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Influence of Soil Moisture and Bioamendments on the Speciation and Bioavailability of Chromium in Contaminated Soils

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Abstract: Chromium (Cr) is a strategic and dangerous heavy metal with many applications in the leather tanning and chemical industries. Cr has gained importance due to the greater understanding of its persistence and toxicity in ecosystems. To protect our environment from severe contamination threats, it is essential to remove Cr. But, before developing a remediation strategy, it is necessary to understand various factors and soil parameters that influence the bioavailability and fractionation of heavy metals. The investigation was conducted in a laboratory closed incubation experiment with bioamendments in a completely randomized design with three replications for 60 days. The study examined the impact of amendments like farmyard manure, composted poultry manure, pressmud compost, and biochar on Cr speciation in contaminated soil under different moisture conditions. The findings revealed that organic amendments substantially impacted soil chemical parameters such as pH, Cr mobility, and bioavailability. The significant reduction of bioavailable fractions was observed in biochar (75 to 80%) amended soil, followed by farmyard manure and poultry manure (60 to 70%). As a result, bioamendments can effectively reduce the bioavailability of Cr in contaminated soil and play a significant role in designing a bioremediation technology for the chromium contaminated soil.

Keywords: Bioremediation, Bioavailability, Chromium contamination, Moisture regimes, Bioamendments

Heavy metal contamination is one of the world's major environmental issues, resulting in crop yield losses. Chromium (Cr) is the seventeenth most abundant element on the planet and the second leading cause of groundwater, soil, and sediment contamination (Avudainayagam et al 2003). When contaminants enter the food chain, they impact human health. Several industrial processes and anthropogenic activities, such as leather tanning, chrome ore mining, fertilizers, pesticides producing factories, electroplating, metal finishing, corrosion control and pigment manufacturing industries releases various forms of chromium in soil and water (Yadav et al 2017). The majority of groundwater samples were unsuitable for irrigation based on index values this is due to anthropogenic activities such as excessive and pesticide are the main sources of chromium (Kumar and Balamurugan 2019). There are two stable forms of chromium, trivalent Cr (III) and hexavalent Cr (VI), which is more toxic and are interconvertible in soil. Cr in some locations shows that greater pollution and human health may be a concern as the landfill matures and the process of maturing continues (Elamin et al 2021).

Similarly, soil contamination caused by tannery wastes in Vellore district and textile industries in Tiruppur District of Tamil Nadu has deteriorated soil health (Rajendiran et al 2015). Cr is one of the heavy metal released through tannery waste, which is highly toxic to humans and plants, and it has been a primary environmental concern for several decades (Tiwari et al 2019). Cr levels in contaminated soils in the Vellore District were extremely high, indicating that the soils surrounding tannery industries are heavily contaminated with Cr (Rangasamy et al 2015, Sathya et al 2021). Large amounts of Cr (16,731-79,865 mg kg^{-1}) were found in surface and subsurface soils in Vellore Districts, where many tanneries exist (Mahimairaja et al 2011). Chromium contamination in soil and water has drastically reduced the crop yields (25 to 40%) over the years (Dotaniya et al 2014). With increased public awareness of Cr poisoning in both animals and humans, there has been a surge in the desire to develop regulatory guidelines and remediation technologies for Cr-contaminated soil and water ecosystems (Rahman and Singh 2019). The reduction of Cr (VI) to Cr (III) and subsequent adsorption as a method for managing Cr contamination in soils has been proposed as an effective method (Premalatha et al 2018). Understanding the bioavailability of Cr (VI) and Cr (III) in soils prompts research into their adsorption and desorption of chromium

(Kamaludeen et al 2003). Clay soil has enormous small pores in which more water is kept and might have promoted microbial activity in the clay soils and remediates the contaminated soils (Salwan Al-Maliki et al 2019). Organic matter in the soil may transform over a period of time. These transformations may have certain effect on the retention or adsorption of Cr in soil. Based on the nature and stability of organic amendments, they can influence metal solid solution phase partitioning and thus alter the bioavailability and environmental fate of metals. Hence, with these facts in view, this research was initiated to quantify the relative adsorption of Chromium by various organic amendments in contaminated soil.

