INTERNATIONAL JOURNAL OF ENVIRONMENT
Volume-4, Issue-1, Dec-Feb 2014/15 ISSN 2091-2854
Received:20 January *Revised:8 February* *Accepted: 14 February*

RHIZOFILTRATION OF HEAVY METALS (CADMIUM, LEAD AND ZINC) FROM FLY ASH LEACHATES USING WATER HYACINTH (*Eichhornia crassipes*)

Amit Kumar Yadav, Bhawana Pathak and M.H. Fulekar*
School of Environment and Sustainable Development, Central University of Gujarat, Gandhinagar, India-382030
*Corresponding author: mhfulekar@yahoo.com

Abstract

Fly ashes are usually contaminated with toxic heavy metals. These metals are leaching out aftercontact with water during wet disposal system, thus polluting the soil, surface and groundwater. In the present study, a hydroponics experiment was conducted to examine the removalof heavy metals Cd, Pb and Zn by *Eichhornia crassipes* grown at various concentration of fly ash ranging from 10, 20 and 40 percent over a period of 30 days. After 30 days, the plants were separately harvested, dried and weighedfor biomass of the roots and shoots. The uptake of each metalwas studied in the root and shoot separately, to determine the bioaccumulation of metals in *Eichhornia crasspies*.The translocation factor was calculated to study the efficiency of the plants forbioaccumulation of each metal in roots and shoot. The results showed that maximum uptake of metals Cd, Pb and Zn by plantwasfoundat the higher concentration (40%) of fly ash.The metals uptake found was 99.16, 166.52 and 741.04 µg g^{-1} tissues in the roots, respectively and 33.46, 41.33 and 255.90 µgg^{-1} tissues in the shoots, respectively and successfullyremoved up to 78% of Cd, 82% of Pb and 70% of Zn.The maximum removal efficiency by plant for Cd, Pb and Zn at lower concentration (10%) of fly ash was 84%, 86% and 75%, respectively.The heavy metals accumulated more in roots than in the shoots by *Eichhornia crassipes*. The maximum bioconcentration factor and translocation factor value of *Eichhornia crappies* for Cd, Pb and Zn were calculated as 705.55, 705.55 and 614.51 and 41.86, 47.18 and 34.53 respectively. The high removal efficiencies of heavy metals Cd, Pb and Zn was find without toxic effect by this aquatic macrophyte, thisplant can be recommended for the actual treatment of fly ash leachatesin ash pond to clean up the aquatic environment.

Keywords: Fly ash, Heavy metals, Rhizofiltration, *Eichhornia crassipes*, Ash pond.

Introduction

In India, the demand for power generation has increased rapidly in recent time due to continuous growth of industrialization, urbanization, major infrastructure and economic development. Due to industrialization the demand for energy has grown at an average of 3.6% per annum over the past 30 years. At the end of December 2012, the installed power generation capacity of India stood at 210951.72MW (Central Electricity Authority, Ministry of Power, Government of India. June 2012). The total demand for electricity in India is expected to cross 950,000 MW by 2030 (http://www.livemint.com/2009). At present about 65% of the electricity consumed in India is generated by thermal power plants accounts two-thirds of the power which includes gas, liquid fuel and coal. The installed capacity of Thermal Power in India, as on June 30, 2011, was 115649.48 MW which is 65.34% of total installed capacity. Coal is the only natural resource and fossil fuel available in abundance. Consequently, it is used widely as a thermal energy source and also as fuel for thermal power plants producing electricity (Mishra, 2004). Current installed base of coal based thermal power is 96,743.38 MW which comes to 54.66% of total installed capacity. In India the electricity generation is mainly dependent upon the coal-based thermal power plants (54.66%) and will continue in the coming several decades due to its large amount reserves (http://www.indianpowersector.com). The coal based thermal power stations generate huge amount of fly ash that is a major issue in India.The coal combustion for the generation of electricity results into 20-30% fly ash as a waste product (Fulekar and Dave, 1990). In India, most of the thermal power plants are using low grade bituminous or sub-bituminous Indian coals with high ash content (30–55%) and low calorific value (3,500–4,000 kcal/kg) (Kumar *et al.*, 2003). This results in generation of huge quantities of ash every year. Present generation of fly ash from coal based thermal power plants is 131 MT/year and it is expected to increase to 300-400 MT/year by 2016-17 (http://www.flyash2012.missionenergy.org). The disposal of fly ash as a residue of combustion of coal in thermal power plant constitutes a greater problem (Iyer, 2002). However, the current utilization of fly ash is only about 55%, mainly in the areas of cement as well as concrete manufacturing and building products, and to some extent in earth fills (Jakka *et al.*, 2011). The rest of fly ash generated by the coal based power station is disposed of by using wet or dry systems. In the dry ash disposal system ash is stored in form of ash mounds and by the action of rain the present of heavy metals get leached and reach to the water of ponds, rivers etc.In the wet disposal system ash is mixed with water and the ash slurry is transported to the disposal area- ash ponds as wet slurry. In ash pond the fly ash come in contact with water continuously and leaching out of heavy metal in ash pond that contaminates to soil, water environment due to heavy metal contamination (Fulekar et al., 2005) and the deterioration of several ecosystem.There are several types of heavy metals which are released from fly ash leachates such as Cadmium, lead, Zinc, Chromium, Copper, Nickel, and Arsenic (Fulekar and Dave, 1985). These metals are of special concern because they are non-degradable. Heavy metals pollution has leads to serious ecological and health problems, thus removal and recovery of heavy metals are very important with respect to environmental and economical considerations. Therefore, the heavy metal pollution from these fly ash deposited ash pond can affect the surrounding population, on prolonged exposure that is challenge for the fast-growing population of the country (Masto *et al.*, 2009). Thus special attention is to be needed to remove these heavy metals emitted from fly ash in ash pond for prevention of environmental pollution (Sharma *et al.*, 1989) and cleanup aquatic environment. Using the conventional physicochemical methods to remove the heavy metal from contaminated water is too expensive due to the high cost of operation and not eco-friendly. The high cost of traditional and engineered remedial approaches has driven interests in ecological application of rhizofiltration of phytoremediation technologies.

Rhizofiltration is the recent technique which has been used as a more sustainable approach for the remediation of aqueous contaminated sites and widely accepted because of its environmental friendliness. Rhizofiltration is the use of plant roots to absorbs, concentrate or precipitate metal contaminants from aqueous medium. Although this technology is more suitable for decontamination of polluted water or removal of organic and inorganic impurities from wastewater by the use of aquatic plants, terrestrial species can also be used by growing hydroponically or on floating platforms in treatment ponds (Salt, *et al.*, 1995). The capacity for rhizofiltration can be increased by using plants with an enhanced ability to translocation of metals within the plant (Straczek *et al.*, 2010). A suitable plant for rhizofiltration should quickly produce significant amount of root biomass with large surface area when grown hydroponically (Vidali, 2001). Lead, Cadmium, Copper, Nickel, Zinc and Chromium, which are primarily retained within the roots under rhizofiltration (Chaudhary *et al.*, 1998).

