



Phytoextraction potential of heavy metals by native wetland plants growing on chlorolignin containing sludge of pulp and paper industry



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ABSTRACT

The results of physico-chemical analysis of pulp and paper mill effluent sedimented sludge revealed the presence of heavy metals (mg l^{-1}) Fe (67.53), Zn (13.90), Cu (2.15), Cr (2.30), Cd (0.255), Mn (11.0), Ni (3.30), and Pb (1.05) along with persistent chlorolignin. The major persistent organic pollutants detected by GC-MS were ethane, 1,1-diethoxy; tetradecanoic acid; furane 2,5-dimethyl; *n*-hexadecanoic acid; nonacosane, trimethylenebis-1,3-dioxolane; 1,3-dioxolane, 2-(phenylmethyl). Twelve representative native plants were noted based on their population number growing on pulp and paper sludge and evaluated for their phytoextraction potential of heavy metals. The result revealed that *Triticum aestivum* was found as root accumulator for all metals except Cu. Similarly, the *Brassica campestris* accumulated all metals maximum in root except Ni, Fe and Pb. While, *Eclipta alba* accumulated majority of metals in their shoot and leaves, But *Solanum nigrum*, *Rumex dentatus* accumulated metals in root and shoot both. *Ranunculus scleratus* accumulated all the tested metals in their aerial parts except Cd and Pb. *Camelina benghalensis* accumulated metals in root except Cd, Pd. Similarly the *Phragmites cummunis* and *Ricinus cummunis* accumulated majority of metals in their shoot and leaves. It was also noted that several evaluated plant showed bioconcentration factor (BCF) greater than one for accumulated metals i.e. Pb in *T. aestivum* (1.285), *C. benghalensis* (5.142), *Cannabis sativa* (3.466), *P. cummunis* (7.180), *R. cummunis* (66.80) was also noted. Furthermore, greater than one translocation factor (TF) for all these plants showed strong evidence for phytoextraction and in situ remediation potential of these plants. The overall order of phytoextraction potential of native wetland plants were *C. sativa* > *P. cummunis* > *C. benghalensis* > *T. aestivum* > *B. campestris* > *E. alba*.

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1. Introduction

Heavy metals are known as a major source of contamination discharged by various industrial activities. These heavy metals and persistent organic pollutants (POPs) are harmful to animals as well as humans due to its tendency to accumulate in the food chain (Singh and Prasad, 2015). The sludge generated from various industries is considered as a source of potentially toxic elements and its disposal is a threat to human due to the presence of several

heavy metals and various unknown organic pollutants. Nowadays the production of sludge is increasing day by day as a result of wastewater treatment, it remains bulky with high moisture contents and their composition may range from high content of organic to minerals and heavy metals depending on their origin. Sometime, after undergoing composting and vermicomposting, the sludge is used as a fertilizer in many countries (Lim et al., 2016). However, trace elements bioavailability beyond the permissible limits has posed a crucial problem in agriculture and environmental studies. Therefore, in the recent past several studies have been reported phytoremediation and phytoextraction of heavy metals from contaminated site by potential plants (Mani and Kumar, 2014; Lone et al., 2008). The native potential plants involved in the uptake of an element is most reliable method for the prediction of availability of a contaminated metal to plants and their application for phytoextraction of heavy metals from contaminated site (Gupta and

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Sinha, 2006; Kabata-Pendias, 2010). However, the mobility of all trace metals and their specific chemical forms or binding properties with various organic co-pollutants are the major factor for controlling phytoextraction and metal accumulation by potential plants. Besides, the soil condition and plant growth parameters also regulate the heavy metal accumulation, moreover the mobility and availability of heavy metals in the soil are generally very low, especially when the soil is having high pH, clay and organic matters which have metal binding tendency (Jung and Thornton, 1996; Rosselli et al., 2003). Among the all potential plants some are used as a food or medicines which are health concern. Thus, the characterization of physico-chemical properties of various sludge and evaluation of potential native plants capable for phytoextraction and distribution of various heavy metals in their various parts is warranted globally for the development of phytoremediation technique for sustainable development. A potential strategy may be used to remediate the contaminated sludge by these plants to remove the pollutants from the habitat or to render them harmless (Salt et al., 1998; Lasat Mitch, 2002). Presence of heavy metals and persistent organic pollutants in pulp and paper mill is global challenge for its safe disposal due to its huge generation from industrial processing though it can be decreased by physico-chemical methods such as coagulation (Subramonian et al., 2014; The et al., 2016) and adsorption (Sajab et al., 2014), but it is not economically feasible due to its energy intensive and cost expensive methods (Horsfall and Abia, 2003). Hence, these traditional treatment systems can be replaced by biological treatment system. Phytoextraction of heavy metals by native wetland plant growing on chlorolignin waste of pulp and paper mill effluent sludge is emerging as simple, cost effective and self-sustaining alternative of the traditional treatment system. Another application of phytoremediation is phytostabilization where plants are used to minimize metal mobility in contaminated soils. However, plants may play an important role in metal removal through absorption, cation exchange, filtration and chemical changes through root accumulation process (Dunbabin and Bowner, 1992; Wright and Otte, 1999). The pulp and paper mill effluent and sludge content high amount of iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), manganese (Mn), nickel (Ni), lead (Pb) (Chandra and Rachna, 2012). The wetland plants such as cattail (*Typha latifolia*), common reed (*Phragmites australis*), and motha (*Cyperus malaccensis*) grows in such condition is an evidence of their potentiality for heavy metals accumulation in their tissues (Ye et al., 2001; Deng et al., 2004; Chandra and Sangeeta, 2010, 2011; Sangeeta and Chandra, 2011). Besides, cattail and common reeds have been successfully used for the phytoremediation of Pb/Zn mine tailings under waterlogged conditions (Ye et al., 1997a,b). Various other wetland plants are also screened for heavy metals accumulation from the natural wetland by several workers (Cardwell et al., 2002; Demirezen and Aksoy, 2004; Deng et al., 2004; Yoon et al., 2006). It is an important to use the native plants of contaminated site for phytoremediation because these plants are naturally adopted in terms of survival, growth and reproduction under the environmental stresses than those introduced from other environment. There has been a continuing interest for searching native plants that are tolerant for heavy metals. However, only few studies have evaluated the phytoremediation potential of native plants under field conditions (Shu et al., 2002; McGrath and Zhao, 2003). Heavy metals can cause severe phytotoxicity and may act as powerful factor for the evolution of tolerant plant populations also. Therefore, it is possible to classify metal-tolerant plant species from natural vegetation in field waste sites that are contaminated with various heavy metals.

