CELLULOSE CHEMISTRY AND TECHNOLOGY

REDUCTION OF POLLUTANTS IN PAPER MILL EFFLUENTS BY AQUATIC PLANTS

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Degradation of organics in waste water was attributed to the microorganisms living in and around the aquatic plant root system through a symbiotic relationship. This relation produced a synergistic effect, resulting in increased degradation rates and removal of organic chemicals from the waste water. Four tropical aquatic plants, namely *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia*, were employed to remove pollutants from a paper mill effluent having BOD and total solids in the ranges of 100-115 mg/L and 500-600 mg/L, respectively. Each of them has an optimum range of growth temperature and most of them cannot tolerate extreme temperatures. The maximum percentage values of BOD removal in a steady state by *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia* were of 82.45 (10-day retention time in September-October), 46.42 (6-day retention time in October-November), 44.34 (6-day retention time in October-November) and 51.31% (10-day retention time in October-November), respectively. The minimum BOD reductions by *Eichhornia* and *Salvinia* were of 22.86 and 22.15% in winter (November-December), and by *Lemna* and *Spirodela* were of 16.14 and 13.80% in summer (April-May), respectively. The maximum total solid mitigation occurred in the case of *Eichhornia*, *i.e.* of 49.8% (September-November), the minimum value being recorded in the case of *Spirodela*, i.e. of 3.7%, compared to all the other species (November-December). Of all studied aquatic plants, *Eichhornia* shows the maximum COD reduction (20.4%) and *Spirodela* – the minimum COD reduction. The highest reduction of total Kjeldahl's nitrogen, phosphorous and potassium removal occurred in September-November and May-June, the lowest being recorded in November-December. The maximum biomass yields for *Eichhornia*, *Spirodela*, *Lemna* and *Salvinia* were of 90.93-108.02, 44.53-45.99 and 56.21-58.99 T(dw)/ha/yr, respectively.

Keywords: paper mill effluent, aquatic plants, BOD, total solids, colour, biomass

INTRODUCTION

Pulp and paper industry is commonly known as an important contributor to the environmental impact, due to its large consumption of energy and chemicals, and also to the generation of effluents with high concentrations of suspended solids, organic load, as well as high toxicity.[1] The pulp bleaching sequences are especially problematic due to the presence of adsorbable organic halides (AOX), total organic chlorides (TOCl) and wood extractives in the effluents.[2] The deliberate discharge and accidental release of harmful chemical compounds into the environment have the potential to disrupt the structure and functioning of the natural ecosystems, while pulp bleaching uses large amounts of chlorine-based and other chemicals, causing several effluent-related problems in the pulp and paper industries.[3] The by-products of such chemicals are chlorinated organic substances, some of which are toxic, mutagenic, persistent, bio-accumulating, thus causing numerous harmful disturbances in biological systems.[4] In response to government and environmental protection groups, paper industries are currently changing practices to minimize the use of chlorine-based chemicals. Several methods are now available to mitigate BOD, colour and total solids, etc., like chemical precipitation, electro deposition, solvent extraction, ultra filtration, ion exchange, distillation and microfiltration, etc.[5]

However, they have no practical significance, due to their high costs. The economic solution for the required finishing treatment of the treated effluent generated by the paper industry is the use of aquatic plants. Crites and Mingee[5] evaluated that the capital cost for constructed wetland ranges from US$ 170-410 per m^3/day, compared to a typical cost range from US$ 800 to 1000 per m^3/day for a secondary treatment. Several studies were devoted to the utility of aquatic plants in the removal of pollutants, but most of them refer to domestic wastes and other wastes.[6-10] Very limited work is available on the treatment of paper mill wastes by aquatic plants.[9] For example, water hyacinth creates mosquito sites and prevents small fish from feeding on mosquito larvae.[11] Water hyacinth also causes a great deal of water loss through evaporation, with estimates of 3.7 and 5.3 times higher than normal evaporation.[12,13] A major part of the degradation treatment of organics is attributed to the microorganisms living on and around the plant root systems. Once microorganisms are established on aquatic plant roots, in most cases, they develop a symbiotic relationship with the higher plants, normally producing a synergistic effect, which increases the degradation rates and the removal of organic chemicals from the wastewater surrounding the plant root systems. Oxygen transfer by plants into the root zone plays a significant role in supporting the aerobic bacteria in the root zone and subsequent degradation of wastewater carbon.[10] For example, the O_2 transport through either pennywort or water hyacinth plants was found to be responsible for 90% of BOD removal, while the remaining 10% of BOD removal was due to O_2 transport directly from the air.[10]