The remediation of chromium contaminated soils is an important issue that helps sustain agriculture and reduces negative environmental impacts (Mahimaraja et al 2011) conducted laboratory experiments to examine the potential of biological wastes in remediating Cr contaminated soils. Their results revealed that 61% (in clay loam soils) and 75% (silt clay loam soils) reductions in the concentration of bioavailable fractions (soluble plus exchangeable) of Cr resulted from the application of coir pith. Sathya and Mahimairaja (2016) also conducted laboratory experiments using bioamendments for the remediation of Nickel. From these experiments, we concluded that the application of biological amendments, namely farmyard manure, composted poultry manure, pressmud compost and biochar, were found to be effective for reducing the bioavailable fractions of Cr, mainly through the formation of organic complexes, demonstrating their great potential in the bioremediation of Cr-contaminated soil. Therefore, in the current study, a bioremediation technology was developed by the addition of biological amendments and evaluated its potential in remediating the Cr contaminated soil, and the influence of soil pH, organic carbon (OC) content on bioavailable fractions of Cr in bio-amended soil was studied through a laboratory closed incubation experiment.

MATERIAL AND METHODS

Study area: The effect of different bio-amendments on the bioavailability of Cr and its fractions were investigated by performing a laboratory closed incubation experiment at the National Agro Foundation Research and Development Centre, Chennai, India (12º.98'84.01" N, 80º.22'26.4" E). The soil samples were air-dried for three days and sifted using a 2-mm sieve to attain equal particle size.

Selection of bioamendments: Bioamendments such as farmyard manure, composted poultry manure, pressmud compost, and biochar were chosen for this study. The bio-amendments were collected from Tamil Nadu Agricultural University Farm, Coimbatore (11°00'45.8"N 76°55'53.8"E). They are used as soil amendment to improve soil quality, fertility and increase soil carbon sequestration. In addition, the recalcitrant nature of bio-amendments increases their long-term potential value as a soil amending material (Liang et al 2021). Furthermore, incorporating bio-amendments into the soil can be used as a soil conditioner because it improves soil fertility due to its high organic carbon content and high nutrient and water sorptive capacity (Chan et al 2020). The selected bioamendments have favorable features, such as their large specific surface area, porous structure, surface functional groups, and high pH, allow them to be utilized as an adsorbent to immobilize heavy metals in soil (Rieuwerts 2007). Important characteristics of the bio-amendments were determined and presented in Table 1.

Incubation experiment: In the incubation experiment, soil was spiked with Potassium Dichromate ($K_2Cr_2O_7$) synthetic salt to achieve a final concentration of 500 mg Cr kg^{-1} and was mixed thoroughly. Then, five hundred grams of Cr salts spiked soil was weighed in a 2 kg plastic container and closed with a polyethylene cover containing small holes for aeration. Three replicates of each treatment were prepared and placed randomly and incubated in the laboratory at 25 ± 2ºC for 60 days. The moisture content of the soil samples were maintained at two different conditions in Field capacity moisture (FC) and Alternate wetting and drying condition (AWD). Then, after three days of equilibiration, selected bioamendments were added by following the treatment details;

Treatment Details

T_1 – Control, T_2- 500 mg kg^{-1} of Cr+ 12.5t ha^{-1} of farmyard manure, T_3- 500 mg kg^{-1} of Cr + 5t ha^{-1} of composted poultry

Table 1. Physico-chemical characteristics of bioamendments

Parameter	Unit	Farm yard manure	Composted poultry manure	Pressmud compost	Biochar
pH	-	7.25±0.009	6.23±0.07	6.27±0.13	7.86±0.19
EC	dS m^{-1}	3.08±0.02	2.35±0.003	2.28±0.03	3.19±0.06
Total nickel	mg kg^{-1}	16.01±0.39	16.26±0.25	13.50±0.29	18.07±0.23
Total chromium	mg kg^{-1}	BDL	0.47±0.001	0.33±0.007	BDL
Total cadmium	mg kg^{-1}	3.69±0.08	3.14±0.02	3.07±0.07	3.86±0.04

Note: BDL- Below Detectable Limit

manure, T_4- 500 mg kg^{-1} of Cr + 5t ha^{-1} of pressmud compost , T_5- 500 mg kg^{-1} of Cr + 5t ha^{-1} of biochar, M1- Field capacity moisture, M2- Alternte wetting and drying conditions

At the end of 0, 15, 30, 45, and 60 days of incubation, the samples were thoroughly mixed, and examined for pH and different fractions of Cr.

Speciation of chromium: Heavy metals transform based on their chemical valence state. As a result, a sequential extraction protocol was used to determine the relative proportions of different forms of Cr. A technique pronounced by Hughes and Noble (1991) was used to determine the species of retained chromium in the soil, and the calculation is depicted below.

