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Analysis and treatment of heavy metals in the effluent of orient paper Mills in Amlai, Shahdol district, Madhya Pradesh

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Abstract
The effluents discharged by Orient Paper Mill Amlai contain notable quantities of metallic cations such as zinc, copper, iron, manganese, lead, and cadmium. The release of these heavy metals without proper treatment poses a significant risk to public health due to their persistence, biomagnification, and accumulation in the food chain. In order to address the problems associated with metal pollution, several processes have been developed for the treatment and disposal of waste materials containing metals. Some plant species have the remarkable ability to accumulate heavy metals like lead, chromium, cadmium, and zinc. Currently, the field of phytoremediation, which utilizes plants to remove pollutants, is approaching a potential commercialization stage. Therefore, it is worth exploring the potential of utilizing *Croton sparsiflorus* to effectively remove even low concentrations of heavy metals present in the wastewater of paper mill effluent soil.

Keywords: Phytoremediation, heavy metals, effluent soil, *Croton sparsiflorus*

1. Introduction

The pulp and paper industry, ranked as the sixth most polluting industry out of the seventeen globally recognized polluters by the esteemed Ministry of Environment and Forests (MOEF), holds a notorious reputation (Medhi *et al.* 2011 and Sharma & Ramotra, 2014) [1, 2]. It is noteworthy to mention that Asia, on a continental scale, reigns supreme in its production of pulp and paper, surpassing all other regions worldwide.

The primary concern plaguing the pulp and paper sector resides in its excessive utilization of freshwater resources and generation of substantial volumes of wastewater (Devaki, R.M. Tech and Dr. Lima Rose Miranda, 2017) [3]. Approximately 1.5 cubic meters of effluent is generated per metric ton of paper produced (Shivayogimath and Joshi, 2015) [4].

The utilization of industrial or household waste in irrigating agricultural crops, particularly in urban and suburban areas, is prevalent due to its easy accessibility, disposal challenges, and limited availability of fresh water (Singh *et al.* 2004 and Rahman *et al.* 2012) [5, 6]. However, this practice is known to significantly increase the presence of heavy metals in the soil and crop plants (Fazeli *et al.* 1998 and Chopra *et al.* 2013) [7, 8]. Heavy metals pose a grave threat due to their non-biodegradable nature, extended biological lifespans, and ability to accumulate in various body tissues (Fytians *et al.* 2001, Tandi *et al.* 2005 and Chopra *et al.* 2009) [9-11]. These metals are particularly hazardous because they readily dissolve in water (Chopra *et al.* 2013, Pathak *et al.* 2012) [8, 12]. Conventional treatments for heavy metal contamination have drawbacks such as low effectiveness at low concentrations, expensive handling, and safe disposal of toxic sludge (Sub *et al.* 2008) [13].

In India, there exist a staggering 666 pulp and paper mills, with an impressive 632 of them relying on agro-residue for their operations (Malla and Mohanty, 2005, Kumar and Chopra, 2012) [14-15]. These mills produce a substantial volume of wastewater, characterized by high levels of biological oxygen demand (BOD) and chemical oxygen demand (COD) Mapanda *et al.* (2005) [16] and Kumar (2010) [17]. The infusion of various substances through the practice of irrigating crops with pulp mill wastewater not only impacts crop growth and soil properties but also influences their mobility within the soil profile (Belorai and Levy, 1971 and Waisel, 1972) [18, 19]. The pulp and paper industry, a prominent player in the industrial landscape, extensively employs lignocellulosic materials and water in its manufacturing processes, leading to the discharge of chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols, and chlorinated hydrocarbons in its effluent (Liss *et al.* 1997) [20].