A promising new method using living aquatic plants to remove metals from water is examined in this study. It has been shown that aquatic plants are quite effective for removing metals from their surrounding waters (Foster, 1976). Several species of aquatic plants such as water hyacinth (*Eichhhornia* sp.), water lettuce (*Pistia* sp.), Duck-weeds (*Lemna* sp., *Spirodella* sp.), and small water fern (*Azolla* sp.) have been used for removal of heavy metals from waste water (Mishra and Tripathi, 2009). The entire above species uptake metals from water and producing an internal concentration several folds greater than surroundings (Miretzky *et al.*, 2004). Water hyacinth (*Eichhornia crassipes*) has great potential for accumulation of heavy metals due to rooted macrophyte and grows in polluted water bodies without noxious weed. In spite of this, *E. crassipes* has been an important choice for rhizofiltration of heavy metals from contaminated water due to its several advantages over than other species (Maine *et al.*, 2001).

In the present research study the aquatic plant *Eichhhornia crassipes* was used for uptake of heavy metals Cd, Pb and Zn by growing in fly ash leachates. The assessment of heavy metals and physico-chemical parameters of leachates have been analyzed. This plant was allowed to grow in fly ash leachates under a control condition to study their heavy metals uptake study for a period of 30 days.Thus, the purpose of this research is to produce a low-cost and eco-friendly adsorbent from aquatic plant for removal of heavy metal from fly ash leachates. Rhizofiltration of heavy metals from fly ash leachates were done to clean up the aquatic environment. This lab research work will be directly applicable to the ash pond for removal of heavy metals to prevent the environmental pollution.

Materials and methods

Fly ashmaterial and leachates

Fly ash samples used in this study were collected from the Gandhinagar Thermal Power Plant, Gujarat in January, 2013. A sample weighing 5 kg was taken under the electrostatic precipitator. Its chemical composition characteristics were determined (Table 1). The ash samples were dried at 110°C in hot air oven for 24 hours and homogenized prior to experiment. The laboratory experiment was set up for the fly ash to determine the leachate constituent of the fly ash. In the leaching experiment, the samples were leached directly using de-ionizes water (Xiang Wei *et al.*, 2012).The fly ash concentrations of 10%, 20% and 40% wereprepared in the containers. For this 100 g, 200 g and 400 g fly ash were taken in different containers made up to the volume with ultrapure (Milli-Q Plus 185 system-treated) water up to 1000 ml respectively. The solution was shaken in a rotator shaker (Innova 42) at 150 rpm at room temperature 25-26°C (Jerzy Jankowski *et al.*, 2006) for 24 h, after which the solution were allowed to stand for 12 h before the leachates were collected (Xiang Wei *et al.*, 2012, Choi *et al.*, 2002).The determination of physicochemical parameters such as pH, total dissolved solid, electrical conductivity, alkalinity, chloride, sulphate, phosphate, ammonia-nitrogen, nitrite-nitrogen and nitrate-nitrogen of fly ash leachates immediately after sample collection (Jerzy Jankowski *et al.*, 2006). These parameters were analyzed by using standard methods for examination by standard methods (APHA, 1998). The samples were analyzed for the concentration of heavy metals Cd, Pb and Zn by atomic absorption spectroscopy (AAS).

Table 1

Physical and Chemical properties of Fly ash-used for experiments.

Physical and Chemical property and mineral as oxide	
SiO_2	63.2%
Al_2O_3	26.3%
$Fe_2O_3 + Fe_3O_4$	5.5%
CaO	0.95%
MgO	1.8%
SO_4	0.50 % (SO_3
TiO_2	Nil
pH value	9.3
Specific gravity	2.6
Fineness	563 cm^2/gram
Loss of Ignition	1.8 %

Bulk density	1.0007mg/m^3

Source: GTPP, Gandinagar

Plant material and pre-cultivation

The *Eichhornia crassipes* plants were collected in February 2103 from a near by unpolluted site in Mahadev Ponds located the district Aanand region of Gujarat State in India. Plants washed thoroughly in running water to avoid any surface contamination, the plants were put in polyethylene bags containing ponds water and transported to the laboratory were cultivated for 3 weeks in plant growth chamber. Prior to pre-cultivation, all plants were washed with running tap water in order to remove the residual particles and bugs and they were further reconditioned in 8L containers filled with tap water and 2 L of sterilized half strength Hoagland solution (Table 2 (Esperin, 1972)). All plants were grown and maintained inplant growth chamber (Meta Lab) for acclimatization, left continuously at 25±2°C, relative humidity 66% and under fluorescent tubes with a light intensity of 2000 lux and a 14h:10h (light: dark) photoperiod (Fernando *et al.*, 2009).

Table 2

Chemical composition of Hoagland solution.

Chemical	Concentration (mg l^{-1})
Macronutrients	
KNO_3	303.3
Ca $(NO_3)_2.4H_2O$	472.2
$NH_4H_2PO_4$	115.0
$MgSO_4.H_2O$	69.2
Micronutrients	
KCl	1.8
H_3BO_3	0.8
MnSO. H_2O	0.1
$CuSO_45H_2O$	0.1
H_2MoO_4	0.1

Source: Esperin (1972).

Hydroponics experimental: uptake and accumulation of heavy metals (Cd, Pb and Zn)

In this study, three different experimental groups which achieved 10, 20 and 40 percent fly ash concentrations were taken in containers. Each group consisted of three glass containers that included three replicates.Totally nine containers were used for three experimental groups.Following a pre-cultivation period, young propagated and healthy *E. crassipes* with about the same size and weight were selected for the removal of Cd, Pb and Zn. The plants were washed thoroughly with ultrapure water prior to the experimentation. Fresh plant was placed carefully in the eachcontainer had one plant. Each container in the experiment groups was filled with 1 L of fly ash leachates.The concentration of heavy metals Cd, Pb and Zn in different percentage of fly ash solution was determined before the beginning of experiment. After plantation solution samples were collected six times during 30 days experiment, periodically on days 0, 1, 7, 14, 21 and 30 of the experiment from each concentration of fly ash for determination of metal concentrations depleting with time span elapsed. Loss of water due to evaporation was made up daily by adding ultrapure water to the mark in the each experimental container.All the experimental sets were kept in the plant growth chamber for 30 days as working schedule was planned for present study. At the end of experiment the plants were harvested and rinsed with tap water followed by ultrapure water to remove dust, sediment and mineral particles. These plants were separated in to roots and shoots, then oven dried at 80°C (Mishra and Tripathi, 2009) for 48 h (APHA, 1998) for remove all moisture to a constant weight. Dry weights of roots and shoots were determined.

