1). A high interaction value depicting sampling effect (p<0.001) over the use of the PFA as an ameliorant was observed. The order of the difference between samples treated with PFA and without PFA was PbNO₃ (21.7 mg L⁻¹), PbSO₄ (21.01 mg L⁻¹), PbCO₃ (17.4 mg L⁻¹), PbS (17 mg L⁻¹) to that of the control (3.3 mg L⁻¹) (Table 2). While a significant difference (p<0.05) was observed between all the samples relative to the control there were no differences between PbSO₄ and PbS (p=0.45), PbCO₃ and PbS (p=0.19) and PbSO₄ and PbCO₃ (p=0.25).

Effect of PFA treatment on pH values of leachate from samples spiked with lead compounds: All Pb spiked soil samples demonstrated an increase in pH when treated with PFA, highlighting a strong alkaline regulatory role for PFA (Fig. 2). A significant difference (p<0.01) on pH values was observed with all the samples when the treatment effect was measured. The highest pH after treatment with PFA was observed on PbSO₄ (8.7±0.05), while the lowest pH value was for samples not spiked or treated with PFA (7.31±0.13). However, immediately on spiking of the soil samples with lead compounds, the pH increased marginally to over 7.5.

Biosensor based toxicity of the leachate Effect of filtration of leachate on biosensor response: All the samples without PFA, when filtered, showed a marginal increase in percentage bioluminescence with the highest effect amongst the spiked samples observed for Pb NO₃ (63.18%±1.62) and the lowest for PbSO₄ (47.17%±3.22) (Table 2). All the controls showed higher luminescence in comparison with the spiked samples indicating lower toxicity levels. However, for unfiltered samples (without PFA), the highest luminescence results (apart from the controls) were observed with PbS (57.2%±1.97) and the lowest with PbSO₄ (22.13%±2.75).

Immediately after the equilibration period (9 d) (following spiking of the samples and the application of PFA), the samples showed a significant increase (p<0.001) in luminescence in all the treatments. The highest percentage luminescence was observed with PbNO₃ (83.74%±1.55) and the lowest with PbS (68.31%±2.43) when filtered and treated with PFA. However, for unfiltered leachates samples treated with PFA, the highest luminescence result was observed with PbNO₃ (74%±1.24), while the lowest was with PbSO₄ (35.05%±2.60).

Further analysis of percentage luminescence data showed that the effects of filtration on samples (not treated with PFA) were higher in comparison to those that were not filtered. The highest difference was observed with PbNO₃ (23.60%) and PbSO₄ (22.05%), with the lowest luminescence noted with PbS (2.24%) (Table 2). However, when filtered samples, were analysed for the effect of PFA (i.e. with/without PFA), the highest differences in mean percentage luminescence were observed with PbSO₄ (29.01%).
Table 2: Analysis (ANOVA and LSD) of luminescence-based toxicity data for leachates from samples treated with/without PFA (filtered/unfiltered)

| Samples      | Without PFA | With PFA |
|--------------|-------------|----------|
|              | Mean Filtered | Mean Unfiltered | Mean Filtered | Mean Unfiltered |
| NoPb         | 89.32 (0.89) | 79.81 (1.82) | 97.05 (2.12) | 88.55 (1.97)   |
| PbS          | 59.44 (2.43) | 57.20 (1.97) | 68.31 (2.43) | 65.05 (2.75)   |
| PbSO₄        | 47.17 (3.22) | 22.13 (2.75) | 76.18 (2.60) | 35.05 (2.60)   |
| PbCO₃        | 50.38 (1.62) | 39.58 (1.47) | 76.07 (3.22) | 60.97 (1.47)   |
| PbNO₃        | 63.18 (1.44) | 41.22 (2.60) | 83.74 (1.55) | 74.14 (1.24)   |

*p value***  ***  ***  ***

LSD (5%)  3.8  3.3  3.07  3.07

Figures in parentheses show standard errors of the mean, *** p< 0.001, N = 9

To further determine the particulate effect on leachate sample toxicity, analysis of the samples that were not treated initially with PFA and remained unfiltered were compared with those that were filtered and treated with PFA. The results as shown earlier demonstrated that filtration improved bioluminescence. Moreover when considering the effect of both filtration and treatment of the samples with PFA, the results demonstrated that, samples that were unfiltered and not treated with PFA only indicated the highest percentage luminescence with PbS (57.20%±1.97) while the lowest was with PbSO₄ (22.13%±1.97). When the same samples were treated with PFA and filtered,% bioluminescence values increased indicating a reduction to toxicity for PbS (68.31%±2.43) and PbSO₄ (76.18%±2.60). However, the highest difference in percentage luminescence between filtered (and treated samples) and unfiltered (and untreated) samples were observed with PbSO₄ (54.05%) and PbNO₃ (44.16%). The lowest difference in luminescence was noted with PbS (11.11%) (Table 2).

