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Removal of Chlorinated Resin and Fatty Acids from Paper Mill wastewater through Constructed Wetland

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Abstract**—**This study evaluates the performance of horizontal subsurface flow constructed wetland (HSSF-CW) for the removal of chlorinated resin and fatty acids (RFAs) from pulp and paper mill wastewater. The dimensions of the treatment system were 3.5 m x 1.5 m x 0.28 m with surface area of 5.25 m^2, filled with fine sand and gravel. The cell was planted with an ornamental plant species *Canna indica*. The removal efficiency of chlorinated RFAs was in the range of 92-96% at the hydraulic retention time (HRT) of 5.9 days. Plant biomass and soil (sand and gravel) were analyzed for chlorinated RFAs content. No chlorinated RFAs were detected in plant biomass but detected in soil samples. Mass balance studies of chlorinated RFAs in HSSF-CW were also carried out.

Keywords**—** *Canna indica*, Chlorinated resin & fatty acids, Constructed wetland, Pulp and paper mill wastewater.

I. INTRODUCTION

THE pulp and paper industries depends mainly on the natural resources, i.e. water, fibrous raw material (e.g. wood, agro-residues), and fossil fuels for the production of paper. It generates a large quantity of wastewater with high organic load and chlorinated toxic compounds that may cause serious environmental impacts upon direct discharge to receiving waters. Wood extractives such as resin and fatty acids (RFAs) make a considerable contribution to aquatic toxicity even at very low concentration [1].

Among the various sections, bleaching accounts for the largest fraction of toxicity [2], [3]. Chlorobleaching (using Cl_2, ClO_2, or other chlorine compounds such as calcium or sodium hypochlorite) of wood pulp causes formation of chlorinated RFAs [4], [5]. The chlorinated RFAs found in bleach plant effluent originate from the fibrous raw material and their amount depends on the type of wood species, bleaching chemical charge applied and on the degree of washing of the unbleached pulp. RFAs occur naturally in plants & trees, mainly in softwoods. Their purpose is to protect wood against insect and microbial damage. Chlorinated RFAs are the major contributors to toxicity of pulp and paper mill effluents to aquatic organisms [6]. These are hydrophobic in nature and have been shown to bioaccumulate in aquatic organisms [7].

The conventional treatment systems in pulp and paper mills include primary and secondary aerobic biological treatment system. It has been observed that the secondary treated effluent still contains high level of toxic compounds. In order to protect wastewater receiving bodies and to meet increasingly stringent discharge limits, it is essential to reduce the toxicity of pulp and paper mills wastewater.

Constructed wetlands (CWs) are simple and low cost systems that can treat domestic and industrial wastewaters of different origins [8]. These systems utilize natural processes to improve the wastewater quality and mainly consist of shallow (usually less than 1 m deep) beds or channels, plants, substrate (soil, sand and gravels) and a variety of microorganisms [9]. CWs are capable to reduce contaminants including inorganic matter, organic matter, toxic compounds, metals and pathogens from different wastewaters. Reduction or removal of contaminants is accomplished by diverse treatment mechanisms including sedimentation, filtration, chemical precipitation, adsorption, microbial interactions and uptake or transformation by plants [10]. Incoming nutrients support the growth of plants, which convert the inorganic components into organic materials and form the basis of CW food chain [11]. Microorganism's play a main role in biochemical transformation of contaminants [12] and their capability in removing toxic organic compounds added to wetlands has been reported [13]-[15]. The efficiency of CWs to remove the contaminants from the wastewater mainly depends on the root zone interactions between soil, contaminants, plant roots and a variety of microorganisms. The soil is the main supporting material for plant and microbial growth. It was observed that fine gravel promotes greater growth of plants and therefore increases the amount of contaminants removal [16]. CWs are less expensive to operate and have low maintenance cost than traditional wastewater treatment systems. Additionally these systems have more aesthetic appearance than traditional wastewater treatment systems [17], [18].

The objective of this study is to evaluate the treatment efficiency of horizontal subsurface flow constructed wetland (HSSF-CW) in terms of chlorinated resin and fatty acids removal from pulp and paper mill wastewater. Additional objectives were to analyze the soil and plant material to study the existence of chlorinated resin and fatty acids.