Heavy metal analysis in plants

Dried plant samples were grounded with a mortar and pestle to powder for facilitate organic matter digestion and stored for wet digestion for the analysis of metals Cd, Pb and Zn. These samples were digested with HNO_3: $HClO_4$ in 5:1 ratio (v/v) at a temperature of 60 to 70°C (APHA, 1998) and diluted to 100 ml with ultrapure waterand stored in polyethylene bottles at 4°C in a refrigerator. The digested plant samples were analyzed for metals Cd, Pb and Zn by means of atomic absorption spectrophotometer (Perkin Elmer).

Data analysis

The translocation factors (TF) described the plant's ability to translocation of heavy metals from the roots the harvestable aerial part (Mattina, *et al.*, 2003). It was calculated by dividing the metal concentration in shoot by the metal concentration in root on a dry weight basis.

The bio-concentration factor (BCF) described as accumulation of heavy metal by plants from surrounding medium. It was calculatedby dividing the metal concentration in plant by metal concentration in the solution (Nand Kumar *et al.*, 1995).

The percentage metal removal was calculated from % removal = $[(C_0 - C_1)/C_0] \times 100$, where C_0 and C_1 are initial and remaining concentrations of metal in solution (mg l^{-1}) (Abdel Halim *et al.*, 2003).

Statistical analysis

Metal concentrations in fly ash solutions were mentioned in mg l^{-1} and concentration in plant parts are mentioned in µg g^{-1} and data were expressed as means of three replicates.

Results

Physicochemical characteristics of fly ash leachates at various concentrations of fly ash

Table 3demonstrates the result of physicochemical analysis of fly ash leachates at 10%, 20% and 40% concentrations of fly ash. The result finding shows that pH was found to decrease from 10% to 40% on increasing concentrations of fly ash solutions. The other parameters such as total dissolved solid, electrical conductivity, alkalinity, total hardness, chloride, sulphate, phosphate, ammonia-nitrogen, nitrite-nitrogen and nitrate-nitrogen were found to increases from 10% to 40% on increasing concentrations of fly ash solutions.

Table 3

Physicochemical characteristics of fly ash leachates at various concentrations of fly ash.

Parameter	10% ash concentration	20% ash concentration	40% ash concentration
Temperature (°C)	24.8	25.2	23.9
pH	8.41	8.15	7.92
Total Dissolved Solid (mg l^{-1})	220	283	350
Electrical Conductivity (µS m^{-1})	441	566	697
Alkalinity (mg l^{-1}as CaCO3)	67.62	88.62	93.92
Total Hardness (mg l^{-1}as CaCO3)	146	274	370
Ca Hardness (mg/l as CaCO3)	104	162	304
Mg Hardness (mg l^{-1}as CaCO3)	42	112	66
Chloride (mg l^{-1})	33.98	34.98	43.96
Sulphate (mg l^{-1})	36.2	52.6	62.4
PO_4^{3-} -P (mg l^{-1})	4.2	7.2	3.8
NH_4^+-N (mg l^{-1})	1.3	1.4	2.1
NO_2^{-}-N (mg l^{-1})	0.014	0.012	0.022
NO_3^{-}-N (mg l^{-1})	1.50	1.58	1.62

Heavy metal concentration (mg l^{-1}) in fly ash leachates at various concentrations of fly ash

Heavy metals (Cd, Pb, and Zn) were determined in fly ash leachates at various concentrations (10%, 20%, and 40%) of fly-ash with the help of AAS (Table 4). There was an increasing in the concentration of Cd, Pb and Zn from 10 to 40 % of fly ash solutions. Cd concentration ranged from 0.12mg $l^{-1}$to 0.22mg l^{-1}, Pb concentration ranged from 0.14mg $l^{-1}$to 0.32mg $l^{-1}$and Zn concentration from 0.87mg $l^{-1}$to 1.68mg l^{-1}. 40% fly ash solution was characterized by high levels of Cd (0.22mg l^{-1}), Pb (0.32mg l^{-1}) and Zn (1.68mg l^{-1}). 10% fly ash was characterized by low levels of Cd (0.12mg l^{-1}), Pb (0.14mg l^{-1}) and Zn (0.87mg l^{-1}).

Heavy metal (Cd, Pb, and Zn) accumulation in Eichornia plants and Translocation Factor (TF) and Bio-concentration Factor (BCF)

Eichorniacrassipes was found to be sensitive to exposure of Cd, Pb, and Zn in fly ash leachates. The heavy metal (Cd, Pb, and Zn) was calculated in tissues on dry weights basis.The concentration of heavy metals in the different portals of the plants harvested from the various concentration of fly- ash leachates show a high level of metal accumulation in the roots in comparison to the shoots. The plants from 40% fly ash leachates were characterized by high levels of Cd, Pb and Zn (Table 4). In the plants from 40% fly ash leachates, Cd accumulated was (99.91µg g^{-1}roots, 33.46 µg g^{-1} shoots), Pb accumulated was (166.52µg g^{-1} roots, 41.33µg g^{-1} shoots) and Zn accumulated was (741.04µg g^{-1}roots, 255.90µg g^{-1}shoots) after 30 days of treatment.The Bio-concentration Factor (BCF) represents the ability of *Eichornia Plant*to extract heavy metals from the ash solution. Metals that are accumulated by plants and largely stored in the rootsfollowed to shootsof plants are indicated by Translocation factor (TF) values (Table 5).

Table 4

Heavy metal concentrations (mg l^{-1}) in fly ash leachates at various concentrations of fly ash.

Heavy Metal	10% ash concentration	20% ash concentration	40% ash concentration
Cd (mg l^{-1})	0.12	0.16	0.22
Pb (mg l^{-1})	0.14	0.20	0.32
Zn (mg l^{-1})	0.87	1.05	1.68

Table 5

Concentration of Cd, Pb and Zn (µg g-1dry wt) accumulated in the roots and shoots of *Eichornia* plantgrown for 30 days upon exposure fly ash leachates and the Translocation Factor (TF) and Bio-concentration Factor (BCF).

