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Remediation of cadmium contaminated irrigation and drinking water: A large scale approach

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ABSTRACT

Cadmium is one of the most troublesome toxic heavy metals. It accumulates in the water reservoirs and agricultural soil as a result of intensive use of Cd contaminated phosphate fertilizers, e.g. in agriculture in the North Central Province (NCP) of Sri Lanka. The hyper-accumulator *Thlaspi caerulescens*, accumulates up to 1000 ppm Cd in shoots without exhibiting toxicity symptoms. The storage rhizomes of year old *Nelumbo nucifera* (lotus) natural vegetation in water reservoirs in NCP accumulated 253 ± 12 mg Cd/kg. Seedlings of lotus grown in 5% Hoagland's solution at 0.75, 1.0 and 1.25 ppm cadmium sulphate showed a significant increase in Cd removal of 0.0334–0.121 ppm/week. However the removal rate of Cd from water failed to increase any further at higher concentrations of Cd in water. The slow growth rate and low rate of phytoextraction demands a more effective but an affordable method of remediation in order to combat the prevailing elevated cadmium levels in NCP that causes chronic renal failure (CRF). We have developed a large scale filtering device using rice husk. We have achieved successful results in sequestering Cd using raw rice husk as well as amorphous silica derived from rice husk.

1. Introduction

Excessive pollution of water resources with heavy metals demands means of efficient and affordable purification. Perhaps this could to be achieved by simulating nature. We conducted studies of the "hyper-accumulators" of heavy metals, as a means of developing strategies to alleviate heavy metal accumulation problems in agricultural land, irrigation and potable water. Existence of plant species with ability to tolerate and survive under extreme exposure to heavy metals without any apparent phytotoxicity is well known (Ahmed et al., 2001; Zhao et al., 2003; Fischerova et al., 2006). Such plants can provide the genetic information that could be used to develop more efficient hyper-accumulators.

The cadmium in aquatic and agricultural environment is posing very serious health problems in many countries, both in the developed and developing world. Long term exposure to cadmium often results in chronic renal failure (CRF) among industrial workers in Sweden and Belgium (Friberg and Vahter, 1983, Lauwerys et al., 1984), among agricultural workers in Thailand (Piyaratana et al., 2008), in Japan (Nogowa et al., 1979) and in Sri Lanka (Bandara et al., 2008). In the North Central Province of Sri Lanka, contamination is associated with regular and intensive use of high cadmium phosphate fertilizer in lowland agriculture.

Although the use of hyper-accumulators for bioremediation has been discussed, thus far very few hyper-accumulators have been identified. Of these, *Thlaspi caerulescens* is one of the best characterized plants being used as a hyper-accumulator of Cd. This plant can tolerate 100 ppm of Cd without any phytotoxicity.

In the NCP, *Nelumbo nucifera* is natural vegetation in all the reservoirs. Bandara et al. (2008) reported that Nelumbo can accumulate seven heavy metals namely, cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn). In a controlled environment study using seedlings of *N. nucifera* grown in 5% Hoagland's solution at 0.75, 1.0 and 1.25 ppm cadmium sulphate solution, a significant removal (0.0334–0.121 ppm per week) was observed. However the cadmium removal rate from the aquatic substrate by Nelumbo roots reached a plateau and did not increase proportionately at higher Cd concentrations (Abeyrathna, 2004).

The apparent slow growth rate of plants, low rates of phytoextraction and the question of disposal of lotus rhizomes stored with cadmium demand more effective and quicker methods of remediation of irrigation and drinking water. It is our objective to design a more effective and a cheaper method of chemically filtering water using agricultural waste that is easily available in the NCP, to meet the urgent need of large scale water purification.

2. Materials and methods

2.1. Filtering medium

Raw dry rice husk was obtained from the rice mills in the Central Province where no cadmium problem is yet reported. The filter medium was prepared using raw rice