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II. Materials and Methods

A. Chemicals

The resin and fatty acids used were obtained from the Aldrich Chemical Company (Milwaukee, USA) and Sigma Chemical Company (St. Louis, USA). Solvents i.e. methanol, diethyl ether and methyl tertiary butyl ether used were HPLC grade. Other reagents used for experimental studies were of analytical reagent grade. Standard solutions of resin and fatty acids were prepared in methanol : diethyl ether (10 : 90) solution.

B. Constructed wetland

For this research study, a pilot-scale horizontal subsurface flow constructed wetland cell was constructed with surface area 5.25 m^2. The dimensions of cell were 3.5 m in length, 1.5 m in width, and effective depth of 0.28 m (Fig. 1). The cell was sealed by a polyethylene liner to avoid leakage and the slope of the bottom of the cell was 1.4% of the length. Near the inlet and outlet zone of the cells a layer of coarse gravel (35 mm) was put to facilitate the distribution and collection of the wastewater respectively. The empty cell was filled with fine sand and gravel with particle size of 0-10 mm. The CW cell was equipped with inlet and outlet hydraulic structures. Wastewater inflow was through perforated PVC pipe, placed across the entire width at the upstream side of the CW cell so that wastewater flow had a uniform distribution across cell. The outlet structure of the cell was an orifice (5 cm diameter) at the bottom of the downstream end of the cell. The plant species i.e. Canna indica was collected from the near by region and planted in the cell by hand at an interval of 30 cm. At the time of plantation the average height and density of the plants were 15 cm and 7 m^{-2} respectively.

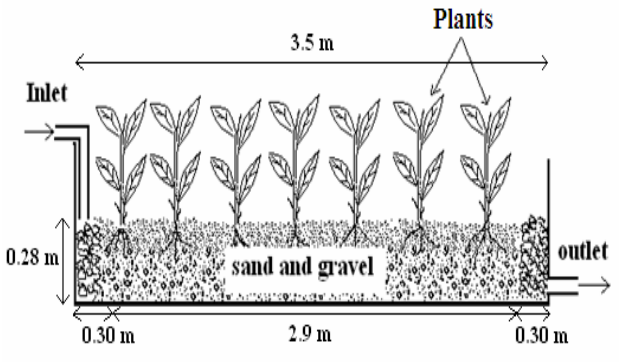

Fig. 1 Schematic diagram of the experimental horizontal subsurface flow constructed wetlands.

C. Wastewater loading

The HSSF-CW cell was loaded with water for five weeks prior to the application of the wastewater, for the growth of plant species. After that wastewater (after primary treatment) from the pulp and paper industry was loaded to the cell for 9 months (April 2010 to December 2010). For initial 7 months, some experiments were done to know the treatment efficiency of the HSSF-CW at different hydraulic retention times (HRT). The data of that was utilized for the optimization of HRT. In last 2 months (November-December), the inlet flow rate was maintained to 100 L/day, corresponding to hydraulic retention time (HRT) of 5.9 day calculated by the given below equation (1) [19]:

$$HRT = nLWd/Q \quad (1)$$

where n is the effective porosity of the media, L is the length of the cell, W is the width of the cell, d is the average depth of the bed and Q is the average flow of wastewater through the cell. The porosity of the substrate was determined at the beginning of the study and was estimated to be 0.27.

D. Water flow measurements and mass balance

Inlet water flow measurements were made daily. Inlet structure of the HSSF-CW cell was fitted with gate valve that enabled manual adjustment of the flows. The inlet water flows from CW was measured by using a measuring cylinder and a stop watch. The flow was adjusted to the desired value if deviated from set flow rate value. Outlet flow was measured twice in the every month by taking readings after every two hours during the 24 hours of the day and the mean was used to represent the outflow for the whole day.

The total loading of chlorinated RFAs to the HSSF-CW was calculated by multiplying the total wastewater feed during experimental period with the average concentration of total chlorinated RFAs. The total mass content of chlorinated RFAs accumulated in soil was calculated by multiplying the total weight of the HSSF-CW soil with the concentration of chlorinated RFAs in unit weight of soil.