Water-soluble fraction (Step1): One gram of air-dried soil sample was weighed in a 50ml polypropylene centrifuge tube and add 25ml of double-distilled water. It was shaken in an end- over-end shaker for 2h at 25 ± 2ºC. Then the samples were centrifuged (8000 rpm) for 10 minutes and filtered (Whatman No. 40). The amount of soluble Cr in the water extract was measured using an Atomic Absorption Spectrophotometer with an air-acetylene flame of VARIAN, AA240 (USEPA, 1979).

Exchangeable fraction (Step2): The amount of 25 ml of 0.5 M KNO_3 was added to the residue from phase 1 and shaken for 16h. As in phase 1, centrifugation, filtration, and calculation were carried out.

Organic fraction (Step 3): To the residue from step 2, 0.5M NaOH was added and shaken for 16h. The centrifugation, filtration is analysed in AAS for the chromium concentration, and calculation were carried out equation 1

Organic plus iron-oxide bound fraction (Step 4): To the residue from step 3, 0.05M Na_2EDTA was added and shaken for 6h. The centrifugation, filtration, and measurement

Residual fraction (Step 5): The soil residue from step 4 was transferred into a 100 ml conical flask utilizing small quantities of water and dried in an oven. 10ml of nitric acid (concentrated) was added and the contents were digested at 110ºC. After digestion, the contents were diluted and filtered using Whatman No.4 filter paper. Cr content in the filtrate was measured. Before and after the extraction, the tube and contents were weighed to determine the volume of entrapped solution and heavy metal transfer between extractants. The following equation was used to calculate the sum of Cr extracted by each extractant.

Cr extracted mg kg^{-1} = C x (E+M) - (C' x M) / soil weight

Where, C - Heavy metal concentration in the extraction solution, E - The extractants mass (g), M - Entrained solution mass (g) carried over from the previous extraction. C - Heavy metal concentration in the extraction solution of the previous step of the sequence.

RESULTS AND DISCUSSION

Characteristics of soil and bioamendments: The pH of the experimental soil was 7.30, with an EC of 0.542 dS m^{-1}. The following four bioamendments were chosen: Biochar, composted poultry manure, pressmud compost, and farmyard manure. The pH varied between 6.23 (composted poultry manure and 7.86 (biochar). The electrical conductivity (EC) was between 2.35 dS m^{-1} (composted poultry manureto 3.19 dS m^{-1} (biochar). The organic carbon content was 24.12% in farmyard manure, which is higher than others when compared to composted poultry manure ,pressmud compost , and biochar.

pH of bioamended soil: The pH of Cr contaminated soil was 7.82, which were significantly increased due to the incorporation of different amendments (Fig. 1). When the soil's pH increases, the soil's negative surface charge increases, resulting in increased adsorption of positively charged Cr. Initially, the pH of the experimental soil on the 0th day without amendments was about 7.65 whereas, after adding organic amendments, pH varied between 7.69 to 7.82. After adding biochar, the soil pH had increased and it is mainly due to the alkaline nature of biochar and contribute to the stabilization of heavy metals (Wang et al 2019). The pH of the soil in the field capacity moisture condition (M1) was higher than the pH of the soil in the alternate wetting and drying condition (M2). The decrease in soil pH could be due to the production of organic acids during the decomposition of soil organic matter and the adding of organic amendments (Fatima et al 2021), while the increase in pH was most likely due to the production of NH_4 and the addition of base ions from bioamendments (Seenivasan et al 2015). Because of the activity of protons and ions, changes in the pH of the solution had an effect on the adsorption of metal ions (Alatabe and Kariem 2021).

Electrical conductivity of bio-amended soil: The initial electrical conductivity of the experimental soil was about 0.48 dS m^{-1}, further after the addition of different amendments the conductivity ranged between 0.35 and 0.54 dS m^{-1}. After 15 days, the EC increased slightly compared to the initial conductivity. However, Electrical conductivity (EC) started decreasing later till the 60th day. The highest EC value (0.86 dS m^{-1}) was recorded in the composted poultry manure added soil, whereas the lowest (0.21 dS m^{-1}) was observed in soil that received pressmud compost at a rate of 5t ha^{-1}. Further, the electrical conductivity under field capacity conditions were slightly less than under alternate wetting drying conditions. Out of all amendments, biochar and pressmud compost exhibited the lowest electrical conductivity; this might be due to the adsorption of some cations and anions of amendments.

