



RESEARCH ARTICLE

Heavy metal adsorption potential of weed compost derived humic substances

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ABSTRACT

The chemical pollution due to anthropogenic origin especially through heavy metals, pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls are serious threats to the environment, and their main sources are industry, transport, and agriculture. Most of these pollutants reach and accumulate air, water and/or soil and threaten the life on this planet. In this context, this paper mainly evaluates the Cadmium (Cd) and Lead (Pb) adsorption potential of weed compost derived humic substances for detoxification of these two heavy metals. Weed compost was produced during August to December from locally available weeds such as *Chromolaena odorata*, *Macaranga peltata*, *Lantana camara*, and *Mikania micrantha* in 3:2:1:1 proportion, and humic substances such as humic acid (HA) and fulvic acid (FA) were extracted using standard procedure. In particular, six different concentrations (2–10 mg) of lead nitrate and cadmium nitrate were used to study the adsorption of Cd^{2+} and Pb^{2+} onto HA and FA. The findings demonstrated that the adsorption of cadmium and lead on humic substances were positively correlated, increased with increase in concentrations of the metal ions. For Cd, HA showed maximum adsorption of 383.5 ppm at 10 mg, while FA showed 340.50 ppm. For Pb, HA and FA showed adsorption of 605.60 ppm and 595.60 ppm, respectively, at 10 mg. Lead adsorption by humic substances surpassed that of cadmium. In addition to heavy metal adsorption, this study also characterized the structural and functional properties of humic substances. The study revealed the heavy metal adsorption potential of weed compost derived humic substances.

Keywords - Cd, Fulvic acid, Heavy metals, Humic acid, Pb, Weed compost

INTRODUCTION

The environment is seriously threatened by chemical contamination, which mostly results from human activity. Among the most dangerous contaminants include pesticides, heavy metals, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). The main sources of these pollutants are transportation, agriculture, and industrial operations. The environmental implications of these pollutants are far-reaching. Heavy metals, such as lead, cadmium, mercury, and arsenic can accumulate in soil, water, and air, causing irreversible damage to ecosystems. Implementing best management practices (BMPs) can prevent heavy metal contamination and reduce environmental impacts. Instead of synthetic fertilizers, use organic amendments like compost, manure, or green manure one of the best methods to reduce heavy metal contamination and at the same time it improves soil

physical properties, nutrient availability, soil carbon storage and microbial activity. The agricultural value of composts is increased when they are added to soil with more humified organic matter because the impacts of this organic matter in the soil persist longer. Two large groups of compounds found in compost are non humic and humic substances. Polysaccharides, sugars, proteins, amino acids, lipids, fatty acids, waxes, pigments and other substances of low molecular weight are non humic substances and heterogeneous with dark coloured substances with high molecular weight is the humic substances.

Humic substances are more stable organic matter which makes up a significant portion of the total soil organic carbon and nitrogen. They can improve soil buffering capacity, increase moisture retention, and supply plants with available nutrients. Moreover, these compounds can also bind metals, alleviating both heavy metal toxicity and metal deficiency in soils (McCarthy2001).

The importance of humic acid in improving agricultural soils is well established, especially in soils with low organic matter. It is an alternative for increasing crop production, and humic acid is a promising natural resource to be utilized.

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Due to the functional groups like OH, COOH, and COO⁻ which aid the humic acid in enhancing the physico-chemical characteristics of the soil and biologically stimulating plant growth. It acts as a catalyst in promoting the activity of microorganisms in soil. Fulvic acid is effective in increasing drought resistance to plants, reducing leaching of fertilizer, stabilizing soil pH and improving uptake of nutrients. The ability of humic substances to form stable complexes has been well accepted. One of the most important parameter controlling heavy metal behavior in soils is the soil organic matter, together with soil pH. The insoluble humic substances bound on heavy metals are relatively immobile, but on the other hand, the metal mobility and bioavailability may increase if binding is on smaller organic molecules (Kabata-Pendias 1993). The formation of metal-humic complexes mainly involved with the carboxylic -COOH and phenolic -OH groups of humic substances. However, the organic matter complexation with both Cd and Pb is more important than their adsorption through cation exchange. The detailed information regarding the interaction of heavy metals with humic substances in soils can be applicable in the development of remediation methods for polluted soils (Halim *et al.* 2003). The migration and bioavailability of pollutants in the soil can be reduced significantly through complexation with organic matter. Fulvic acid has strong complexation with heavy metals and significantly affect the adsorption-desorption behavior of heavy metals in soil because of solubility of fulvic acid-metal complex (wang *et al.* 2017). The phenolic and carboxyl groups on the molecular chain of humic acid interact with cationic metal to form spherical compounds, which claimed the soil remediation mechanism of humic acid. The humic acid is considered to have the greatest affinity with Pb²⁺, Cu²⁺ (Yates and von Wandruszka's 1999).