E. Wastewater, soil and plant biomass analysis

Wastewater samples were collected at the inlet and the outlet of the CW system. Wastewater samples were analyzed immediately in the laboratory for pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), color, and chlorinated resin and fatty acids. CW plant biomass and soil samples (sand and gravels) were collected at the end of the experiment and analyzed for chlorinated resin and fatty acids. pH was determined by Toshniwal pH meter and color measurement was performed spectrometrically on a double beam spectrophotometer (Spekol 2000, Analytic Jena). For COD and BOD determination standard methods were employed [20].

Extraction of chlorinated RFAs from wastewater was achieved as suggested by Voss and Rapsomatiotis [21]. The inlet and outlet wastewaters (100 mL) were adjusted to pH 9 and extracted with equal volume of methyl tertiary butyl ether for 1 h. For the extraction of chlorinated RFAs from plant biomass and soil samples, 7 gm OD (Oven Dried) and 10 gm OD samples, respectively, were weighed in cellulose thimble and placed in a Soxhlet apparatus. The samples were then extracted for 24 h with hexane (250 mL). Following extraction, the solvent was then evaporated almost to dryness

by using vacuum rotatory evaporator. After extraction, all samples of chlorinated RFAs as methyl esters [22], were injected into the Optima-1-MS fused silica capillary column and were analyzed using gas chromatograph (Trace GC Ultra, Thermo Electron Corporation). The GC conditions are given in Table I. Retention times (RT) were determined using standard solutions of various chlorophenolics.

TABLE I.
GC CONDITIONS FOR THE ANALYSIS OF CHLORINATED RESIN AND FATTY ACIDS

Parameters	Conditions
Detector	FID
Carrier gas	Nitrogen
Sample injected (µL)	0.5
Injection mode	Split less
Column dimensions	30 m x 0.25 mm
Film thickness	0.25 µm
Injector and detector temperature (^{0}C)	300
Column temperature (^{0}C)	190 for 4 min
	190-210 at 1 ^{0}C min^{-1}
	210-230 at 2 ^{0}C min^{-1}
	230-250 at 3 ^{0}C min^{-1}
	250 for 15 min

III. RESULTS AND DISCUSSION

A. Wastewater analysis

The characteristics of the wastewater feed to the HSSF-CW during the experimental period (November 2010-December 2010) are shown in Table II. The values of RT of standards of chlorinated RFAs are given in Table III. The quantities of various chlorinated RFAs detected in the CW inlet and outlet wastewater are shown in Table IV. Two chlorinated fatty acids (cFA) i.e. 9,10-dichlorostearic acid and 9,10,12,13-tetrachlorostearic acid and two chlorinated resin acids (cRA) i.e. chlorodehydroabietic acid and 12,14-dichlorodehydroabietic acid were identified in the pulp and paper mill wastewater feed to the inlet of HSSF-CW. Among all RFAs, the concentration of 9,10-dichlorostearic acid was highest with average value of 39.56 µg L^{-1}. The results indicate that the total content of cFA was higher in comparison to cRA in the inlet feed wastewater. At HRT of 5.9 days, the chlorinated RFAs removal efficiency varied between 92-96% as shown in Fig. 2. The highest removal was observed in case of 9,10-dichlorostearic acid (95.68%) and lowest removal was observed in case of 9,10,12,13-tetrachlorostearic acid (92.12%).

Chlorinated RFAs are almost insoluble in water and may also be removed by a number of separation processes including adsorption/absorption when pass through the substrate of CW. The degree of sorption and its rate are dependent on the characteristics of both the organic matter and the solid surface (plants, substrate and litter) [23]. As organic in nature, chlorinated RFAs could be used as food for microorganisms e.g. *Pseudomonas* sp., *Sphingomonas* sp. [24], [25]. The microorganisms attached to the root zone of the plants also play a very important role in the degradation of organic matter i.e. conversion of organic carbon to carbon dioxide, for this purpose oxygen is supplied by the plant's root zone [26]. The extent of microbial degradation of organic compounds within a CW is also expected to strongly depend on the physico-chemical properties (such as water solubility, concentration) of the contaminant [27]. These compounds become soluble after some initial reductive dechlorination steps, and thus can be easily degraded by microbial interactions.