Starting from such considerations, a study was conducted to mitigate BOD, COD, total solids, total Kjeldahl's nitrogen, P and K in a paper mill effluent using agro-waste as a raw material, conducted from primary clarifier by four different aquatic plants: *Eichhornia, Lemna, Spirodela* and *Salvinia.*

EXPERIMENTAL

General scheme of experiments

Experiments were planned to observe the removal of pollutants from the treated effluent of a paper mill by aquatic plants. To this end, the (treated) effluent samples were drawn from the ETP of a medium-sized kraft paper mill using agro-waste, with no chemical recovery. Four different species of locally growing aquatic plants (weeds/macrophytes) were employed, namely *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia*. For each loading rate (hydraulic retention time (HRT), *viz*. 2, 4, 6, 8 and 10 days) and weed, an experimental basin or pond was used. Simultaneously, removals were also observed in blank ponds (one for each HRT) not seeded with any kind of plant. The studies were carried out at laboratory-scale macrophyte ponds consisting of 3 L plastic basins, of which 2 L volumes were used for the hydraulic loading. For obtaining a 2-day retention time, the 2 L volume from the basin was replaced completely by fresh flow, for 2 days, but in a few uniform batches. The hydraulic loading of each basin with the effluent sample was carried out twice a day, to create an effect of continuous-flow operations of the ponds. Before loading, the required volume, taken out of each basin pond, was used as a sample, to test the various parameters.

BOD removals and pH were measured by collecting and analyzing samples every alternate day. The removal of other pollutants was observed once in the beginning and once towards the end of the run. Before effectively starting basin loading, the aquatic plants to be seeded were thoroughly acclimatised with the wastewater. Loading of the basins in a run was continued until a steady state of BOD removals was reached, that is, when a near constant value of BOD removal was obtained. This was considered to be the end of the run. However, the run was continued for a few more days beyond the steady-state time. This steady-state value gave the percentage removal of BOD in the given basin. This scheme of experimental runs was repeated at various times of the year, to observe the seasonal effect on the performance of different plants. Each time before starting a fresh series of runs, the characterization of the wastewater was carried out, as to the most important parameters. For allowing adequate space for the growth of the plants, an about 50% area was kept free of plants in the experimental basins.

Localization and climatic conditions

The studies were carried out in the Department of Paper Technology, IIT Roorkee, Saharanpur Campus, Saharanpur, in cold winter months and summer months, moderated by the effect of the Shivaliks hills. The rainfall, on an average of 1050 mm, occurs mainly between July and September. The temperature ranges from 2.5 to 24 ºC in winter, and from 23 to 45 ºC in summer, respectively.

Source of sampling collection and sample storage

For each run series, 250 L from the required sample of the treated effluent from a small kraft paper mill was collected in 10 and 20 L plastic containers, stored in a cooling cabinet at 4-10 °C, then wholly analyzed.

Tests and analytical procedure

Every time, a fresh batch of effluent samples was collected from the paper mill, in the beginning and end of the run, the following parameters being measured: total solids (IS 3025: Part 15: 1984 Methods of Sampling and Test (physical and chemical) for the water and wastewater – Total residue), dissolved solids (IS 3025: Part 16: 1984 Methods of Sampling and Test (physical and chemical) for water and wastewater – Filterable residue), suspended solids (IS 3025: Part 17: 1984 Methods of Sampling and Test (physical and chemical) for water and wastewater – Non-filterable residue (total suspended solids), chemical oxygen demand (IS 3025: Part 58: 2006 Methods of Sampling and Test (physical and chemical) for water and wastewater – COD), biochemical oxygen demand (IS 3025: Part 44: 1993 Methods of Sampling and Test (physical and chemical) for water and wastewater – BOD), total Kjeldahl nitrogen (IS 3025: Part 34: 1988 Methods of Sampling and Test (physical and chemical) for water and wastewater – Nitrogen), as per Bureau of Indian Standards.