Due to their structure and properties, they can interact with metal ions and, with them, form relatively stable complexes, and these substances are thus responsible for the so-called self-cleaning ability of soils and it can be used as an environmental friendly adsorbent for heavy metals (Klucakova and Pavlikova 2017).

Sustainable remediation strategies for treating soil are required due to high levels of heavy metals in soil, which otherwise leads to pollution of drinking water and contamination of food chain. The effect of several composts derived from source-separated and mixed municipal wastes in the presence and absence of lime were evaluated in a highly acidic heavily

contaminated soil with As, Cu, Pb, and Zn. The results of the study indicated that PTE (potentially toxic element) amelioration was enhanced by compost, but at the same time lime had little effect and even exacerbated PTE mobilization (e.g., As) (Farrell and Jones 2010). Bioremediation experiments are generally carried out to reduce heavy metal bioavailability in contaminated soils utilizing manures and compost originated from different sources. A significant reduction in the concentrations of Cd in the shoots and roots of amaranth was observed by the application of 10–20 t/ha farmyard manure in a sandy loam soil (Alamgir *et al.* 2011). Similarly, application of manure decreased plant tissue concentration of three metals (Cu, Zn, and Pb) in *Chenopodium album* L. (Walker *et al.* 2004).

Toxic heavy metal such as Cd is used in electroplating industries, manufacturing vinyl plastics, metal and even in mining operations. The industrial wastes always contain significant amounts of Cd and Pb. One of the best methods to remove toxic metals like Cd and Pb is chelating with the humic substances such as humic and fulvic acids. Considering the above facts, and the superior quality of weed composts (Sujatha *et al.* 2021), the present study aimed to explore the Cadmium (Cd) and Lead (Pb) adsorption potential of weed compost derived humic substances such as humic acid (HA) and fulvic acid (FA) for detoxification of these two heavy metals

MATERIALS AND METHODS

This study was conducted at Kerala Forest Research Institute, Kerala, India during the year 2023. The compost was produced from locally available weeds such as *Chromolaena odorata*, *Macaranga peltata*, *Lantana camara*, and *Mikania micrantha* in 3:2:1:1 proportion using farm derived inoculum namely *jeevamrutham* as described by (Sujatha *et al.* 2021). The methodology employed for the extraction and characterization of humic and fulvic acids from the compost is outlined below.

Extraction of humic substances

The complex HA and FA present in the weed compost were extracted according to guide lines suggested by international humic substance society and (Satisha and Devarajan 2011).

Fifty g of sample was mixed with 500ml 0.1M NaOH (1:10) and shaken for 24hrs in a shaker. This mixture was then centrifuged at 3000 rpm for 15 mins. The alkaline supernatant was then collected, and the insoluble materials discarded. The pH of this alkaline supernatant containing both HA and FA was

noted, and acidified using conc. HCl to make the pH 1. Once the pH became stable, it was allowed to precipitate. When the HA was completely precipitated, the clear supernatant containing fulvic acid was collected, and centrifuged at 3000rpm for 30min.

The clear supernatant FA and the precipitate HA were collected, and dried in hot air oven.

Spectroscopic characterization of HA and FA

The E_4/E_6 ratio of HA and FA were measured in the visible (200–800nm) by Ultraviolet-Visible Spectroscopy (AgilentCary5000) (Dick and Burba 1999). One mg of HA and FA were dissolved in 10ml of 0.05N NaHCO_3 and the absorbance at 465 and 665 nm were measured. Fourier-transform infrared spectra (Thermo Nicolet Avatar 370) of HA and FA were recorded with a resolution of 4 cm^{-1} , at 4,000 to 400 cm^{-1} in KBr pellets method using DTGS detector.

Adsorption of heavy metals

The concentrations of Cadmium (Cd) and Lead (Pb) in the samples were determined using atomic absorption spectrophotometry (Varian 240 spectrophotometer) (Carbonell *et al.* 2009b). Element-specific cathode lamps and fuel oxidant systems were employed to ensure accurate analysis.