Metal	Concentrations of metal in fly ash leachates (µg ml^{-1})	Concentrations of metal uptake by plant(µg g^{-1}dw)		Plant dry weight(g)		TF (%)	BCF
		Roots	Shoots	Roots	Shoots		
Cd	10% (0.120)	60.810	23.856	0.1184	0.1006	39.23	705.55
	20% (0.160)	75.078	31.434	0.1252	0.1018	41.86	665.70
	40% (0.220)	99.916	33.464	0.1201	0.1016	33.49	606.27
Pb	10% (0.140)	70.945	27.833	0.1184	0.1006	39.23	705.55
	20% (0.200)	87.440	41.257	0.1252	0.1018	47.18	643.48
	40% (0.320)	166.527	41.338	0.1201	0.1016	24.28	649.57
Zn	10% (0.870)	405.405	129.224	0.1184	0.1006	31.87	614.51
	20% (1.050)	463.258	147.347	0.1252	0.1018	31.80	581.52

40% (1.680)	741.049	255.905	0.1201	0.1016	34.53	593.42

Concentrations of heavy metals (Cd, Pb, Zn) in different % of fly ash solution after 1st day, 7th day, 14th day, 21st day and 30th day during rhizofiltration

The plants were grown for a period of one month and solution sample were withdrawn from each concentration at 0th, 1st, 7th, 14th, 21st and 30th day of treatment. These samples were used for the analysis of heavy metals (Cd, Pb and Zn) concentration (Table 6).At 10% fly ash leachates the concentration of Cd depleted ranged from 0.12mg l^{-1} to 0.02mg l^{-1}, the concentration of Pb depleted ranged from 0.14mg $l^{-1}$to 0.02mg $l^{-1}$and the concentration of Zn depleted ranged from 0.87mg l^{-1} to 0.22mg l^{-1}. The removal percentage of Cd, Pb and Zn was 84%, 86% and 75%, respectively. At 20% fly ash leachates the concentration of Cd depleted ranged from 0.16 ppm to 0.03 ppm, the concentration of Pb depleted ranged from 0.20mg $l^{-1}$to 0.03mg $l^{-1}$and the concentration of Zn depleted ranged from 1.05mg $l^{-1}$to 0.30mg l^{-1}. The removal percentage of Cd, Pb and Zn was 82%, 85% and 87%, respectively. At 40% fly ash leachates the concentration of Cd depleted ranged from 0.22mg l^{-1} to 0.05mg l^{-1}, the concentration of Pb depleted ranged from 0.32mg l^{-1} to 0.06mg $l^{-1}$and the concentration of Zn depleted ranged from 1.68mg $l^{-1}$to 0.51 mg l^{-1}. The removal percentage of Cd, Pb and Zn was 78%, 82% and 70%, respectively.

Table 6

Concentration of Cd, Pb and Zn (mg l^{-1}) in 10%, 20% and 40% fly ash leachates after 0th, 1st, 7th, 14th, 21st and 30th day of hydroponics experiment.

Heavy Metal	Fly ash leachates	0th day	1st day	7th day	14th day	21st day	30th day
Cd (mg l^{-1})	10%	0.12	0.09	0.07	0.05	0.03	0.02
	20%	0.16	0.12	0.07	0.06	0.04	0.03
	40%	0.22	0.16	0.12	0.09	0.06	0.05
Pb(mg l^{-1})	10%	0.14	0.11	0.09	0.07	0.04	0.02
	20%	0.20	0.16	0.12	0.07	0.04	0.03
	40%	0.32	0.24	0.18	0.12	0.08	0.06
Zn (mg l^{-1})	10%	0.87	0.74	0.62	0.52	0.31	0.22
	20%	1.05	0.84	0.68	0.54	0.34	0.30
	40%	1.68	1.36	1.15	0.87	0.68	0.51

Discussion

The fly ash generated by the process of coal combustion in thermal power stations is being mainly disposed off by the wet methods. In this cases the fly ash come in contact with water and heavy metals present therein are leached and contaminate the soil water environment. The removal of heavy metals by rhizofiltration is a recent technique being employed in present study. The physical and chemical component of fly ash of GTPP used for the research is given in Table 1. This shows that the fly ash is a ferro-alumino-silicate mineral. Table 3 demonstrates the physico-chemical parameters of fly ash leachate studied at varying percentage of 10%, 20% and 40% solution. The research finding showed that pH was fond to decrease from 10% to 40% fly ash solution. Other parameters like TDS, electrical conductivity, alkalinity, total hardness, Ca hardness, Mg hardness, chloride, sulphate, phosphate, ammonia-nitrogen, nitrite-nitrogen and nitrate-nitrogen recorded a slightly increases at the increasing concentration from 10% to 40% fly ash concentration solution. The concentrations of heavy metals in the fly ash solutions of 10%, 20% and 40% are given in Table 4. Fig.1 shows that on increasing concentrations solution from 10% to 40% the amount of leached metal is increased. It also demonstrates in each fly ash solution, leaching of metals was increasing Cd <Pb< Zn. The leached experiment indicated that that the mechanisms such as oxidation, reduction, precipitation and hydroxylation take place simultaneously during the leaching period in aquatic environment (Fulekar and Dave 1983). In the process of rhizofilttration of heavy metal contaminants in water are absorbed or precipitated onto or into the plant roots. Study conducted by (Fulekar and Jadia, 2005) has shown the significance of rhizofiltration. Another experiment performed on water hyacinth (Mishra *et al.*, 2008) also shows the importance of rhizofiltration against heavy metal pollution.The release of heavy metal from fly ash in natural water system will be influenced by pH of fly ash, bonding between the element and fly ash, its chemical form and the physic-chemical of the water (Fulekar *et al.*, 1983).

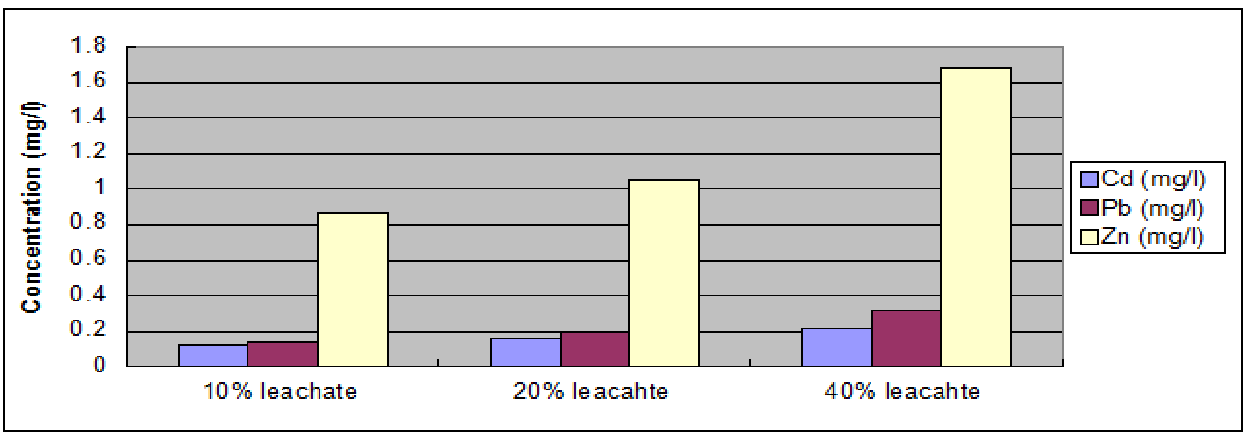


Fig.1(a) Heavy metal concentrations (mg l^{-1}) in various percentages of fly ash leachates.