The pulp and paper industry is major source of environmental pollution. In addition, during the course of paper production 150–200 m³ sludge is generated per ton of paper production (Pokhrel and Viraraghavan, 2004). In India there are about 625 pulp

and paper industries which produce approx. 1800–2400 m³ sludge per ton of paper production annually, but the sludge has been reported for high content of different toxic heavy metal which may accumulate in different plants and soil. This lead to cause health hazards through food chain. Several heavy metals and persistent organic pollutants are reported as pollutants in wastewater and sludge both (Chandra et al., 2011). However, the chemical properties of disposed persistent pollutants are still unknown therefore bioremediation is a challenge for safe disposal. Moreover, the lignocellulosic waste and humic substances have strong binding tendency with heavy metals which reduces the metal availability to growing plant species. Furthermore, the heavy metal remains reduced in disposed fresh sludge at alkaline condition. However the luxuriant growth of some native plants of pulp paper effluent sludge indicated the phytoextraction potential of various heavy metals and bioremediation of complex hazards sludge containing the mixture of various metal and persistent organic co-pollutants. Mazumdar and Das (2015) has reported the phytoremediation of Pb, Zn, Fe and Mg with 25 wetland plants species from the pulp and paper mill contaminated site in North East, India, which is relatively temperate region. In this study floating and marginal wetland plants were collected from the site for metal accumulation. The effluent and sludge characteristic with heavy metal content varies from industry to industry, due to variation in raw material and paper manufacturing process. Moreover, the metal accumulation by wetland plants is regulated by the environmental factors and nutritional constituent of waste. But, the knowledge of different heavy metals for phytoremediation pattern and magnitude is still unknown; hence the immediate objectives of this study is to investigate the heavy metal phytoextraction potential by native wetland plants growing on chlorolignin containing organic pollutants rich sludge discharged from pulp and paper industry and heavy metal content in the disposed pulp paper industry sludge. Furthermore, to investigate the comparative phytoremediation potential of different plants growing on sludge. In addition the analysis of various heavy metals accumulation pattern in different parts of plants growing on sludge and finally to explore the possibility for monitoring of heavy metals pollution by growing native plants at sludge disposal site for prevention of environmental pollution in aquatic resources.

Therefore, the present study has been carried out at the pulp and paper sludge disposal site of industry. Further, the persistent organic pollutants (POPs) and heavy metals were detected by Gas Chromatography-Mass Spectrometry (GC-MS) analysis and Atomic Absorption Spectrophotometer (AAS) respectively, after extraction with suitable solvents and acid digestion methods. Simultaneously the potentially growing plants were uprooted and heavy metal analysis was done in different parts of plants.

2. Materials and methods

2.1. Collection of sludge sample and native plants

The sludge samples were collected from M/s Century pulp and paper mill Ltd., Lalkuwan, Nainital, Uttarakhand, India. The sludge sample was collected in pre-sterile plastic bag (capacity 20 kg) (Tarson Production Pvt. Ltd., USA) from sludge bed of discharging wastewater after secondary treatment from the treatment plant of pulp and paper mill. Twelve growing native plants on the sludge, based on their coverage at the site together with the associated sludge sample were collected and it was washed thoroughly by sterile distilled water and CaCl₂ solution to remove the adherent sludge particles. The selected plants were identified by standard taxonomic tools and confirmed by plant taxonomist from CSIR-National Botanical Research Institute, Govt of India.

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