To investigate the adsorption of heavy metals by humic substances, 20 mg of humic acid and fulvic acid samples were prepared and mixed separately with different concentrations of lead nitrate (PbNO_3) and cadmium nitrate (CdNO_3) salts. Six different concentrations of each salt (2 mg, 4 mg, 5 mg, 6mg, 8mg, and 10mg) were considered. Each different concentrations (mg) of the metal salts along with 10 ml of distilled water is dissolved with 20 mg of each humic substances separately and stirred well by a magnetic stirrer.

The solutions were then centrifuged at 6500 rpm for 30 minutes to separate the solid and liquid phases. The supernatant was collected and analysed using atomic absorption spectroscopy (AAS) to determine the concentrations of Pb^{2+} and Cd^{2+} ions. This experimental procedure allowed for the investigation of the adsorption of cadmium and lead ions on humic acid and fulvic acid samples at different salt concentrations.

RESULTS AND DISCUSSION

The weed compost was produced from locally available weeds as reported by (Sujatha *et al.* 2021) and humic substances such as humic acid and fulvic acid were extracted from it.

Characterization of humic substances

Fractions of humic and fulvic acids extracted from weed compost were identified using Ultraviolet-Visible Spectroscopy and Fourier-transform infrared spectroscopy (FTIR) spectroscopy

The E_4/E_6 ratio of humic acid and fulvic acid samples were scanned in the 200–3000 nm region using Ultraviolet-Visible spectrophotometer. The absorbance ratio was considered as a traditional parameter in the case of humic substances to estimate its degree of humification and/or its molecular size. In order to characterize humic substances with respect of aromaticity, E_4/E_6 ratio is a valid and informative index. Further, the magnitude of the E_4/E_6 ratio of humic substances is related to the relative concentration of condensed aromatic rings in these materials frequently suggested in soils. As suggested by (Dick and Burba 1999) the ratio between absorbance (E_4/E_6 ratio) at 465 and 645 nm was determined.

The higher E_4/E_6 ratio of fulvic acid than humic acid (**Table 1**) indicates greater proportion of aliphatic natured substances, and an equivalent finding was made by (Satisha and Devarajan 2011).

Table 1. E_4/E_6 ratios of fulvic and humic acids

	Absorbance at 465 nm	Absorbance at 665 nm	E_4/E_6 ratio
FA	0.0288	0.0031	9.29
HA	0.3793	0.0973	3.89

Therefore, the high E_4/E_6 ratios of humic substances supposedly indicates a relatively low concentration of condensed ring structures, which reflects a low degree of aromatic condensation and thus, infers the presence of relatively large proportions of aliphatic structures.

Fourier-transform infrared spectroscopy (FTIR) spectroscopy is a powerful tool that can be used in the identification of complex compounds and it serve as a qualitative tool for monitoring functional groups and bands of fulvic acids and humic acids. The IR spectra of the two humic fractions are shown in (**Figure 1** and **Figure 2**). They have a diversity of bands more or less typical to those distinguishing the humic materials. Major absorption bands are in the regions of 3400–3300/ cm^{-1} (H-bonded OH groups), 2940–2900/ cm^{-1} (aliphatic C–H stretching), 1750–1720/ cm^{-1} (CO stretching of COOH), 1620/ cm^{-1} (aromatic CC, COO-, H-bonded CO), 1280–1230/ cm^{-1} (C–O stretching and OH deformation of COOH) and 1040/ cm^{-1} (C–O stretching of polysaccharide). It is clear from the spectra that fulvic acid is characterized by absorption near 1767/ cm^{-1} , which implies the

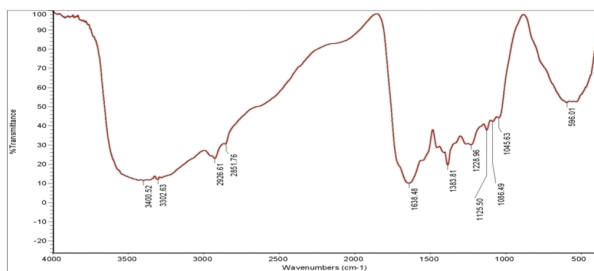


Figure 1. Fourier-transform infrared spectra of humic acid

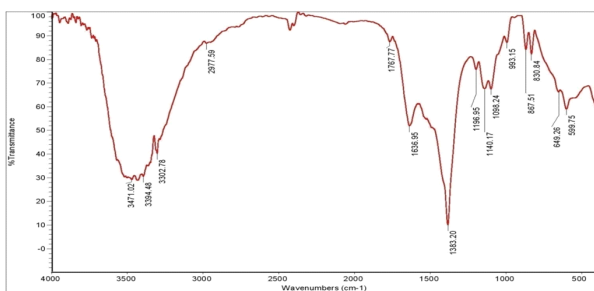


Figure 2. Fourier-transform infrared spectra of fulvic acid

dominant carboxylate groups. The spectra evidently show predominance of OH, COOH and COO-groups which are the most characteristic features of humic materials.

