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Removal of Cadmium from a Sea-food Effluent Contaminated Soil by Indigenous Biological Adsorbents Assessed with Soil Microbial Biomass

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Abstract: Low-cost indigenous biological materials such as Dried Biomass of Azolla (DBA), Composted Coir Pith (CCP) and Dried Rice Husk (DRH) were tried as adsorbents for the removal of cadmium (Cd) from a sea-food effluent contaminated soil of south India. Soil incubation with indigenous biological materials significantly decreased the Cd concentration in contaminated soil as compared with non- incubated control. However, the concentration was far low in soils incubated with DBA followed by CCP. Furthermore, the Cd concentration of soil decreased with incubation time. Comparison of the Cd removal from soil revealed that the removal of Cd in treatment incubated with DBA and CCP was more or less on par. The kinetics of Cd adsorption followed the first-order rate expression given by Lagergren. Highest k_{ad} value was noticed in treatment incubated with DBA followed by CCP. The present study revealed a significant inverse relationship between soil Cd concentration and soil microbial biomass carbon (SMBC). The SMBC significantly increased in treatments incubated with DBA and CCP.

Key words: Cadmium, biological adsorbents, soil microbial biomass.

Introduction

Rapid industrialization, urbanization and modern agricultural practices contribute to the increased disposal of cadmium (Cd) into soil (Buchaver, 1973; Alloway, 1995; Paz-Gonazález et al*.,* 2000). The harmful effects of Cd in humans include a number of acute and chronic disorders such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy (Kadirvelu, 1998). In plants it affects growth, dry matter accumulation, nutrient uptake and antioxidant system (Lin et al*.,* 2007; Soultana and Christos, 2009). Elevated level of Cd in soil has a toxic effect on the soil microbial communities which play an important role in soil nutrient cycling and therefore affects soil fertility (Brookes, 1995; Nannipieri et al*.,* 1997; Giller et al*.,* 1998; Moreno et al*.,* 2002).

With the better awareness of the problems associated with Cd came an increase in research studies related to the methods of removing Cd from the environment. The use of locally available inexpensive biological materials in sorbing contaminants has emerged as a new concept (Bailey et al*.,* 1999). For example, abundantly available indigenous adsorbents such as activated carbon (Leyva-Ramos et al*.,* 1995), agricultural by-products (Samantaroy et al*.,* 1997) and waste materials (Namasivayam and Yamuna, 1995) have been tried for this purpose. Most of these studies have utilized this potential to remove contaminants from industrial waste waters with different composition and characteristics (Namasivayam and Yamuna, 1995; Kadirvelu et al*.,* 2001; Kadirvelu and Namasivayam, 2003). Nevertheless, the literature is still insufficient to cover the use of locally available cheap biological

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materials as sorbants of contaminants in soil except a few reports (Manna et al*.,* 2001; Kumpiene et al*.,* 2007).

The term soil microbial biomass (SMB), i.e. the living part of soil organic matter is used to describe the total mass of microorganisms present in a soil (Brookes, 1995). The importance of SMB in soil functioning is well recognized (Dalal, 1998; Stockdale and Brookes, 2006) and SMB has long been suggested to be a significantly more sensitive indicator of changing soil conditions than the total organic matter content (Powlson and Jenkinson, 1976). In ecotoxicological studies, the SMB has been proposed as a sensitive endpoint to define the impact of contaminants such as heavy metals on soil biological functioning (Brookes, 1995; Giller et al*.,* 1998). The size of SMB pool is routinely measured and expressed as carbon contained in the SMB (SMBC).

We hypothesize that soil with high level of Cd would show shift in microbial community as compared to soil with lower metal levels, and that remediated soils could show recovery of the microbial community. To test this hypothesis we measured the removal of Cd from contaminated soil by three indigenous biological adsorbents and changes in the size of SMBC at different stages of incubation.

Materials and Methods

Experimental Soil

Seafood effluent contaminated soil which had a comparatively high value for Cd was collected within 500 sq m of the seafood processing units located at Alappuzha, India. Soil from five regions of the location were mixed uniformly and freed from debris by passing through a 2 mm sieve before filling in plastic troughs of approximately 18 cm diameter and 8 cm depth. The characteristics of the experimental soil are given in Table 1. The experiment consisted of four treatments (three adsorbent amended treatments and one without any adsorbent (control).