Effect of PFA on pH (less or above pH 5.0) adjustment: The effect of PFA on filtered/unfiltered samples was demonstrated when the same samples were further subjected to pH adjustment. They all showed significant (p<0.001) results on adjustment of pH less or above 5.0 (Fig. 3i) and ii)). This observation illustrated that pH management could be used as another potential tool in the intervention of lead contamination.

When the samples were further adjusted at pH > 5.0, higher luminescence was observed for the reference material (double deionised water), No Pb (filtered and Unfiltered) with and without PFA, filtered PbSO₄, PbNO₃ and PbCO₃ with PFA (Fig. 3i). The lowest percentage luminescence was observed with PbSO₄ for both filtered and unfiltered samples. However, for samples adjusted to pH<5.0, the highest bioluminescence for filtered/unfiltered was observed for PbS treated with PFA (114%) while the lowest luminescence was observed with PbNO₃ filtered (35%) and unfiltered (23.5%) and treated with PFA (Fig. 3ii).


DISCUSSION

Many metals are known to be particularly harmful to human health. There is, therefore, a pressing need for efficient treatment strategies to reduce the toxicity of metal contaminated soil using cost effective techniques e.g. naturally available ameliorants (e.g. PFA). PFA is known to be alkaline which further aids retention of metals. PFA has almost no biodegradable organic material and produces no gas as a product of such degradation. Chaudhuri et al. [41] studied the mobility and bioavailability of selected heavy metals in coal ash and sewage sludge-amended acid soil and concluded that soil quality was enhanced with the addition of either sludge or ash or their mixtures, with no possible threat to increased bioavailability and mobility of metals. In addition, PFA may be used as an amendment to improve physical and chemical characteristics of sandy soils. When applied at sufficient rates (e.g. to achieve 10% w/w in surface layers) to sandy soils, Pathan et al. [21] found that Fly Ash altered texture and increased water-holding capacity. However, Fly Ash samples from different sources (e.g. Australia) showed considerable variation in several properties [21]. Depending on the source used to amend soils, Fly Ash may also provide P and aid nutrient retention by increasing the P retention index and/or cation exchange capacity. That composition of Fly Ash varies depending on the quality of coal used and the operating conditions [10]. For example, PFA from a Thermal Power Station was found to consist of elements essential to plant growth like Ca, Fe, Mg, K but also of other such as B, Se, Mo and metals that can be toxic to the plants [42]. PFA in most of the cases exhibits similar physical and chemical characteristics (Table 1) as demonstrated in samples collected from India.

To comprehend in the current study, the ameliorant potential of PFA (in terms of intercepting mobile lead) for soil matrices spiked with various Pb compounds (PbSO₄, PbNO₃, PbS and PbCO₃), data from the leachate collected after 9 d were compared (i.e. for samples with/without PFA). The order of concentration (mg L⁻¹) of Pb (in decreasing order) was; PbNO₃>PbSO₄>PbS>PbCO₃ but, on addition of PFA, the largest difference in concentration (mg L⁻¹) between the control and the treated samples was of the order PbNO₃>PbSO₄>PbCO₃>PbS. The order exhibited the same pattern except for the PbS and PbCO₃ samples.

The increase in soil pH from 6.00 to above 8.00 observed during the current study on addition of Fly Ash, was similarly reported by Page et al. [13] who, in their experiments with calcareous and acidic soils, revealed that Fly Ash addition also increased the pH of the calcareous soils from 8.0 to 10.8 and that of the acidic soils from 5.4 to 9.9. In India for example, most of the Fly Ash produced is alkaline in nature and also an application of these to agricultural soils could

When individual samples treated with PFA were measured, treatment effect on pH adjusted (i.e. pH less than and above 5) lead spiked samples was significant (p<0.05) only with PbS and PbNO₃ (Fig. 4) suggesting most probably that pH did not affect the overall adsorption potential of PFA for the other samples.

Fig. 3: i) Effect of Filtration and pH above 5 on the toxicity of leachate from soil amended with various lead compounds and treated with or without PFA. ii) Effect of Filtration and pH below 5 on the toxicity of leachate from soil amended with various lead compounds and treated with or without PFA

Fig. 4: The comparative effect of pH adjustment on the toxicity of leachate from the lead spiked soils treated with PFA
possibly increase the soil pH\textsuperscript{[36]}. This property of Fly Ash can be exploited to neutralize acidic soil\textsuperscript{[38,43]}. The effect of Fly Ash addition effectively raises the pH and if applied to acidic soil, should reduce the metal solubility and hence availability to plants.