Potassium and phosphorus concentrations were measured by atomic absorption spectroscopy (AAS).

RESULTS AND DISCUSSION

The characteristics of the effluents collected from an agro-based mill are presented in Table 1. The treated effluents from the effluent treatment plant from a paper mill had BOD and TS values ranging from 100 to 115 mg/L and from 500 to 660 mg/L, respectively.

Removal of solids and COD

The maximum and minimum removal values of total solids, dissolved solids, suspended solids and COD in a steady state, by *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia*, are presented in Table 2. The maximum removal of total solids, dissolved solids and suspended solids is observed in the case of *Eichhornia*, between September-October (10-day retention time), while minimum removal is observed in the case of *Spirodela*, between May-June (6-day retention time). Out of *Spirodela* and *Lemna*, *Lemna* contributes to a higher removal of solids. *Salvinia* shows the best results between October-November, when the temperature is moderate (10-day retention time). Most of the plants show the maximum removal of solids in September, October and November. The worst results are obtained in November-December and May-June. The maximum removal of total solids, dissolved solids and suspended solids is observed for the blank run (having no plants), between May-June *i.e*. 20.5, 22.0 and 15.3%, respectively, in a steady state. The variations in the removal of different solids by the same plant may be due to the different climatic conditions and loading rates, while the variations in the removal attained with different plants in the same run series are possibly due to the different capabilities of various plants to remove the pollutants.

Table 1
Characteristics of effluent samples obtained from effluent treatment plant of a paper mill

Sl. No.	Parameter	Value
1	BOD, mg/L	100-115
2	COD, mg/L	320-370
3	TS (total solids), mg/L	500-660
4	SS (suspended solids), mg/L	110-150
5	DS (dissolved solids), mg/L	390-510
6	Colour, PCU	210-230
7	pH	7.20-7.28
8	TKN (total Kjeldahl nitrogen)	12-15
9	Phosphorus, mg/L	5-7
10	Potassium, mg/L	4-5

Table 2 also reveals that *Eichhornia* attains the maximum COD removal between September-October, the minimum COD removal efficiency being obtained in the *Spirodela* ponds in May-June. Of the two species of duckweed, *i.e*. *Lemna* and *Spirodela*, *Lemna* gives a higher COD removal. In the case of the blank run, the maximum removal of COD is of 32.6% in May-June, while the minimum COD removal observed is of only 5.8%. Run-to-run differences in the percentage removal of COD for a given plant may be due to different environmental conditions and loading rates.

Table 2
Removal of total solids, dissolved solids, suspended solids and COD in the effluent, compared to blank in steady state

Aquatic plant	Maximum removal observed in steady state					Minimum removal observed in steady state				
	TS, %	DS, %	SS, %	COD	Season	TS, %	DS,%	SS,%	COD	Season
Blank	20.5	22.0	15.3	5.8	May-Jun.	3.6	4.0	2.1	5.8	Nov.-Dec.
Eichhornia	48.1	49.8	42.0	20.4	Sept.-Oct.	13.4	13.5	13.0	20.4	Nov.-Dec.
Lemna	24.6	25.5	21.3	12.5	Oct.-Nov.	7.0	7.3	5.9	12.5	May-Jun.
Spirodela	26.4	27.5	22.6	7.5	Oct.-Nov.	3.7	3.7	3.1	7.5	Nov.-Dec.
Salvinia	29.8	30.6	26.8	19.6	Oct.-Nov.	12.4	12.8	11.2	19.6	Nov.-Dec.

Removal of BOD, nitrogen, phosphorus and potassium, and biomass yield

As the run proceeds, a steady state is reached when BOD removal becomes nearly constant. The value of the steady-state BOD removal attained is specific to different runs. Typical values of BOD removal for the *Eichhornia* run series 1 are listed in Table 3. In all cases, BOD removal increases with the time of the run, but at a decreasing rate. This trend leads to the attainment of a constant value, referred to as steady-state value, after about 10-12 days. The steady-state percentage of BOD removed and the corresponding time vary with the type of aquatic plant and with the other experimental conditions. The maximum BOD removal in a steady state is of 82.45% in the case of *Eichhornia*, while in the case of blank, the maximum BOD reduction in a steady state is of 38.80%. In *Lemna* experiments, the maximum percentage of BOD removal (in a steady state) is attained at a hydraulic retention time of 6 and 10 days. The maximum BOD retention reached is of 46.42%. In *Salvinia* runs, the maximum BOD removal on attainment of a steady state is observed after 10 days, while the maximum percentage of BOD removal is of 51.31%.