In the realm of environmental cleanup, the practice of using plants, known as phytoremediation, has garnered significant attention. This method proves to be both cost-effective and environmentally friendly, making it an attractive option for addressing a wide range of hazardous pollutants (Pilen-Smits, *et al.* 1999) [21]. The key to successful phytoremediation lies in identifying plant species that are native to the area of concern and possess the ability to withstand and accumulate high levels of heavy metals (Baker and Whiting, 2002) [22]. Phytoremediation is an emerging technology specifically designed for remediating soils contaminated with metals. It involves the utilization of green plants, along with their associated microbiota, soil amendments, and agronomic techniques, to eliminate, contain, or neutralize environmental contaminants (Cunningham and Berti, 1993) [23]. The efficacy of phytoremediation in the context of heavy metal accumulation has been explored through the study of the *Croton sparsiflorus* plant. Additionally, the impact of introducing biosolids such as vermicompost on the plant's ability to bioaccumulate heavy metals has been investigated, along with the evaluation of heavy metal concentrations in the soil after treatment.

2. Materials and Methods

2.1 Collection of materials

The garden soils are gathered from nearest places. The effluent is collected from Orient paper mill located at Amlai, Shahdol (M.P.). *Croton sparsiflorus* seeds are collected from this plant Amlai, Pokhrinala, Amlai CT Part. Vermicompost was prepared with cow dung using earthworm species *Eurdius euginae*. Seeds were germinated in experimental pots and watered. On fifteenth, thirtieth, forty fifth and sixtieth days the plants were harvested from pots and the concentration of heavy metals Chromium (Cr), Lead (Pb), Cadmium (Cd) and Zinc (Zn) of the samples were noted.

2.2 Experimental setup

The seedlings were exposed to different concentrations of heavy metal chromium to find the toxicity. Chromium at high concentrations of 200 and 300 mg/kg showed high toxicity that the plants died. The various experimental setup used for the present study are listed below:

Table 1: Experimental setup.

S. No.	Pot No.	GS (kg)	CS Seeds (g)	VC (kg)	PME (ml)	Plant harvested (days)
1.	A1	1	2	-	50	15
2.	A2	1	2	-	50	30
3.	A3	1	2	-	50	45
4.	A4	1	2	-	50	60
5.	B1	½	2	½	50	15
6.	B2	½	2	½	50	30
7.	B3	½	2	½	50	45
8.	B4	½	2	½	50	60
9.	C1	1	2	-	100	15
10.	C2	1	2	-	100	30
11.	C3	1	2	-	100	45
12.	C4	1	2	-	100	60
13.	D1	½	2	½	100	15
14.	D2	½	2	½	100	30
15.	D3	½	2	½	100	45
16.	D4	½	2	½	100	60
17.	E1	1	2	-	200	15
18.	E2	1	2	-	200	30
19.	E3	1	2	-	200	45
20.	E4	1	2	-	200	60
21.	F1	½	2	½	200	15
22.	F2	½	2	½	200	30
23.	F3	½	2	½	200	45
24.	F4	½	2	½	200	60

GS – Garden Soil, CS – *Croton Sparsiflorus*, VC – Vermi Compost, PME – Paper Mill Effluent

2.3 Heavy metal analysis of soil samples

Soil samples of each pot were air dried, crushed and pass through 0.2 mm sieve and stored in Zip lock covers for analysis. Heavy metals present in all the samples were analyzed by AAS (Atomic Absorption Spectroscopy).

3. Results and Discussion

The concentration of heavy metals are varies in paper mill effluent (Pb > Zn > Cr > Cd). Heavy metals concentration are decreases largely in B, D and F type (15-60 days) pots, because it consists of vermicompost which is used to growing plant and accumulation of heavy metals. So, the well growing plants which accumulate heavy metals easily than other pots (A, C and E type). Finally, excess amount of heavy metals in soil are remediated by combination of vermicompost with garden soil.

Table 2: Physico–chemical characteristics of the effluent collected from the paper industry.