Biological Adsorbents

Three cheap and locally available biological materials viz. Dried biomass of Azolla (DBA) (pH 8.3; C 49.6%), Composted coir pith (CCP) (pH 6.1; C 25%) and Dried rice husk (DRH) (pH 5.8; C 35%) were used as adsorbents. Each adsorbent was rightly incorporated to soil at a rate estimated to deliver 5 g kg^{-1} soil. The biological materials were steam-sterilized prior to incorporation with soil. The troughs were incubated at 30 °C and moisture level was maintained at field capacity throughout the incubation period.

Table 1: Characteristics of the soil

Parameter	*Value*
Soil type	Sandy (Entisol)
Temperature (°C)	28
pH (H_2O)	7.2
EC (dSm^{-1})	0.74
Organic C (g kg^{-1})	8.70
Available N (mg g^{-1})	0.84
Available P (mg g^{-1})	0.75
Available K (mg g^{-1})	0.08
Available Cd (mg kg^{-1})	0.07

Soil Sampling

Soil sampling was performed at 10 days interval. Final sampling was done at the termination of the experiment at 30 days after incubation (DAI). Approximately 20 g soil samples were taken randomly from three regions of the trough and pooled to get a composite sample. The samples were stored at 4 °C till analysis.

Sample Analyses

Soil Cd Concentration

Available Cd in soil was extracted by 0.005M diethylenetriaminopentaacetic acid (DTPA) (Lindsay and Norvell, 1978). The concentration of Cd in clear extract was measured by atomic absorption spectrophotometry using an air-acetylene flame.

Soil Microbial Biomass

Soil microbial biomass carbon was determined by the chloroform-fumigation extraction method (Vance et al., 1987). Twenty (20.0) grams (dry weight equivalent) of soil were fumigated with ethanol-free chloroform for 48 h. Both fumigated and non-fumigated soils were extracted with 50 mL of 0.5 M K_2SO_4 by shaking for 30 min on an end-to-end shaker. The TOC analyzer was used to determine the organic C (C_{org}) in the extracts. The SMBC was calculated as follows:

$$\text{SMBC} = (C_{org} \text{ in fumigated soil} - C_{org} \text{ in non-fumigated soil})/k_{ec}$$

where k_{ec} = 0.33, the factor used here to convert the extracted organic C to MBC (Sparling and West, 1988). SMBC was expressed as mg C kg^{-1} dry soil.

Adsorption Studies

Reduction of Cd in soils incubated with biological materials over non-incubated control was noted at different stages and the difference was expressed as percentage. Similarly soil Cd concentration in each treatment was monitored and the decrease in concentration was considered as the removal by the adsorbent. Adsorption kinetics of each indigenous adsorbent was evaluated by Lagergren's equation (Lagergren, 1898).

$$\log_{10}(q_e - q) = \log_{10}q_e - (k_{ad}/2.303)/t$$

where q_e and q are the amount of Cd removed by the adsorbent (mg g^{-1}) at equilibrium time and at time t (day) respectively and k_{ad} is the rate constant for adsorption.

Statistical Analyses

The statistical design was completely randomized with treatment and incubation days as main effects. Analysis of variance (ANOVA), comparison of means (Fisher's least significant difference (LSD) test; $\alpha = 0.05$) and simple regression procedures were performed using Statgraphics Centurion XV software.

Results and Discussion

Soil Incubation with Biological Adsorbents and Soil Cd Concentration

Soil Cd concentration significantly decreased in all treatments incubated with biological materials as compared with control (Table 2). However, the concentration was far low in soils incubated with DBA followed by CCP. The percentage reduction of Cd over control under incubation with various biological materials is shown in Figure 1. When Cd removal under various treatments was compared, the removal of Cd in treatment incubated with DBA and CCP was more or less on par (Figure 2). The potential of biological materials as adsorbents of contaminants has been utilized to remove contaminants from industrial waste waters (Arulanantham et al., 1989; Marshall et al., 1993; Kadirvelu et al., 2001). However the use of such materials in sorbing contaminants of terrestrial systems is very less attempted. In the present study out of the three biological materials tried as adsorbents, two of them were found to be very effective in reducing Cd content in soil probably due to the reason that the alkaline nature of the materials can reduce metal mobility and availability in soil by adsorption, complexation or a combination thereof (Basta et al., 2005). Furthermore, the Cd concentration of soil decreased with incubation time with the biological adsorbents. This is in agreement with the finding of Kadirvelu et al. (2001) that the percentage adsorption of toxic heavy metals such as Hg, Pb, Ni and Cu from industrial waste waters on to coirpith increased with time.