Soil organic carbon of bio-amended soil: Results from the laboratory closed incubation experiment have shown that the incorporation of bioamendments had remarkably enhanced the soil organic carbon (SOC). Initially, the SOC content ranged between 0.41% (T_1) and 0.68% (T_4). After 60 days of the incubation period, the organic carbon content ranged between 0.88% (T_5) to 1.18% (T_1). Hence, at the end of 60 days, the highest SOC (1.25%) was observed in biochar incorporated soil under alternate wetting and drying, whereas the lowest (0.21%) was observed in the control soil under field capacity moisture. It could be ascribed to the amount of the functional groups there in the biochar, larger specific surface area, and higher porosity of the soil, which paved the way for a higher rate of Cr adsorption (Sathya and Mahimairaja 2016). Similar results were also reported in the work of Shenbagavalli and Mahimairaja (2012) and the improvement in the organic carbon content due to the incorporation of organic amendments was also reported by Liu et al (2016) and Joshi et al (2017.) Out of all amendments, biochar has markedly increased the soil organic carbon than others Similartrend was observed by Lehmann (2007).,

Influence of bio-amendments on the bioavailability of Cr under two different moisture regimes: The bioavailability of chromium chemical fractions is divided into three categories: readily bioavailable, potentially bioavailable, and unavailable fractions, as well as the impact of bio-amendments in chromium contaminated soil. In both the field capacity moisture and alternate wetting and drying conditions, the higher concentration was observed on initial day and decreased at 60th day of the incubation period. According to the classification, the readily available chromium in the analyzed soils decreased over time (Shahid et al 2017). The farmyard manure @ 12.5t ha^{-1} (T_2) showed a higher readily available fraction than all the other treatments in field capacity moisture conditions. Heavy metal binding in various fractions varies greatly depending on their bioavailability and chemical activity (Olaniran et al 2013). In both the conditions, the concentration of unavailable chromium fractions was higher at the beginning and at the later stages. It is feasible that the higher concentration of unavailable chromium fractions is due to a significantly less mobile state (Nawab et al 2016).

Water-soluble fraction: The water-soluble fraction was higher in soil under field capacity moisture conditions at the initial and final stages. There was an increasing trend in all the treatments towards the days from 0th to 60th day of the incubation period (Fig. 2). Initially, a high concentration of H_2O – Cr was observed under both moisture conditions, which ranged from 91.66 to 95.53 mg kg^{-1}. Application of different bioamendments markedly reduced the concentration of H_2O – Cr. During 60 days of incubation under field capacity moisture conditions, the H_2O–Cr concentrations were found to decrease up to 82.25 mg kg^{-1} with the application of farmyard manure at a rate of 12.5 t ha^{-1}. However, it was high in the soil during the incubation under alternate wetting and drying. Under field capacity moisture, the water-soluble Cr gradually decreased over time up to the 45th day of incubation. Based on pH, total metal concentration, and organic matter content, the soluble concentration of Cr could be predicted (Davamani et al 2016). Hence, the reduction may be attributed to the effect of bioamendments in transforming H_2O-Cr to organic plus iron oxide from (Na_2EDTA - Cr) and residual form (HNO_3 - Cr), respectively. The production of insoluble chromium humic acid complexes may explain the decrease in the concentration of the water soluble fraction of Cr during incubation (Huang et al 2019).

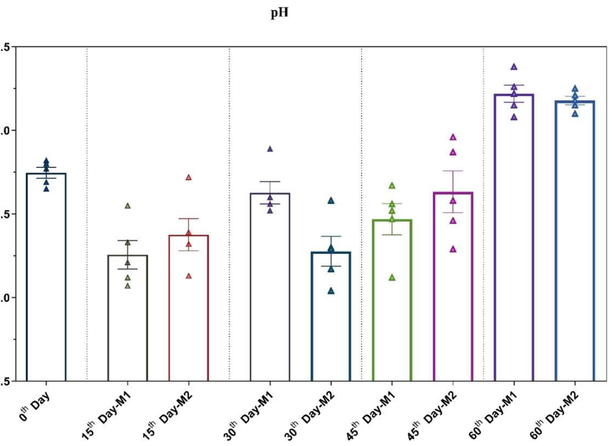

Fig. 1. Effect of bioamendments on soil pH of chromium contaminated soil under two different moisture conditions