As an ameliorant, PFA’s impact on the bioavailability of various Pb compounds was assessed by the use of a genetically modified biosensor lux-marked \textit{E. coli} HB101 pUCD607. The choice of the biosensor was appropriate due to its robust, wide pH ranges (3.0–10.00) and sensitivity in measuring the toxicity of the final leachate collected\textsuperscript{[50]}. The results indicated that prior to the application of PFA to the samples leachate; filtration had the highest effect for PbSO\textsubscript{4} treated soil with a 113.15% increase in luminescence (i.e. from 22.13 to 47.17%). However, this result, which suggested the adsorption of PbSO\textsubscript{4} on the particulate matter of the soil matrix, still demonstrated the toxic nature of the leachate from lead spiked soil. When the unfiltered leachate (indicating lowest luminescence values) from PFA amended soils were tested, the highest increase (86.49%) due to PFA was observed with PbNO\textsubscript{3} (i.e. luminescence increasing from 39.58 to 74.14%). This observation suggested that, when PFA was used as an ameliorant for unfiltered Pb spiked samples, all lead compounds (except PbSO\textsubscript{4} (35±2.60%)) compounds were rendered less toxic by generating less bioavailable lead in the leachate. However, when the same samples treated with PFA were filtered all the samples increased their luminescence with PbSO\textsubscript{4} (which earlier had low luminescence) showing the highest percentage increase (244.24%).

Bataillard \textit{et al.}\textsuperscript{[41]} reported that when lead was added as sulphate, between 10 and 20% of lead particles dissolved, regardless of the soil type with lead sulphide progressively oxidising over time. The low dissolution of lead sulphate could explain the immediate effect of filtration by causing increased luminescence, suggesting that most of the metal was held in the colloidal medium. This observation was critical indicating that while the application of PFA, as an ameliorant was effective, filtration as a technique improved the reduction of toxicity even further after the application of PFA but not before. Overall, the application of PFA appeared to reduce metal release from heavily contaminated soils rendering the final leachate less toxic. Shende \textit{et al.}\textsuperscript{[45]} used alkaline Fly Ash to reduce the metal toxicity of contaminated soil through immobilization of heavy metals. However, these workers found that when the Fly Ash application exceeded 5% on a weight for weight basis in soil, crop growth was significantly reduced. The pot culture studies were carried out with maize (\textit{Zea mays}) crop grown in acidic sandy loam (pH 4.9) and calcareous silty clay (pH 7.9) soils treated with known concentrations of heavy metals (viz. cadmium, copper, nickel and zinc). The adsorption properties of PFA are related to PFA’s ability in immobilizing heavy metals and in studies by Wang \textit{et al.}\textsuperscript{[46]} on characterisation of the metal adsorption capability of class F coal Fly Ash, it was established that the surface physical-chemical characteristics of a class F coal Fly Ash had a quantitative relationship with metal adsorption. During the same study, the adsorption results indicated that metal adsorption was in the linear range of the Langmuir isotherm if the total metal in the system was less than 10% of the total metal binding site. In addition, the results showed that, the presence of cationic metal ions does not affect the adsorption of cationic metal ions by the Fly Ash.

Filtration was primarily used to investigate the impact of the particulate matter on bioavailability of the heavy metals and efficacy of PFA as an ameliorant. Thus in other related studies investigating grain size and how the silt size range of Fly Ash affects the bulk density of soil, Chang \textit{et al.}\textsuperscript{[47]} observed that among five soil types, Reyes silty clay showed an increase in bulk density from 0.89 to 1.01 when the corresponding rates of Fly Ash amendment increased from 0 to 100%. Page \textit{et al.}\textsuperscript{[13,48]} reported that Fly Ash amendment to a variety of agricultural soils tended to decrease the bulk density. Optimum bulk density in turn improves the soil porosity, the workability of the soil, the root penetration and the moisture retention capacity of the soil. Changes in soil texture could be expected in both agricultural soils as well as strip-mined soils. It was generally observed that both sandy and clayey soils tend to become loamy in texture\textsuperscript{[49]} when PFA is added in the U.S. where the average silt content in Fly Ash is about 63.2%\textsuperscript{[35]}, although in India, this content ranges from about 16%\textsuperscript{[50]} to 45%\textsuperscript{[51]}.

**CONCLUSION**

The aim of the study was to investigate the effect of PFA on the leaching of lead from soils amended with various lead compounds (PbS, PbSO\textsubscript{4}, PbNO\textsubscript{3} and PbCO\textsubscript{3}). PFA was found to be a useful ameliorant and to be both efficient and effective for all the lead compounds tested. Its use was also found to offer a potentially valuable alternative as an environmental management tool in reducing the unsightly mounds that can develop due to scarcity of PFA disposal land sites. The application of PFA as an ameliorant to lead spiked soils during the study showed great potential as an \textit{in situ} technique to remediation of contaminated sites. For example when leachate filtration was measured for toxicity after the application of PFA, a drastic improvement of bioluminescence levels were observed. This suggesting that PFA was precipitating the metals in the soil matrices into unavailable toxic colloidal fraction. Further improvement in the reduction of the toxic material was demonstrated through filtration of the samples after treatment with PFA. Essentially this
technique managed to remove the colloidal bound toxic particulate matter effectively as indicated with the results shown. However, the most important aspect that needs to be considered is to establish the source of the PFA, as certain sources could possibly impart certain toxic elements, defeating the primary purpose of amelioration.

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