Table 2: Changes in Cd concentration as influenced by the incubation with organic adsorbents in contaminated soil

Treatment	*Cd (mg kg^{-1} soil)*		
	10 DAI	*20 DAI*	*30 DAI*
CON	0.058a	0.056a	0.049a
DBA	0.044c	0.041b	0.036b
CCP	0.045c	0.043b	0.038b
DRH	0.051b	0.051a	0.048a

Means within a row followed by the same letter are not significantly different at $P = 0.05$ level by Fisher's LSD.

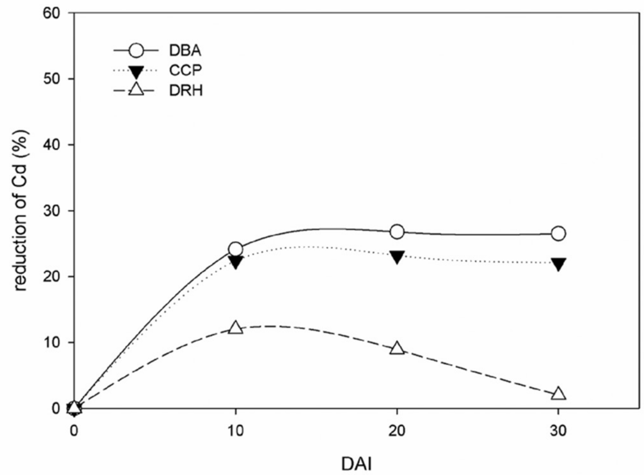

Figure 1: Effect of incubation with indigenous biological adsorbents on the reduction of Cd in contaminated soil.

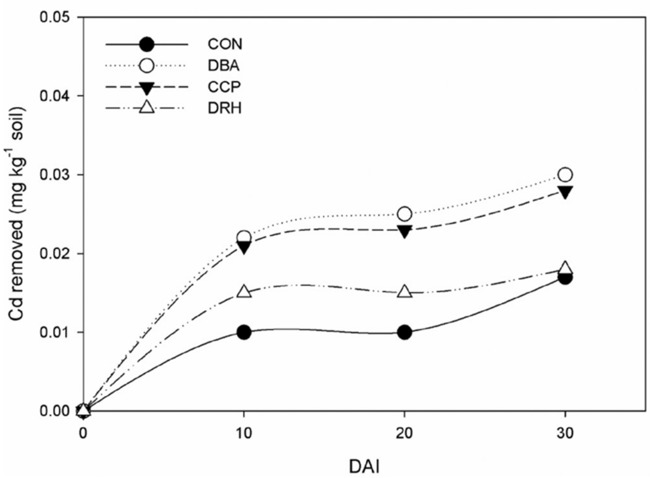

Figure 2: Effect of incubation with indigenous biological adsorbents on the removal of Cd from contaminated soil.

Adsorption Kinetics

The kinetics of Cd adsorption on the biological materials followed the first-order rate expression given by Lagergren (Lagergren, 1898). Linear plots of log $(q_e - q)$ vs days show the applicability of the Lagergren equation to different adsorbent materials as shown in Figure 3. Highest k_{ad} value was noticed in treatment received DBA followed by CCP (Table 3). The k_{ad} value remained low in treatment received rice husk as adsorbent.

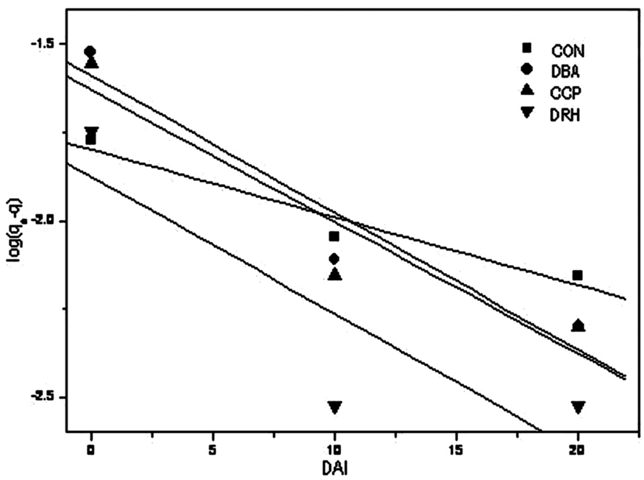

Figure 3: Lagergren plot for the adsorption of Cd under different treatments.