TABLE II
AVERAGE VALUES OF THE HSSF-CW INLET WASTEWATER PARAMETERS WITH STANDARD DEVIATION

Parameters	Inlet
pH	7.7 ± 0.17
COD (mg/L)	1011 ± 81.50
Color (Pt-Co unit)	2553 ± 237.69
BOD (mg/L)	248 ± 15.10

TABLE III.
RETENTION TIME (RT) OF CHLORINATED RFAS (AS METHYL ESTERS) IN OPTIMA-1-MS FUSED SILICA CAPILLARY COLUMN

S. No.	Name of the compound	RT (minutes)
1	9,10-Dichlorostearic acid[a]	29.74
2	Chlorodehydroabietic acid[b]	30.24
3	12,14-Dichlorodehydroabietic acid[b]	37.56
4	9,10,12,13-Tetrachlorostearic acid[a]	41.31

[a] chloro fatty acid, [b] chloro resin acid

TABLE IV
AVERAGE CONCENTRATIONS OF CHLORINATED RESIN AND FATTY ACIDS DETECTED IN THE INLET AND OUTLET WASTEWATER OF HSSF-CW

S. No.	Name of the compound	Inlet[a] (µg L^{-1})	Outlet[a] (µg L^{-1})
1	9,10-Dichlorostearic acid	39.56	1.71
2	Chlorodehydroabietic acid	19.62	1.38
3	12,14-Dichlorodehydroabietic acid	6.75	0.34
4	9,10,12,13-Tetrachlorostearic acid	17.90	1.41

[a] average of four readings

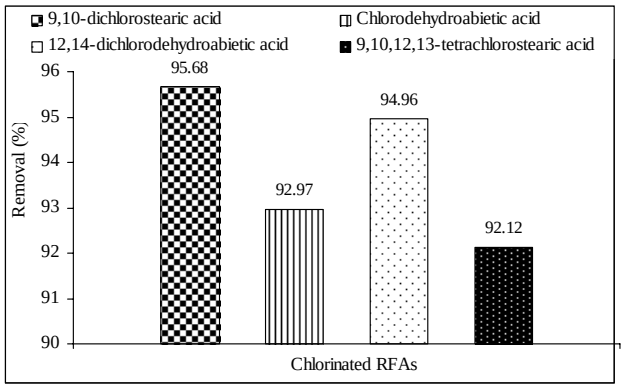

Fig. 2 Removal of chlorinated resin and fatty acids through HSSF-CW at HRT of 5.9 days

B. Plant and soil analysis

Plant biomass was analyzed for chlorinated RFAs content but no chlorinated RFAs were detected in the plant biomass of *Canna indica.* It means that plants do not play any direct role in the removal of chlorinated RFAs from pulp and paper mill wastewater but indirectly they may provide aerobic conditions to the microorganisms in the root zone for the degradation of chlorinated RFAs in CW. Uptake of any organic compounds into plant tissue is predominantly affected by the lipophilic nature, which can be characterized by the octanol water partition coefficient (Kow) [28]. Hydrophobic organic compounds with a log Kow > 4 are believed not to be significantly taken up through the plant cell membrane because of significant retention within the root epidermis [29].

The concentrations of chlorinated RFAs detected in HSSF-CW soil are shown in Table V. Among all chlorinated RFAs, the concentration of 9,10,12,13-tetrachlorostearic acid was highest with value of 122.94 µg OD Kg^{-1} of soil and the lowest concentration of chlorodehydroabietic acid with value of 18.55 µg OD Kg^{-1} of soil. The results indicate that the total content of cFA was higher in comparison to cRA in the HSSF-CW soil. The average inlet wastewater concentration of chlorodehydroabietic acid (19.62 µg L^{-1}) was more than the concentration of 12,14-dichlorodehydroabietic acid **(**6.75 µg L^{-1}) and 9,10,12,13-tetrachlorostearic acid (17.90 µg L^{-1}) but in soil it's concentration was lowest. It may be due to its high degradation rate in comparison to other high chlorine content RFAs in HSSF-CW soil. The high concentration of 9,10,12,13-tetrachlorostearic acid in soil shows its low biodegradation by microbes due to its high chlorine content and very low or no water solubility, resulting from binding to the soil matrix [30], [31]. The aerobic degradation rate is relatively slower for highly chlorinated compounds in comparison to low chlorinated compounds [32]. Adsorption of organic compounds to soil may result from the physical or chemical adhesion of molecules to the surfaces of solid bodies, or from partitioning of dissolved molecules between the aqueous phase and soil organic matter. The extent of sorption depends on the compound's hydrophobic nature as well as on the chemical structure, the organic carbon content, composition of soil organic matter [27] and the organic carbon partition coefficient (Koc) [33].