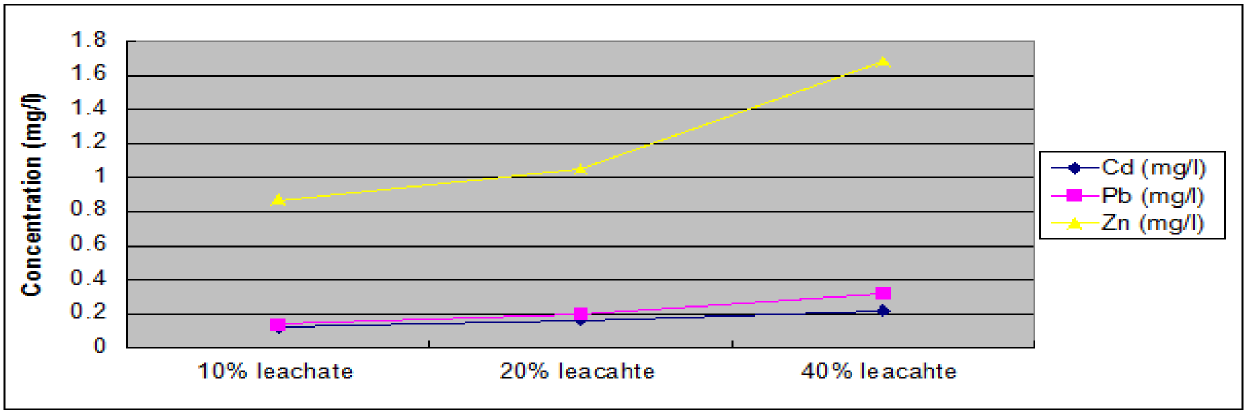


Fig.1 (b).Variation in Heavy metal concentrations (mg l^{-1}) in various percentages of fly ash leachate.

In the present study *Eichornia crassipes* were grown in hydroponic culture in the presence of increasing concentration of fly ash leachates which has increasing ratio of heavy metals Cd, Pb and Zn concentrations to evaluates removal of Cd, Pb and Zn from various concentrations of fly ash leachates.The result presented in this study indicated that uptake of metals Cd, Pb and Zn by *Eichornia crassipes* after 30 days of hydroponics treatment at various concentrations of fly ash leachates are summarized in Table 5. Fig. 2 shows the accumulation of Cd, Pb and Zn was lesser in shoots than roots (shoots < roots). A general increase trend in metal accumulation occurred with the increasing metal concentrations in solutions. The maximum concentrations of Cd, Pb and Zn reached 99.16, 166.52 and 741.04µg g^{-1}in the roots, and 33.46, 41.33 and 255.90 µg g^{-1}in the shoots of E.crrasipes, respectively. It shows plants has accumulation of metals in increasing order of Cd <Pb< Zn. In this study, the translocation factors were calculated on the 30^{th} days of experiment for *Eichornia plants* (Table 5). The results show that maximum translocation factor of Cd, Pb and Zn reached 42%, 47% and 35% respectively for *Eichornia* plants and increasing order of Zn < Cd <Pb. The translocation factor can be a major criterion in the judgments of plants for phytoremediation. Plants with a higher translocation factor can be considered as a better candidate for phytoremediation (Mishra et al. 2008). In this study, the bioconcentration factors also were calculated on the 30^{th}days of experiment for *Eichornia* plants (Table 5). The results show that maximum bio-concentration factor of Cd, Pb and Zn reached 705, 705 and 614 respectively for *Eichornia* plants and increasing order of Zn < Cd = Pb. Bioconcentration factor shows the ratio of heavy metal accumulated by plants to the dissolved in surrounding medium.