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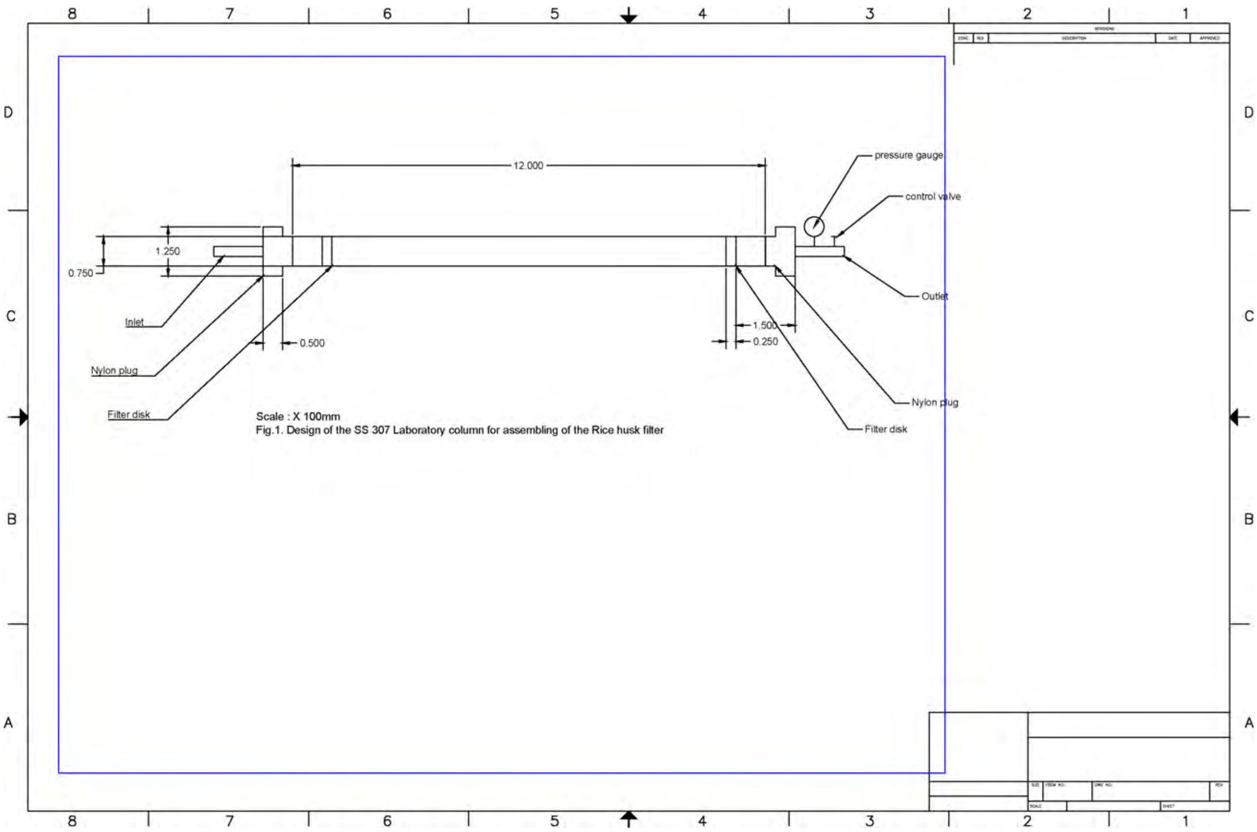

Fig. 1. Design of the SS 307 Laboratory column for assembling of the rice husk filter.

husk, open fired husk obtained by firing husk at ambient conditions, and controlled fired husk. Preparation of controlled fired rice husk filtering medium was done by firing several batches of raw dry rice husk in a muffle furnace (Heraeus Muffle Furnace MR 170E, 1000 °C, 220 V, 3 kW) under hypoxic conditions (a maximum of 0.924 l of oxygen under ambient pressure per burning) at 500 °C.

2.2. Filtering device

A laboratory version of the field filtering unit was constructed using Austenitic chromium-nickel alloys SS 307 (“stainless steel”). Filtering medium was packed in the stainless steel column of 1200 mm long length with a 750 mm pipe diameter and a wall thickness of 5 mm. The ends of the column were sealed with solid nylon 6-6 plugs, with openings for inlet and outlet SS pipes to facilitate attachments of pressure gauges and other control valves. The quantity of substrate used in the column varied according to the material (Fig. 1). A total of 1542 g of controlled fired rice husk was tightly packed into the SS column prior to treatment, using a manually operated packing device to obtain a packing density of 0.291 g/cm^3. Other filter substrates used were also packed in the same manner: 895 g of raw husk – packing density 0.168 g/cm^3 and, 1760 g of open fired husk with the packing density of 0.331 g/cm^3.

2.3. Input and output pipe lines

All pipe lines, pressure pumps and the containers used in the experiment were made of SS 307 or higher. An open basin of 100 l capacity made of SS 307 was used to store water. A positive displacement piston pressure pump with tubes made of SS 307 or above with a capacity 1600 psi was selected to provide a pumping pressure of 600 psi. Therefore no backpressure was developed in the columns.