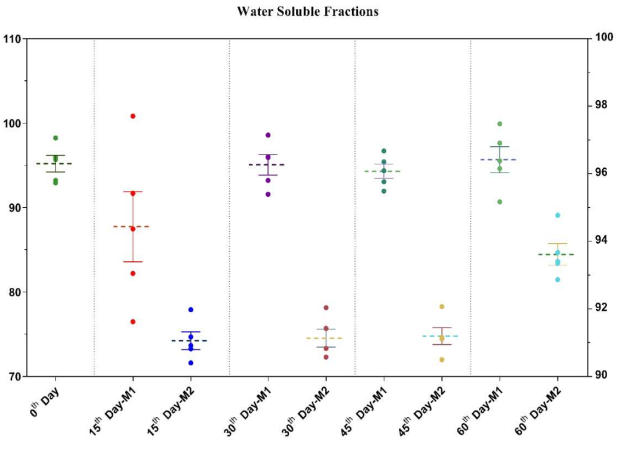

Fig. 2. Effect of bioamendments on water-soluble fractions of chromium contaminated soil under two different moisture conditions

Exchangeable fraction of chromium: The concentration of exchangeable chromium increased on the 15th day from the initial stage and then decreased at 30th and 45th days, which further increased at 60th day under field capacity moisture conditions (Fig. 3). The concentration of exchangeable Cr as extracted by using 0.5M KNO_3 ranged from 94.07 to 104.77 mg kg^{-1}. Both the moisture contents and various organic amendments had significant effect on exchangeable fraction of Cr. In general the concentration of exchangeable Cr was found decreased upto 30th day of incubation and thereafter it was found to increase at 60th day. Such effect was more pronounced in soil under alternate wetting and drying condition. The concentration of metals in this phase indicates the impact of metals on the environment (Sherene 2010). Both moisture and bioamendments significantly impacts the exchangeable fraction of Cr. It was found high in the pressmud compost amended soil and low in the control soil under alternate wetting and drying condition. The reduction in exchangeable Cr might be due to its adsorption on soil particles and its transformation to other species of Cr (Kotaś and Stasicka 2000). The adsorption of metals decreases as the pH of the soil decreases, increasing the available fraction (Zhang et al 2018). The metal transformation primarily influences soil type, moisture content, and incubation time in soil. The exchangeable fractions of fraction is a reliable indicator of the bioavailability of metals (Beesley et al 2011).

Organic fraction of chromium: There was a marked changes in the organic Cr content due to the application of bio-amendments (Fig. 4). The organic fraction of Cr was extracted by 0.5M NaOH and the concentration of NaOH-Cr decreased drastically from 137.54 mg kg^{-1} (control) to 76.38 mg kg^{-1} (bioamended soil). The organic fraction was higher in soil under alternate wetting and drying conditions than under field capacity moisture condition. In alternate wetting and drying conditions, the highest organic Cr (101.98 mg kg^{-1}) was obtained in the soil treated with pressmud compost and the lowest value (71.28 mg kg^{-1}) in the control soil after 60 days of incubation. The changes in organic Cr could also be attributed to changes in soil chemical properties and the chelating ability of organic matter present in the applied bioamendments (Cervera-Mata et al 2022). Complexation, adsorption, and precipitation, among other physicochemical reactions between metals, amendments and soils, are commonly decreased the metal availability in the different soil conditios and the experimental time (Adriano et al 2004). Different physico-chemical processes between metals and soils, such as complexation, adsorption, and precipitation, are generally attributed for the decrease in metal availability over time (Shahid et al 2017)

Organic plus iron oxide bound chromium: The concentration of metals in the organic plus iron oxide bound chromium indicates the impact of metals on the environment. Both moisture conditions and amendments significantly impact the organic plus iron oxide fraction of Cr (Fig. 5). Applying different bio-amendments resulted in significant changes in Cr's organic plus iron oxide fraction. In both under field capacity moisture and alternate wetting & drying, the concentration of organic plus iron oxide bound Ni was found decreased and increased alternatively over a period of time. The characteristics and nature of organic carbon in different bioamendments significantly impacted Cr biotransformation in soil, resulting in different concentrations of the amendments added to the soil. The complexation or chelation of Cr with organic materials is responsible for the change in the organic plus iron oxide bound fraction of Cr (Sellappa Gounder et al 2021). During the mineralization of organic amendments, the metal could precipitate as

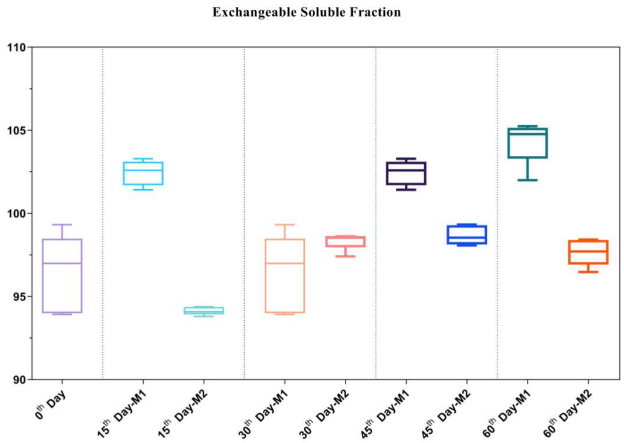

Fig. 3. Effect of bioamendments on exchangeable fraction of chromium contaminated soil under two different moisture conditions