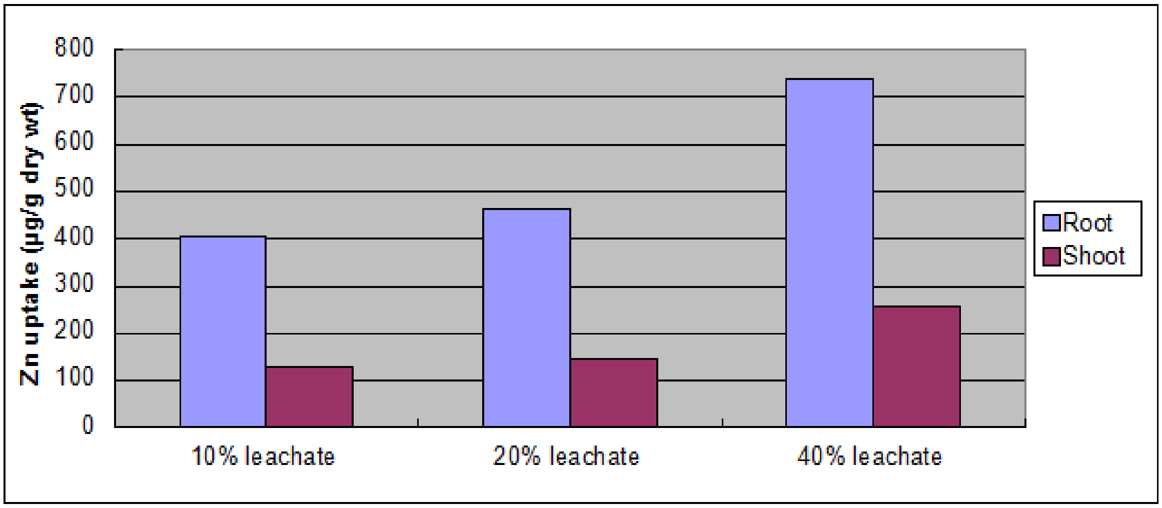
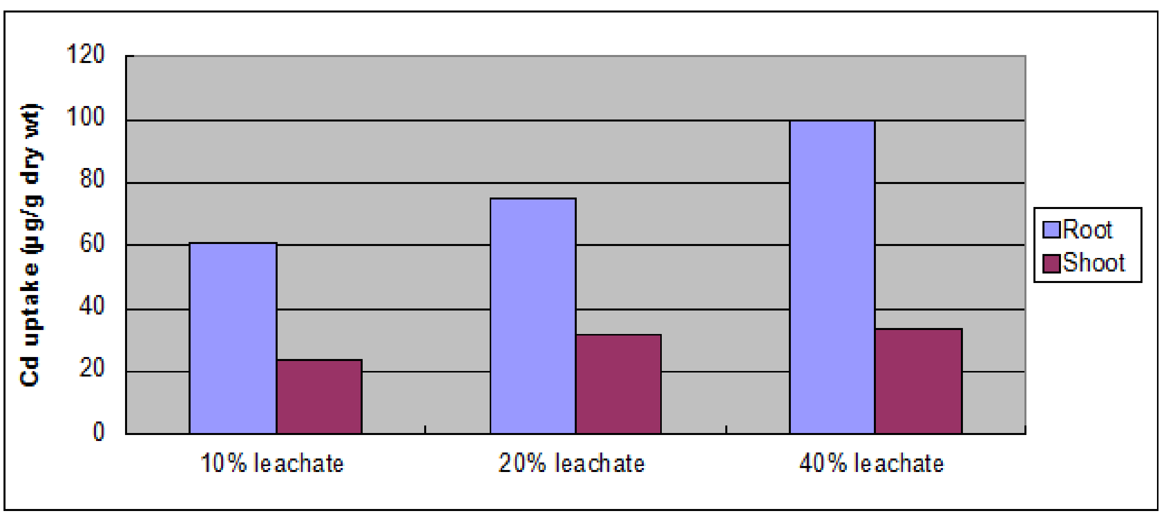
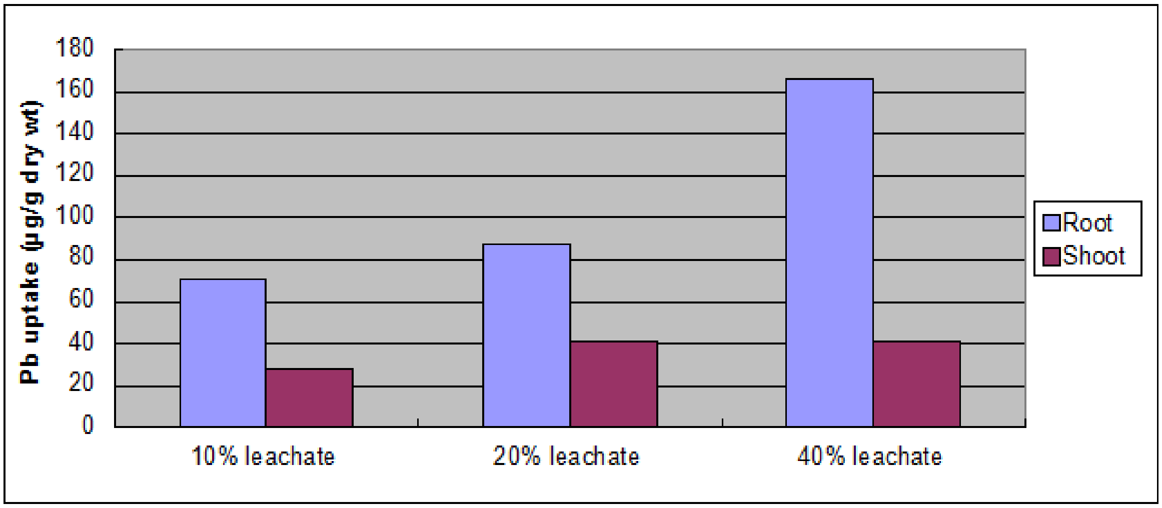


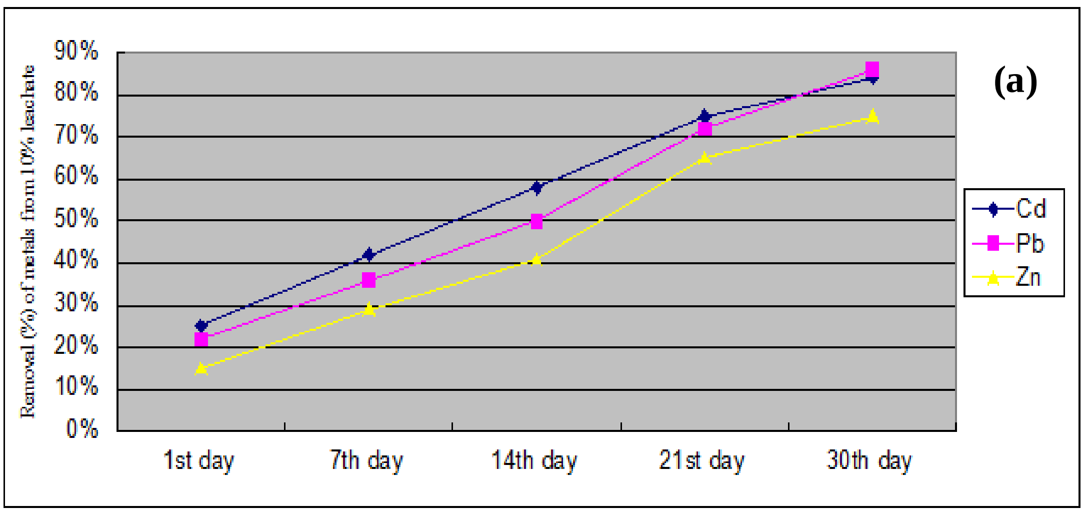
Fig. 2 Cd, Pb and Zn accumulation in the dry biomass of roots and shoots of *Eichornia*plants cultivated in hydroponics media containing various percentages of fly ash leachates.

Removal efficiency of the plant at various concentrations (10%, 20% and 40%) of fly ash concentrations solutions used for experiment is shown in Fig 3. Result revealed increasing trend of removal with the increasing incubation period. Analysis of metal concentration with increasing time has suggested that metal concentrations decreased from day 1 to day 30 day in different experimental sets. High removal of Cd, Pb and Zn by *Eichornia crassipes* were observed at 10%, 20% and 40% of fly ash concentrations solutions. The results obtained from the present study indicated that metal removal percentage for Cd was highest 84%, Pb was highest 86% and Zn was highest 75% at 10% fly ash concentrations solutions. This species was able to remove the 78-84% Cd, 82-86% Pb and 70-75% Zn in 30 days treatment period. The removal efficiencies for Cd, Pb and Zn varied with varying concentration of fly ash concentrations solutions.