S. No	Name of the parameter	Sample details
Physical parameter		
1	Colour	>1hue
2	Odour	Unpleasant
3	Turbidity	30.6NTU
4	Total dissolved solids (mg/l)	432
5	pH	7.84
6	Electrical conductivity (µmhos/cm)	284.6
7	BOD (mg/l)	15.5
8	COD (mg/l)	64.69
Heavy metals		
9	Zinc (mg/l)	3.35
10	Chromium (mg/l)	2.48
11	Lead (mg/l)	6.16
12	Cadmium (mg/l)	1.27

Table 3: Heavy metal concentrations in various soil samples.

S. No	Pot No.	Cr	Cd	Pb	Zn	Reduction of concentration (Days)
1	A1	2.45	1.32	5.87	3.36	15
2	A2	2.20	1.27	4.96	2.94	30
3	A3	1.57	1.06	3.49	2.55	45
4	A4	1.34	0.83	2.86	2.32	60
5	B1	2.42	1.32	5.46	3.03	15
6	B2	1.31	0.94	4.32	2.88	30
7	B3	0.08	0.16	2.37	0.65	45
8	B4	0.05	0.11	2.03	0.58	60
9	C1	2.52	1.27	5.94	3.36	15
10	C2	2.27	1.19	4.67	3.23	30
11	C3	1.96	0.97	3.77	2.86	45
12	C4	1.55	0.88	2.77	2.67	60
13	D1	2.38	1.33	6.19	3.10	15
14	D2	2.03	0.97	5.56	2.87	30
15	D3	0.11	0.28	2.27	0.76	45
16	D4	0.04	0.18	1.99	0.64	60
17	E1	2.52	1.35	5.67	3.39	15
18	E2	2.36	1.29	4.84	3.26	30
19	E3	1.95	1.18	3.93	2.88	45
20	E4	1.66	0.94	2.92	2.56	60
21	F1	2.47	1.36	6.17	3.16	15
22	F2	2.14	0.86	5.67	2.83	30
23	F3	0.92	0.58	3.55	0.86	45
24	F4	0.08	0.46	1.92	0.66	60

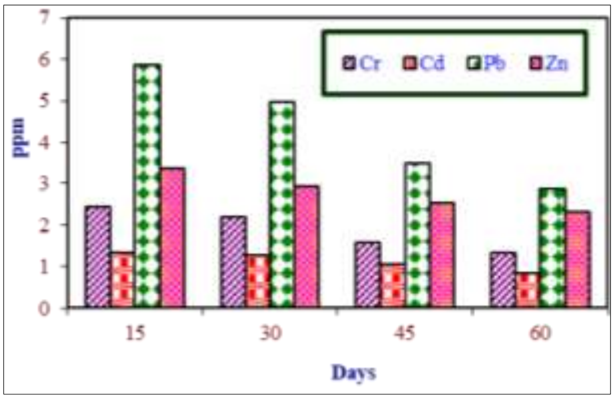

Fig 1: Reduction of heavy metal concentrations in pot A1 to A4.

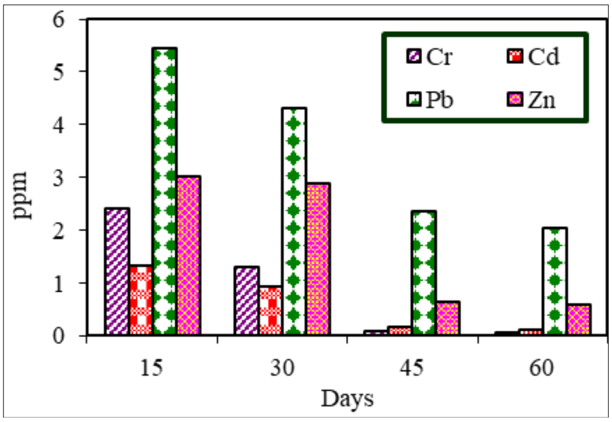

Fig 2: Reduction of heavy metal concentrations in pot B1 to B4.