Adsorption of heavy metals

Adsorption of heavy metals such as Cd^{2+} and Pb^{2+} on HA and FA extracted from weed compost was tested in different concentrations of respective metallic salts, such as cadmium nitrate and lead nitrate. The data obtained are given in the (Tables 2-5).

Results of cadmium adsorption by HA at different concentrations are shown in (Table 2). The amount of cadmium adsorbed by HA increases with increasing cadmium concentration, from 84.91 ppm at 2 mg to 383.5 ppm at 10 mg. The efficiency remains relatively high across all concentrations.

Table 2. Adsorption of Cd on HA

Weight of HA (mg)	Concentration of salt (mg)	Total Cadmium (ppm)	Free Cadmium (ppm)	Cadmium adsorbed (ppm)
20	2	95	10.09	84.91
	4	190	17.51	172.49
	5	237	23	214
	6	285	30.09	254.91
	8	380	52.73	327.27
	10	475	91.5	383.5

The results of cadmium adsorption by FA at various cadmium salt concentrations are shown in (Table 3). The amount of cadmium adsorbed by FA increases with increasing cadmium concentration, from 62.74 ppm at 2 mg to 340.50 ppm at 10 mg.

Table 3. Adsorption of Cd on FA

Weight of FA (mg)	Concentration of salt (mg)	Total Cadmium (ppm)	Free Cadmium (ppm)	Cadmium adsorbed (ppm)
20	2	95	32.26	62.74
	4	190	46.10	143.90
	5	237	55	182
	6	285	65.87	219.13
	8	380	94.12	285.88
	10	475	134.5	340.50

The amount of cadmium adsorbed by FA is lower than that adsorbed by HA at the same concentrations. Humic acid adsorbed 383.50 ppm of cadmium while fulvic acid adsorbed 340.50 ppm of cadmium in 10 mg of salt. Compared to FA, HA has a higher adsorption efficiency. Whereas FA's adsorption efficiency was 71%, HA was 80%.

It is inferred from the data that adsorption of Cd on HA and FA increases with increase in the concentration of metal ions (Figure 3 and Figure 4). The adsorption was remarkably higher on HA than FA.

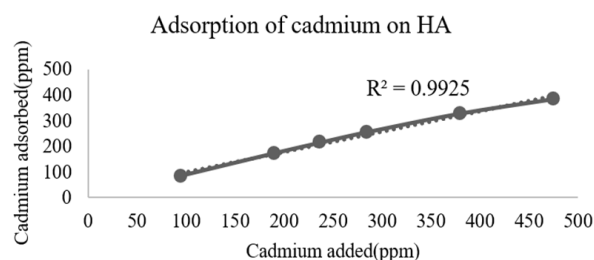


Figure 3. Humic acid-Cadmium (Cd)

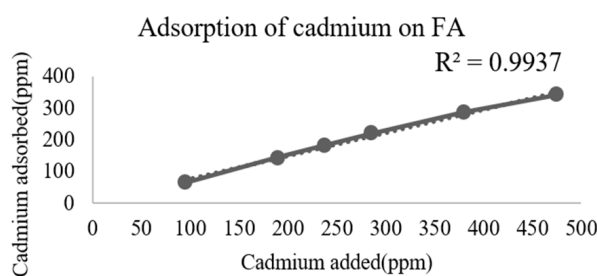


Figure 4. Fulvic acid- Cadmium (Cd)

The findings of Lead (Pb) adsorption on HA at various Lead salt concentrations are shown in the (Table 4). With an increase in lead concentration, the amount of lead absorbed by HA rises from 122.94 ppm at 2 mg to 605.60 ppm at 10 mg. The results suggest that HA is highly effective in adsorbing lead ions from solution, with an average adsorption efficiency of 97%. The adsorption capacity of HA increases with increasing lead concentration, indicating its potential as a natural adsorbent for lead removal.