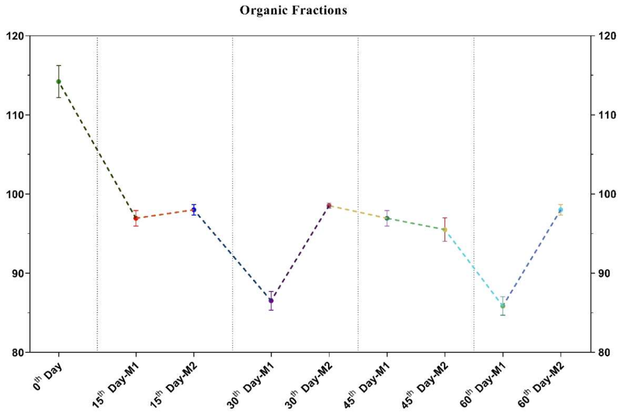

Fig. 4. Effect of bioamendments on organic fraction of chromium contaminated soil under two different moisture conditions

inorganic compounds. During the mineralization of bioamendments, the metal might precipitate as inorganic molecules (Lwin et al 2018). The complexation or chelation of Cr with organic matter is responsible for the variation in Cr's organic plus iron oxide bound fraction (Almås et al 2000). During the mineralization of organic amendments, the metal could precipitate as inorganic compounds (Walker et al 2003). The rate of Cr (VI) reduction was also affected by several factors, including pH, temperature, and the carbon and nutrient sources (Parameswari et al 2009, Megharaj et al 2003).

Residual fractions of chromium: The concentration of residual frations of Cr in the soil under field capacity moisture was significantly higher than in the soil under alternate wetting and drying conditions (Fig. 6). The significant increase in the residual Cr can be attributed to the sorption of Cr. Initially, the concentration was about 87.92mg kg^{-1}. However, after the 15th day, the concentration increased compared to the intial stage and further increased up to the 60th day. The residual fraction is a major carrier of metals in most ecological systems. The moisture conditions and organic amendments significantly affected the soil chemical properties. Under both moisture conditions, the residual Cr was found to increase gradually from the 0th day to the 45th day, and after that, it was found to decrease at the 60th day of incubation. Under both moisture conditions, the residual Cr concentration was highest in the soil treated with biochar and lowest in the soil supplied with pressmud compost after 60 days of incubation. Biochar has been shown to adsorb and retain a higher level of heavy metals than other materials (Zhang et al 2013).

Furthermore, because it is the most prevalent speciation process, the solid phase of Cr accounts for most Cr in the soil (Sarkar et al 2019). Thus, biochar significantly reduced chromium fractions, which may be due to their high cations exchange capacity (CEC) and surface area, which facilitates Cr adsorption. In contrast, the other amendments increased Cr bioavailability by soluble organic matter fractions and organic acid production during decomposition (Amir et al 2005). Because it is the most dominant speciation process, the solid phase of Cr is associated with the largest fraction of Cr in soil. In addition, it has low mobility in the soil (Sherene 2010).

Pearson's correlation analysis of soil parameters on the initial day (0th day) in both the conditions (M1): Pearson's correlation coefficient analyzes the relationship between different physicochemical properties and heavy metal concentrations. The soil pH is positively correlated with EC, SOC, organic Iron Oxide chromium, residual chromium and strongly positively correlated with exchangeable chromium. However, it has a strong negative relationship with water-soluble chromium and organic chromium. The correlation of pH has a good level of statistical significance (Fig. 7), with soil organic chromium fraction. The result was in agreement with previous studies of Chen et al (2015). Water-soluble chromium fractions are negatively correlated with pH and organic iron oxide chromium fractions but have a positive relationship with organic chromium fractions. Exchangeable chromium fraction is positively correlated with pH, and it has a negative relationship between organic and organic iron oxide chromium fractions. Since the neutral and alkaline soils have higher concentrations of clay minerals and oxides than acidic soils, Cr redistribution from readily available to potentially available is less in the available fraction (Shahid et al 2017). Organic iron oxide chromium fraction is positively correlated with pH, SOC and strongly negatively with water-soluble chromium fraction. Residual chromium fraction is negatively correlated with SOC and organic iron oxide chromium fractions. Neina (2019) observed negative