TABLE V
CHLORINATED RFAS DETECTED IN CW SOIL

S. No.	Name of the compound	Soil[a] (µg OD Kg^{-1})
1	9,10-Dichlorostearic acid	26.90
2	Chlorodehydroabietic acid	18.55
3	12,14-Dichlorodehydroabietic acid	32.71
4	9,10,12,13-Tetrachlorostearic acid	122.94

C. Mass balance of chlorinated RFAs

The total mass content of chlorinated RFAs loaded to HSSF-CW was 2131.79 mg. Out of this, 19.53% got accumulated in the soil, 2.48% came through outlet of the HSSF-CW and about 78% was degraded as shown in Fig. 3. Results show that large fraction of the total loading got degraded in HSSF-CW at HRT of 5.9 days. The kinetics of different physical (adsorption/absorption), chemical (oxidation/reduction) and biological processes (aerobic/anaerobic) decides the actual degradation or accumulation in the CW treatment system. In early stages of CW operation, sorption onto soil substrate is higher due to the high adsorption capacity of previously unexposed substrate [34]. When no sorption–desorption equilibrium is reached, the system acts as a sink for the contaminant. After attaining steady-state conditions, pollutants will still be retained by reversible sorption processes, but further net loss of pollutants will not occur. This retention may increase the pollutants residence time within the CW and support biodegradation by increasing exposure to degrading microorganisms [27], [35].

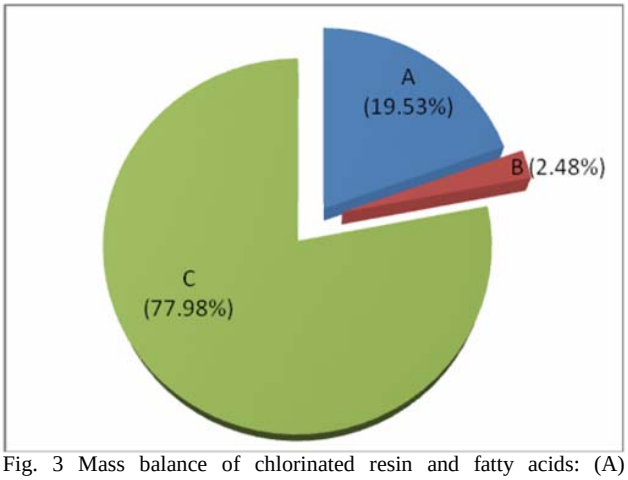

Fig. 3 Mass balance of chlorinated resin and fatty acids: (A) accumulated in soil, (B) in outlet wastewater and (C) degraded in HSSF-CW

IV. CONCLUSION

Horizontal subsurface flow constructed wetlands have good potential for the removal of chlorinated resin and fatty acids from pulp and paper mill wastewater. At HRT of 5.9 days, the removal efficiency varied between 92-96%. The highest removal was observed in case of 9,10-dichlorostearic acid (95.68%) and lowest for 9,10,12,13-tetrachlorostearic acid (92.12%). Plants do not play any direct role in the removal of chlorinated RFAs from pulp and paper mill wastewater but indirectly they may provide aerobic conditions to the microorganisms in the root zone for the degradation of chlorinated RFAs in CWs. The most probable mechanisms for the removal of chlorinated RFAs were adsorption/absorption and microbial degradation occurring in the root zone of the plants. *Canna indica* grew well in the HSSF-CW during the experimental period.

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