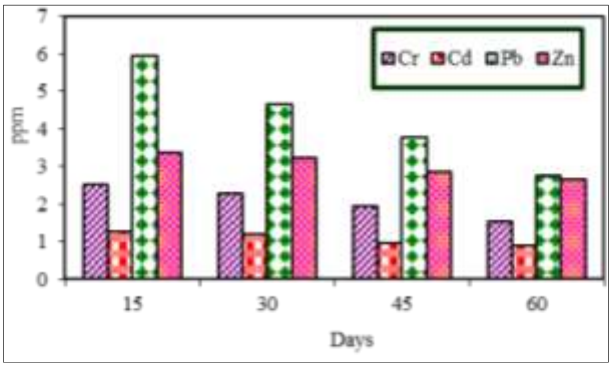

Fig 3: Reduction of heavy metal concentrations in pot C1 to C4.

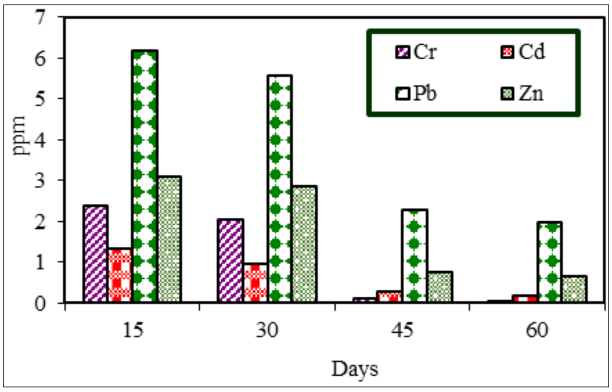

Fig 4: Reduction of heavy metal concentrations in pot D1 to D4.

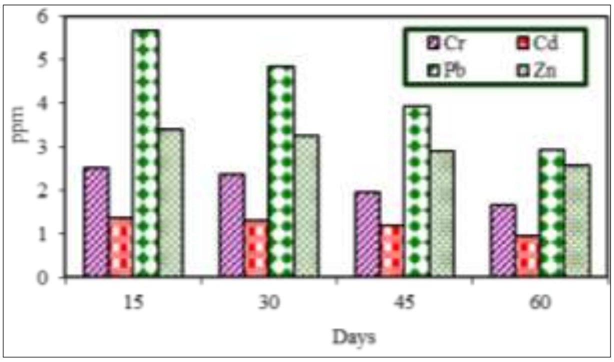

Fig 5: Reduction of heavy metal concentrations in pot E1 to E4.

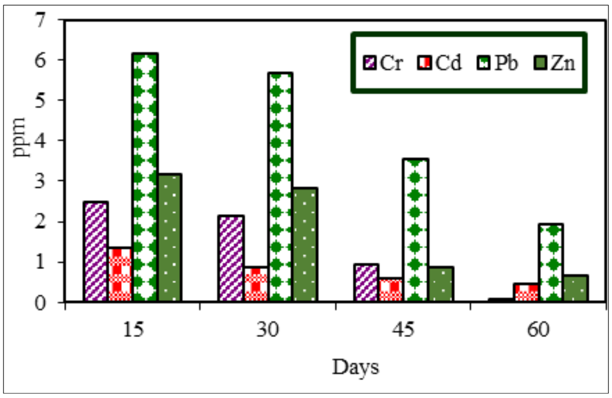

Fig 6: Reduction of heavy metal concentrations in pot F1 to F4.

4. Conclusion
The study found that when earthworm compost is mixed with garden soil, the amount of harmful metals in it gradually decreases. This makes it a good choice for growing healthy plants and getting rid of heavy metals in 15-60 days. However, other types of pots (A, C, and E) are not as good at removing heavy metals from polluted soil because they do it more slowly than the compost and soil mix. The study also found that a certain plant called *Croton sparsiflorus* is really good at taking in and getting rid of the toxic metals from soil that has been polluted by a paper mill. This is a big step towards finding a cheap and effective way to clean up polluted soil.

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