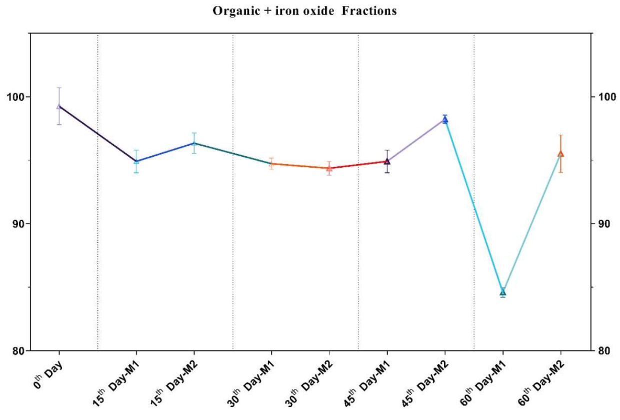

Fig. 5. Effect of bioamendments on organic plus iron oxide fraction of chromium contaminated soil under two different moisture conditions

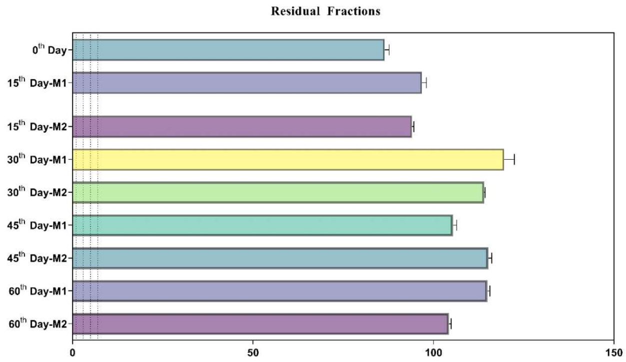

Fig. 6. Effect of bioamendments on residual fraction of chromium contaminated soil under two different moisture conditions

relationship between soil pH and metal ion availability and mobility in the soil solution.

Pearson's correlation analysis of soil parameters on the initial day (0th day) in both the conditions (M2): The soil pH is negatively correlated with the water-soluble chromium fraction and organic chromium fraction, and it has a positive relationship with the exchangeable chromium fraction. Water-soluble chromium and iron oxide bound chromium, on the other hand, showed a positive correlation. It is because there are more available and mobile Cr fractions (Barman et al 2020). The high pH value favoured the retention of additional metals on the soil surface in alkaline soil (Choppala et al 2018). Water-soluble chromium fraction is negatively correlated with pH, organic iron oxide chromium fractions. Exchangeable chromium fraction is positively correlated with pH and SOC. Organic chromium fraction is negatively correlated with pH, and exchangeable chromium fraction. The negative correlation might be due to the concentrations of non-available fractions increased.

In contrast, the concentrations of available fractions decreased, so Pearson's correlation analysis revealed a positive relationship between non-available fractions and pH and a negative relationship between organic chromium fraction and pH (Chen et al 2018). Organic iron oxide chromium fraction is negatively correlated with EC, water-soluble chromium fraction and residual chromium fraction. The strong link between exchangeable soil metals could indicate contamination at similar levels and from similar sources (Li et al 2009). Residual chromium fraction is negatively correlated with SOC and organic iron oxide Chromium fraction. In M2 moisture conditions, pH is highly negatively correlated with organic chromium fractions with high levels of significance and the same results were observed in M1 moisture conditions.

Pearson's correlation analysis of soil parameters on the final day (60th day) in both the conditions (M1): The soil pH is positively correlated with SOC and strongly negatively correlated with organic chromium fractions and iron oxide chromium fractions (Fig. 8). Low pH levels can increase the soil's water-soluble and organic Cr fractions (Król et al 2020). Water-soluble chromium fractions are negatively correlated with exchangeable chromium fractions. Water-soluble and exchangeable chromium metals in soil show a significant chemical fraction with a positive correlation between pH and EC (Yang et al 2019). The exchangeable chromium fraction has a negative relationship water-soluble chromium fraction. pH is negatively correlated with EC, water-soluble chromium fraction, and has a strong positive relationship with SOC. Though the parameters have a strong relationship, it is not statistically significant.