Table 3: Adsorption rate constants

Treatment	Rate constant k_{ad} (day^{-1})
CON	4.435×10^{-2}
DBA	8.961×10^{-2}
CCP	8.616×10^{-2}
DRH	7.553×10^{-2}

Effect of Soil Incubation with Biological Materials on Microbial Communities

The present study revealed a significant ($r = -0.490$; $P < 0.001$) inverse relationship between soil Cd concentration and SMBC (Figure 4). There is accumulating evidence that heavy metals decrease the proportion of microbial biomass in total soil organic matter and the ratio of soil microbial carbon to organic carbon has been proposed as a useful measure of soil pollution by heavy metals (Brooks, 1995). The SMBC significantly increased in treatments incubated with biological materials such as DBA and CCP (Table 4) with a maximum increase in its percentage at 30 DAI (Figure 5). The possible explanation to this is that the biological materials counteracted the toxic effect of Cd due to the better

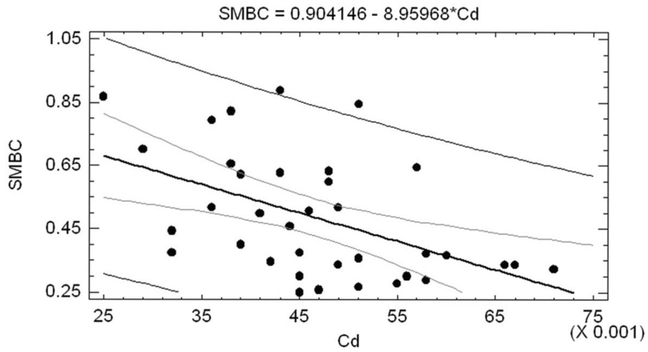

Figure 4: Plot of fitted model showing the relationship between soil Cd concentration and SMBC.

adsorption onto these materials (Kadirvelu, 1998; Kadirvelu et al., 2001) or by the release of soluble organic carbon during its decomposition (Martens, 2000; deMora et al., 2005). Manna et al. (2001) in a similar study with the addition of wheat straw into metal (Cd and Pb) contaminated soil observed an increase in SMBC from 65.5 to 93.5%.

Table 4: Changes in SMBC as influenced by the incubation with organic adsorbents in contaminated soil

Treatment	*SMBC (mg kg^{-1})*		
	10 DAI	*20 DAI*	*30 DAI*
CON	0.287bc	0.337c	0.337c
DBA	0.459a	0.508b	0.794a
CCP	0.371ab	0.628a	0.843a
DRH	0.266c	0.357c	0.633b

Means within a row followed by the same letter are not significantly different at $P = 0.05$ level by Fisher's LSD.

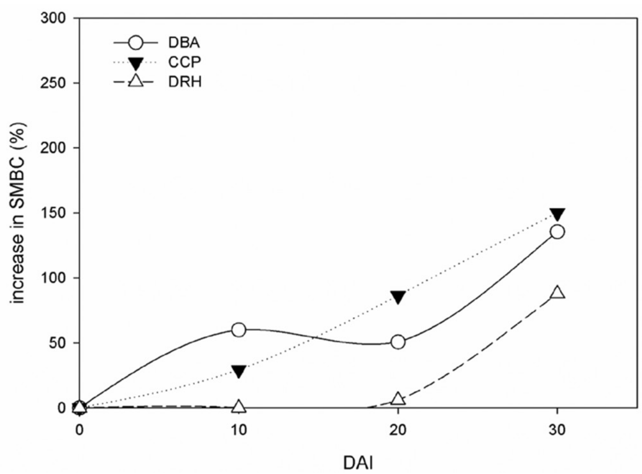

Figure 5: Changes in SMBC as influenced by the incubation with indigenous biological adsorbents in contaminated soil.

Conclusions

The study provides a meaningful insight into the potential use of cheap indigenous biological materials in sorbing Cd from contaminated soil. Soil incubation with DBA and CCP effectively reduced the Cd concentration in soil and improved SMBC. *Azolla* is a common weed causing menace in rice field and coirpith—a solid waste arising from coconut fibre processing industries. After its very limited use in basin management and in coconut gardens and potting mixture in nurseries, a major quantity is left as waste which often poses major environmental concern. By way of using them as adsorbents of contaminants, the materials otherwise would have been discarded as waste is effectively utilized.

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