Pb uptake (µg/g dry wt)
180
160
140
120
100
80
60
40
20
0
10% leachate
20% leachate
40% leachate
Root
Shoot



(a)
Removal (%) of metals from 10% leachate
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1st day
7th day
14th day
21st day
30th day
Cd
Pb
Zn

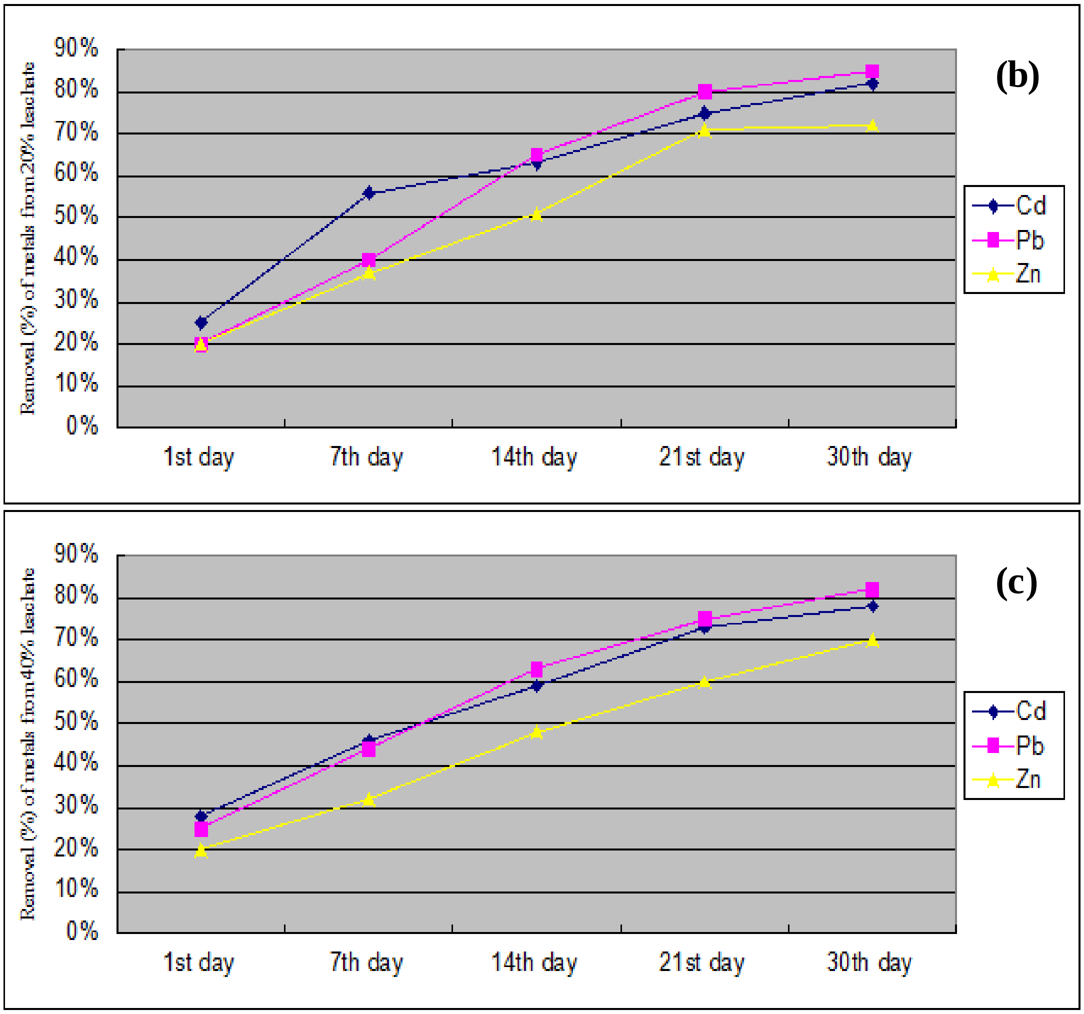


Fig. 3 Removal % of heavy metal (Cd, Pb, and Zn) from 10%, 20% and 40% fly ash leachates after 0^{th}, 1^{st}, 7^{th}, 14^{th}, 21^{st} and 30^{th} day of treatment.

Fig.3 (a) shows the Cd, Pb and Zn removal percentage from 10% fly ash solutions over time. After 1d, 7d, 14d, 21d and 30d the Cd removal was 25%, 42%, 58%, 75% and 84% , the Pb removal was 22%, 36%, 50%, 72% and 86% and the Zn removal was 15%, 29%, 41%, 65% and 75% respectively from 10% of fly ash concentration solution. The final removal of Cd, Pb and Zn was 84%, 86% and 75%, respectively. Fig.3 (b) shows the Cd, Pb and Zn removal percentage from 20% fly ash concentrations solutions over time. After 1d, 7d, 14d, 21d and 30d the Cd removal was 25%, 56%, 63%, 75% and 82% , the Pb removal was 20%, 40%, 65%, 80% and 85%, and the Zn removal was 20%, 37%, 51%, 71%, and 72%, respectively from 20% of fly ash concentration solution. The final removal of Cd, Pb and Zn was 82%, 85% and 72%, respectively. Fig.3(c)shows the Cd, Pb and Zn removal percentage from 40% solutions over time. After 1d, 7d, 14d, 21d and 30d the Cd removal was 28%, 46%, 59%, 73% and 78%, the Pb removal was 25%, 44%, 63%, 75%, and 82%, and the Zn removal was 20%, 32%, 48%, 60% and 70%, respectively from 40% of fly ash concentration solution. The final removal of Cd, Pb and Zn was 78%, 82% and 70%, respectively.It all showed that removal was highest at the first 7^{th} days and then decreased continuously after 30^{th} days of the exposure treatment. The result has shown that the quantity of Cd, Pb and Zn accumulated by plants increased with increased with the increase of concentrations of fly ash concentrations solutions.

Heavy metal Cd, Pb and Zn accumulation at various concentrationof fly ash leachate was not have associated with production of some morphological symptoms of toxicity such as yellowish of leaves, growth retardation and chlorosis in plants due to low quantity of heavy metals in fly ash leachates. The higher bioconcentration factor, translocation factor and high relative growth rate of tested species enable them to accumulate large amount of hazardous metals in their harvested parts and if not disposed properly, the accumulated heavy metals may back to the systems. At the end of the growth period, plant biomass must be harvested, dried or incinerated, and the contaminated-enriched materials should be deposited in a special dump. Recovery of heavy metals from harvested plant parts is another technology.

Conclusion

The present work proved *Eichornia crassipes* as a good accumulator of Cd, Pb and Zn efficiently and survives in polluted contaminated water bodies. This macrophyte has accumulated Cd, Pb and Zn up to 134µg g^{-1}, 209µg/g, and 997µg g^{-1}at 40% concentration of fly ash leachates after 30 day and successfully removed up to 84% of Cd, 86% Pb and 75% Zn respectively. Regardless of the concentrations of treatment in accumulating heavy metal accumulation in water hyacinth followed the order: roots > shoots. The accumulation pattern of Cd, Pb and Zn in whole plants of *Eichornia crassipes* during the hydroponics experiment of the present study increased from Cd <Pb< Zn and the removal % was in order of Zn < Cd <Pb. Cadmium, Lead and Zinc accumulated at various percentage of fly ash leachates which was not associated with production of some morphological symptoms of toxicity such as yellowing of leaves, growth retardation and chlorosis. On the basis of results *Eichornia crassipes* can be recommended for the removal of heavy metal (Cd, Pb and Zn) from fly ash effluents, however, a suitable harvesting and hazardous material disposal system will be required for meaning full results. Furthermore studies are needed to evaluate the on-site application of this free- floating rhizofiltration technique and may assure their full utilization in this context.