Table 3
Removal of BOD in steady state and time required to reach steady state for *Eichhornia*

HRT series, days	BOD removed in steady state, %	Time to reach steady state, days	Applied BOD loading, kg/ha/day
2	48.25	18	65.12
4	69.40	16	32.56
6	70.73	16	21.71
8	72.25	14	16.28
10	73.67	12	13.02

Table 4
Maximum removal of BOD in steady state and time required to reach steady state by *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia*

Aquatic plant	HRT series, days	Maximum steady-state percentage of BOD removed	Periods
Blank	8	38.80	May-Jun.
Eichhornia	10	82.45	Sept.-Oct.
Lemna	6	46.42	Oct.-Nov.
Spirodela	6	44.34	Oct.-Nov.
Salvinia	10	51.31	Sept.-Oct.

Table 5
Minimum removal of BOD in steady state and time required to reach steady state by *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia*

Aquatic plant	HRT series, days	Minimum steady-state percentage of BOD removed	Period
Blank	2	5.92	Nov.-Dec.
Eichhornia	2	22.86	Nov.-Dec.
Lemna	2	16.14	Apr.-May
Spirodela	2	13.18	Apr.-May
Salvinia	2	22.15	Nov.-Dec.

Table 6
Maximum and minimum removal of total Kjeldahl N, P and K by *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia* in a paper mill effluent, in steady state

Aquatic plant	Maximum removal in steady state, %			Minimum removal in steady state, %		
	Total Kjeldahl N	P	K	Total Kjeldahl N	P	K
Blank	27.5	18.0	14.6	4.1	3.9	2.0
Eichhornia	64.8	45.5	41.5	18.0	11.8	12.5
Lemna	36.1	24.1	22.5	10.0	6.0	4.9
Spirodela	32.8	22.4	21.4	5.8	4.0	2.4
Salvinia	41.6	29.1	27.7	16.4	9.8	10.0

Table 7
Biomass yield of *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia*

Aquatic plant	Biomass yield, tonnes (dry mass)/ha/yr	
	Maximum	Minimum
Eichhornia	108.02	90.93
Lemna	58.99	56.21
Spirodela	45.99	44.53
Salvinia	65.50	63.45

Likewise, *Spirodella* shows a maximum percentage of BOD removal (44.34%) in a steady state.

The maximum removal of BOD (82.45%) in a steady state occurs, in the case of *Eichhornia*, in September-October, values of 46.42 and 44.34% being recorded for *Lemna* and *Spirodela*, respectively, in October-November, and of 51.31% for *Salvinia*, in September-October (Table 4). The minimum BOD removal for *Eichhornia*, *Lemna*, *Spirodela* and *Salvinia* is of 22.86 (November-December), 16.14 (April-May), 13.18 (April-May) and 22.15% (November-December), respectively (Table 5).

Table 6 shows that the minimum removal of total Kjeldahl N, P and K occurs in the months of November-December and May-June, while the maximum removal occurs in October-December, November-December, May-June and September-October, as depending upon the plant species.

The observation was made that, among different weeds, the biomass yield in *Eichhornia* runs is maximum, lying between 90.93 and 108.02 T (dw)/ha/yr, while the *Spirodela*, *Lemna* and *Salvinia* yields are lower, *viz*. from 44.53 to 45.99, 56.21 to 58.99 and 63.45 to 66.50 T (dw)/ha/yr, respectively (Table 7).

CONCLUSIONS

Aquatic plants, namely *Eichhornia*, *Spirodela*, *Lemna* and *Salvinia*, *Eichhornia*, show the maximum reduction in total solids, BOD, COD and total Kjeldahl N, P and K of paper mill effluents in different seasons. Therefore, these aquatic plants may be grown in a lagoon, forming different beds for each plant, to remove maximum pollutants throughout the year. This process may be adopted for small-scale pulp and paper industry, where the option of chemical recovery is not feasible.

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