Pearson's correlation analysis of soil parameters on the final day (60th day) in both the conditions (M2): Soil organic carbon (SOC) has a strong positive relationship with pH and a strong negative relationship with the water-soluble chromium fraction. The pH and SOM concentration had a significant impact on the binding of heavy metals in various forms (Ettler et al 2007). The pH, SOC, and organic chromium fractions are negatively correlated with the water-soluble chromium fraction. The exchangeable chromium fraction is related to pH, EC, and SOC in a positive way. Organic chromium fraction is negatively correlated with pH,

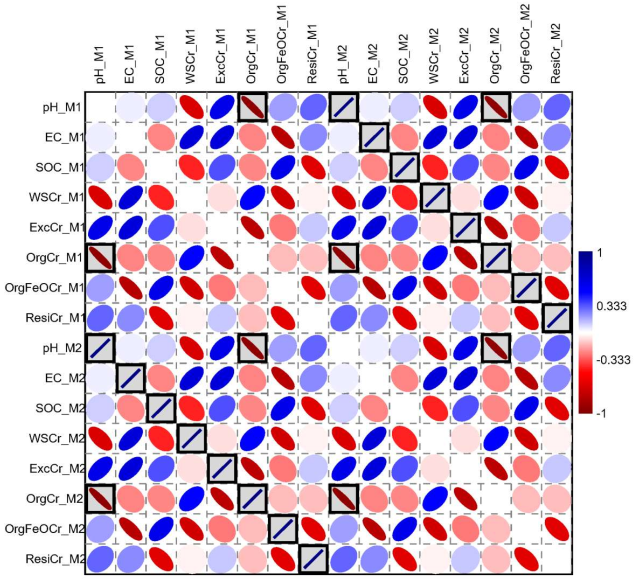

Fig. 7. Pearson's correlation analysis of soil parameters on the initial day (0th day) in both the conditions

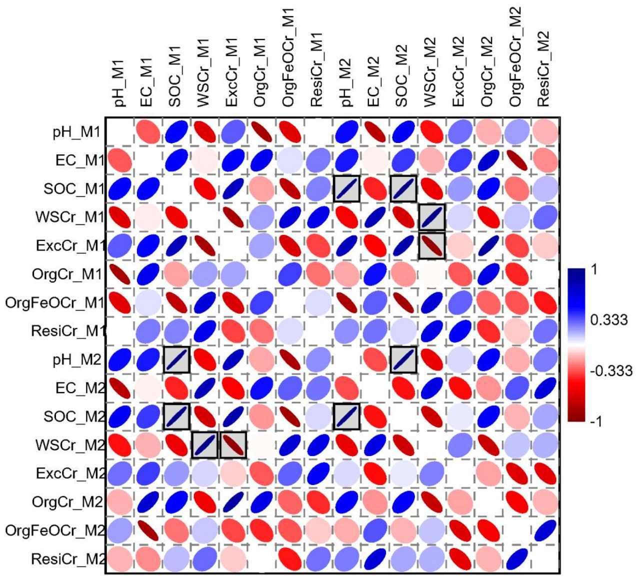

Fig. 8. Pearson's correlation analysis of soil parameters on the final day (60th day) in both the conditions

exchangeable chromium fraction. A significant negative correlation exists between chromium in the soil and chromium adsorption with amendments, indicating that metal removal from the soil is strongly linked to chromium adsorption with amendments (Ullah et al 2020). Organic iron oxide chromium fraction is negatively correlated with EC, water-soluble chromium fraction and residual chromium fraction. Soils with a negative correlation between pH and changes in the soil water-soluble and organic chromium fractions have a higher level of chromium (Shaheen and Rinklebe 2014). Residual chromium fraction is negatively correlated with the exchangeable chromium fraction. pH is highly positively correlated with SOC ..

CONCLUSION

Bioremediation is a more efficient method of removing metal contaminants and converting them to harmless substances and is efficient, eco-friendly and cost-effective strategies for remediation of Cr contaminated environment. The application of organic amendments to agricultural soils regularly improves their physical, chemical, and biological fertility. The organic amendments used for this study are cost savings and locally available products that farmers can use effectively to remediate chromium-contaminated soil. The organic acids producee during the decomposition of bioamendments reduced soil pH and increased the Cr bioavailability. The use of bioamendments resulted in 80 per cent reduction in the concentrations of bioavailable fractions such as water-soluble – Cr (H_2O – Cr) and exchangeable fractions (KNO_3–Cr) in contaminated soils under two different moisture conditions. Organic amendments have the potential to remediate Cr-contaminated soil based on Cr mobilization or immobilization. The soil pH and bioavailable fractions of Cr showed a positive correlation in our study. If the amendment increases Cr bioavailability, we can use phytoremediation technology. These contaminated lands must be remediated to maintain agricultural production and environmental health. As a result, using bioamendments to remediate chromium contaminated soils could provide a novel solution to the soil pollution problem.

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