Table 4. Adsorption of Pb on HA

Weight of HA (mg)	Concentration of salt (mg)	Total Lead (ppm)	Free Lead (ppm)	Lead adsorbed (ppm)
20	2	125.12	2.18	122.94
	4	250.24	3.79	246.45
	5	312.8	5	307.80
	6	375.36	6.60	368.76
	8	500.48	11.49	488.99
	10	625.6	20	605.60

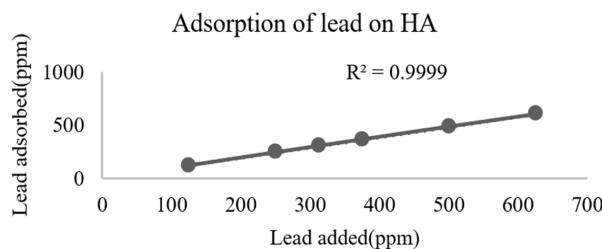
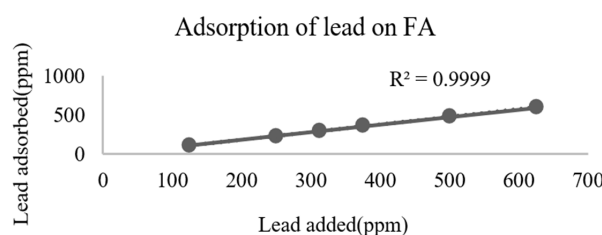
The results of lead (Pb) adsorption by FA at various cadmium salt concentrations are shown in (Table 5). With an increase in lead concentration, FA adsorbed more lead from 115.22 ppm at 2 mg to 595.60 ppm at 10 mg. The amount of lead adsorbed by FA is lower than that adsorbed by HA at the same concentrations. HA adsorbed 605.60 ppm of lead and FA adsorbed 595.60 ppm of lead in 10 mg of salt. The adsorption efficiency of HA is slightly higher than that of FA. The adsorption efficiency of HA was 96.8% at 10 mg of salt, whereas FA's was about 95.2%. Overall, the results suggest that both HA and FA are effective in adsorbing lead ions from solution, but HA has a slightly higher adsorption efficiency.

Table 5. Adsorption of Pb on FA

Weight of FA (mg)	Concentration of salt (mg)	Total Lead (ppm)	Free Lead (ppm)	Lead adsorbed (ppm)
20	2	125.12	9.90	115.22
	4	250.24	13.06	237.18
	5	312.8	15	297.80
	6	375.36	17.23	358.13
	8	500.48	22.74	477.74
	10	625.6	30	595.60

The data in general indicated that, as the concentration of the Pb^{2+} increased, their adsorption on both HA and FA also increased (Figure 5 and Figure 6).

The research studies on humic substances interactions with heavy metals from natural bulk material like compost counts few. The metal ions and humic acids interactions are complex in nature due to their heterogeneous, polyelectrolyte and polydispersive character by (Klucakova and Pavlikova 2017). Due to predominance of OH, COOH and COO-groups humic acid can interact with the heavy metals in soil (Hizal and apek 2006).

**Figure 5. Humic acid-Lead (Pb)****Figure 6. Fulvic acid-Lead (Pb)**

Conclusion

Humic acid is a kind of organic matter, whose inner structure contains not only abundant benzene ring but also some complex functional groups such as hydroxyl group(-OH), carboxyl group (R-COOH) which can provide electrons to coordinate with heavy metals to form into complex compounds or chelates. The coordination mentioned in the results positively related to the concentration of metal ions. Meanwhile, humic acid can easily be adsorbed on the surface of soil colloid. Therefore, adsorption sites in soil particle will increase. It is the combined effects of coordination and adsorption that makes the concentration of available heavy metals decrease in a comparatively large scale. The humic substances can bond with metal ions in several different ways from the net negative charge on the surface of a humic particle with purely electrostatic, nonspecific interaction of metal cation to specific interactions in the formation of complexes and chelates with functional groups (Klucakova and Pekar 2006).

The results suggest that both HA and FA are effective in adsorbing cadmium and lead ions from solution, but HA has a slightly higher adsorption efficiency. Among two toxic heavy metals, adsorption capacity of HA is greater than FA indicating its potential as a natural adsorbent for heavy metal removal and more potential for lead removal.

The humic substances act as a natural barrier for the pollution due to anthropogenic origin. The active functional groups such as OH, COOH and COO-groups present in the humic substances adsorb the pollutants leading to the detoxification. The weed

compost was additionally endowed with higher content of phytochemicals which lead to the formation of humic substances with active functional groups for detoxification of heavy metals.

Based on the study it is revealed that humic substances produced from weed compost have great potential in detoxifying the pollution due to heavy metals.

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