2.4. Pre-test processing of filter medium

The filtering medium used must be free of any cadmium that could interfere in the test analysis. Therefore the substrates prepared were thoroughly cleaned by continuous running of reverse osmosis (RO) treated deionized water through the packed column at 600 psi with each of the substrates (at a flow rate of 1200 l/h for raw rice husk, 666 l/h for controlled fired rice husk and 225 l/h for open fired rice husk) until the conductivity of the input water and output water from the columns reported the same value of 10 μs/cm at pH 7.2 at 23 °C.

2.5. Filtration procedure

Efficiency of the filtration procedure was assessed by continuously pumping 100 l of deionized water containing 6857 mg of cadmium sulphate octahydrate through the packed column as described in Section 2.3 above, for a period of 10 h, with hourly sampling for cadmium analysis using graphite furnace AAS. The open fired rice husk packed filter could tolerate 600 psi only for a period of 3 h due to build up of very high pressure within the system. There was no increase in pressure in the other two columns namely the controlled fired rice husk and raw rice husk packed columns. It is probably due to higher porosity in filter material compared to the finer open fired rice husk. The packing density of the columns was highest in open fired rice husk. The total flow volume over the 10 h period was 6660 l in the controlled fired rice husk column and 12,000 l through the raw rice husk column. The total flow volume in open fired rice husk column was 675 l in 3 h.

2.6. Analytical methods

Each water sample collected hourly was well mixed by vortexing at 23 ± 1 °C. Two 20 ml working samples were taken for analysis and stored in 25 ml acid washed cadmium free glass vials at 4 °C, until analysis for cadmium was done as described by “Standard Methods for Examination of Water and Waste Water” by Greenberg et al. (1992). The standard cadmium solution AA standard BDH Spectrosol at 1000 mg/l supplied by BDH, U.K. was used. Samples were fed into the GBC 932 Plus Atomic Absorption Spectrometer and aspirated into the air-acetylene flame. The detection limit of the AAS was set at 0.2 mg/l or mg/kg and the Graphite Furnace GBC GF 3000 with a detection limit 0.15 μg/l or μg/kg was used. The quality control measures were followed for cadmium extraction and analysis at all steps of the analytical process and also in sampling as described by EPA, USA (1983).

3. Results

Results of the filter media we used were very encouraging. The cadmium content in rice husk prior to cleaning with deionized reverse osmosis water were in raw rice husk 0.78 μg/kg of Cd, open fired rice husk 2.34 μg/kg of Cd and in control fired rice husk 1.35 μg/kg of Cd (on dry weight basis). The continuous circulation of 100 l of contaminated water with a known amount of Cd showed gradual purification with each run through the column. The analy-

Table 1
The cadmium concentration in mg/liter in the samples of filtrate obtained after filtering cadmium added water through raw rice husk, controlled fired rice husk and open fired rice husk filter medium.

Hour	Filter substrate used in the SS column		
	Controlled fired rice husk	Open fired rice husk	Raw rice husk
0[a]	18.44 ± 3.60	18.44 ± 3.60	18.44 ± 3.60
1	1.15 ± 0.38	2.34 ± 1.08	13.1 ± 1.52
2	0.44 ± 0.24	2.18 ± 1.66	0.99 ± 0.24
3	1.19 ± 0.44	13.5 ± 0.97	11.4 ± 1.2

[a] 0 h represent the cadmium concentration of water before passing through the filter. Data are mean of five separate analysis and represented as mean ± SD.

sis of water samples obtained hourly during the filtration process and the filter material after completion is given in Table 1.

4. Discussion

During the second hour of operation of the filter under a pressure of 600 psi, gave the best results of Cd filtration. After pumping 1350 l of, Cd contaminated water with a flow rate 666 l/h we observed that the amount of Cd adsorbate from water is reaching a plateau. The surface chemistry of amorphous silica absorbent has been reviewed by Zhuravlev (2000). The Zhuravlev model could use to determine the kind of the chemisorptions pattern of the column under the restoration of the hydroxyl covering and also to assess the OH groups inside the SiO_2 skeleton. It has been established that adsorption and other surface properties per unit surface area of silica are identical. It could be that the adsorption is either ionic or physico-chemical, and under the conditions operated in this study Cd is adsorbing and desorbing continuously. Therefore it is possible that filters arranged in a series at any given point could filter the cadmium out of water.