Acknowledgement

One of the authors (Amit Kumar Yadav) is grateful to University Grant Commission (UGC), for their financial assistance. Authors are also thankful to authorities of Thermal Power Plant, Gandhinagar for their permission to visit fly ash station and for providing fly ash sample regarding the study.

References

A P H A (American Public Health Association), 1998. Standard methods for the examination of water and waste water. *20th ed. American Public Health Association, Washington, DC, USA.*

Abdel Halim, S.H., Shehata, A.M.A., El Shahat, M.F., 2003. Removal of lead ions from industrial waste water by different types of natural materials. *Water Research* 37, 1678–1683.

Chaudhry, T.M., Hayes, W.J., Khan, A.G., Khoo, C.S., 1998. Phytoremediation focusing on accumulator plants that remediate metal contaminated soils. *Austraaslian Journal of Ecotoxicology*, 4, 37-51.

Choi, S.K., Lee, S., Song, Y.K., Moon, H.S., 2002. Leaching characteristics of selected Korean fly ashes and its implications for the ground water composition near the ash disposal mound. *Fuel*, 81, 1083-1090.

Esperin, E., 1972. Mineral Nutrition of Plants: Principles and Perspective. *John Wiley, New York* .

Fernando, R., Espinoza, Q., Martin, N., Stutz, G., Tirao, G., 2009. Root uptake and reduction of hexavalent chromium by aquatic macrophytes as assessed by high-resolution X-ray emission. *Water Research*, 4159-4166.

Foster, P., 1976. Concentrations and concentration factors of heavy metals in brown algae. *Environmental Pollutes*, 10, 45–53.

Fulekar, M.H. and Dave J.M., 1990. Environmental impact assessment of fly ash from coal-fired power plants. *Encology*, 4, 25-34.

Fulekar, M.H. and Dave, J.M., 1985. Arsenic content in fly ash and its relationship with physico-chemical characteristics of ash effluents. *Asian Environment*, 6(5), 35–38.

Fulekar, M.H., Jadia, C.D., Kakhanis, M., 2005. Rhizofiltration of heavy metals from coal ash leachate. *Asian Journal of Water, Environment and Polltion*, 3(1), 91-94.

Fulekar, M.H., Naik, D.S., Dave, J.M., 1983. Physico-chemical characteristics of sluicing water in ash pond. *Chemical Era*, 19(2), 28-31.

Iyer, R., 2002. The surface chemistry of leaching coal fly ash. *Journal of Hazardous Materials*, B 93, 321-329.

Jakka, R.S., Ramana, G.V. Datta, M., 2011. Seismic slope stability of embankments constructed with ash pond. *Geotechnical Geology Engineering*, 29, 821-835.

Jerzy Jankowski, Colin, R., Ward, D.F., Sarah, G., 2006. Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems. *Fuel*, 185, 243-256.

Kumar, V., Kumar, A., Mathur, M., 2003. Management of fly ash in India: A Perspective. Proceedings of Third *International Conference on Fly Ash Utilization and Disposal, New Delhi*, 1, 1-18.

Maine, M.A., Duarte, M.V., Sune, N.L., 2001. Cadmium uptake by floating macrophytes. *Water Research*, 35(11), 2629-2634.

Masto, Reginald E., Ramesh, C., Ram, L.C., 2009. Bulk use of pond ash for cultivation of wheat maize–eggplant crops in sequence on a fallow land. *Resources, Conservation and Recycling*, 54, 134–139.

Mattina, M.J.I., Lannucci Berger, W., Musante, C., White, J.C., 2003. Concurrent plant uptake of heavy metals and persistent organic pollutants from soil. *Environmental Pollution*, 124, 375–378.

Miretzky, P., Saralegui, A., Cirelli, F.A., 2004. Aquatic macrophytes potential for the simultaneous removal of heavy metals (Buenos Aires, Argentina). *Chemosphere*, 57/8, 997-1005.

Mishra, U.C., 2004. Environmental impact of coal industry and thermal power plants in India. Journal of *Environmental Radioactctivity*, 72(1-2), 35-40.

Mishra, V.K. and Tripathi, B.D., 2009. Accumulation of chromium and Zinc from aqueous solutions using water hyacinth (Eichornia crassipes). *Journal of Hazardous Material*, 164, 1059-1063.

Mishra, V.K., Upadhyaya, A.R., Pandey, S.K., Tripathi, B.D., 2008. Heavy metal pollution induced due to coal mining effluent on surrounding aquatic ecosystem and its management due through naturally occurring aquatic macrophyte. *Bioresource Technology*, 99, 930-936.

Nanda Kumar, P.B.A., Dushenkov, V., Motto, H., Raskin, I., 1995. Phytoextraction: the use of plants to remove heavy metals from soils. *Environmental Science Technology*, 29, 1232–1238.

Salt, D. E., Blaylock, M., Kumar, M., P. B. A. N., Dushenkov, S., Ensley, B., Chet, I., Raskin, I., 1995. Phytoremediation: A novel strategy for the removal of toxic metals from the environment. *Biotechnology*, 13, 468–474.

Sharma, S., Jayalakshmi, C.P., Fulekar, M.H., 1989. Fly ash dynamics in soil-water system. *Critical Reviews in Environmental Control*, 19(3) , 251-272.

Straczek, A., Duquene, L., Wegrzynek, D., Chinea-Cano, E., Wannijn, J. Navez, J., Vandenhove, H., 2010. Differences in U root-to-shoot translocation between plant species explained by U distribution in roots. *Journal of Environmental Radioactivity*, 101(3), 258-266.

Vidali, M., 2001. Bioremediation: An overview. *Pure Appllied Chemistry*, 73, 1163-1172.

Xiang Wei, Han, B., Zhou, D., Nzihou, A., 2012. Physicochemical properties and heavy metals leachability of fly ash from coal-fired power plant. *International Journal of Mining Science and Technology*, 22, 405–409.

http://www.cea.nic.in/reports/monthly/executive_rep/jun12/8.pdf. Central Electricity Authority, Ministry of Power, Government of India. June 2012.

http://www.flyash2012.missionenergy.org

http://www.indianpowersector.com

http://www.livemint.com/2009.