In rice milling, about 78% of weight is processed rice, broken rice and bran. Rest of the weight of rice is husk – 22%. Husk is also used as a fuel in the rice mills to generate steam for the parboiling process. Husk contains about 75% organic volatile matter. The balance remains as ash during the firing process, yielding rice husk ash (RHA). RHA in turn contains around 85–90% amorphous silica.

The ash content in BG 300 and BG 400, the common rice varieties used in Sri Lanka, was reported to vary from 25 to 45% depending on the firing conditions used (Bandara, 1994). The ash obtained is 92–95% silica (Mehta, 1978). Silica from RHA is highly porous and lightweight, with a very high external surface area and excellent absorbent properties. Burned rice husk is generally referred to as (RHA); however the type of ash varies in its properties of adsorption according to the burning technique used. The structural properties of silica in the RHA depend on the conditions (time, temperature, etc.) of combustion and rice variety used. At 500–800 °C, amorphous silica is formed. At temperatures greater than this, crystalline silica results. In our study we used three different forms, raw husk, amorphous and crystalline silica from RHA.

Since the raw rice husk is very freely available and cost involved would be only for logistics, it would be possible to replace the filters regularly with fresh material. We propose that large scale filters could be fixed at the sluice gate and use the pressure of the reservoir. Or the filters could be installed upstream of rice fields at intakes from the distribution canal. Both would filter out cadmium carried by the irrigation water.

For example, filter specifications required at the irrigation distribution output near the dam for Cd remediation of a large reservoir, Kalawewa with a capacity of 123 million cubic meters of water when at spill level (DSWRPP-Sri Lanka, 2010) would be, size of filter 2 m × 2 m × 22.1 m; capacity of filter 88.35 m^3 to be renewed at the beginning of the cropping season or every 4 months, with a total requirement of 103 Mt controlled fired RHA to sequester 3.1 Mt of Cd. In this estimation, the Cd in water was taken as 25 μg/l, the extreme level reported in Mahaweli river, the main source of water to Kalawewa reservoir (Bandara et al., 2010). Similarly we envisaged that 304 g of controlled fired RHA packed in a 100 cm length × 3.65 cm diameter column, could filter Cd in drinking water for a family of five persons for a year. However, with regard to filtering Cd from drinking water, volume flow/adsorption chart should be developed in view of the low concentrations of Cd in water.

The domestic level used filters should be collected and processed to leach out Cd from filter media with sulphuric acid prior to recycling in the environment (Ren et al., 2009). It is also possible to sequester Cd in used RHA absorbent in hyper-accumulator plants in order to prevent recontamination of the food chain. There is a potential industrial use of the discarded filter medium, the amorphous silica in the cement industry (Bandara, 1994). Further studies to evaluate desorption patterns are already in progress.

At the present time non-point pollution, and the pollution caused by cadmium that is released into the reservoir water from sediments are difficult to clean, and there is a urgent need for quick and affordable purification process. The work reported here needs further improvement after conducting pilot experiments both at field level associated with irrigation system and also at domestic level with regard to filtering potable drinking water, prior to commercialization. It would be much cheaper to install rice husk filters at all distribution points to prevent entry of cadmium into the food chain, than the enormous cost involved in the mitigation of suffering of chronic renal failure patients by regular dialysis.

It was observed that the best adsorption of Cd is by the controlled fired rice husk, having an average rate of cadmium adsorption 30 mg/g of controlled fired silica. The efficient adsorption is due to the amorphous silica content of the medium. Amorphous silica is biological in origin and it is in an unstructured condition. The unstructured condition facilitates adsorption of cadmium perfectly. In the later stage of filtering process, however, the medium releases Cd again, after reaching saturation.

Open fired rice husk contains only structured silica, which does not provide as many sites for Cd binding. Hence Cd binding in completely burned rice husk is very poor. It is similar to raw rice husk due to its porous structure, but does not favor Cd adsorption. Control fired rice husk can be obtained as a by-product of the energy industry. Rice husk can be used as the raw material for thermal power generation or electricity generation. If technology were adapted to provide the facility for controlled firing of rice husk in normal harnessing of energy, the ash by-product could be used as the filter media for large scale removal of Cd from irrigation water.

Rice husk is freely available in any country that grows and processes rice. It is an unavoidable environmental waste problem. Rice husk ash could be a major environment threat causing damage to the land and the surrounding area in which it is dumped. Many other ways are also being considered for disposal by making commercial use of rice husk ash.

Conflicts of interest statement

We have no conflicts of interest with regard to technical and scientific material discussed in this manuscript.

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