Effectiveness of *Azolla caroliniana* for treating paper mill effluent

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ABSTRACT

This study was focused on removal of various parameters in a paper mill effluent using the method called bioremediation by *Azolla Caroliniana*. The experimental investigations have been carried out by using *Azolla Caroliniana* for conducted the sorption study with various dilution ratio (2, 4, 6, 8, and 10), pH (3, 4, 5, 6, 7, 8 and 9) and biomass (200, 400, 600, 800 and 1000 g). The results showed that the maximum percentage removal of various parameters in a paper mill effluent was obtained at the optimum dilution ratio of 6, pH of 8 and biomass 800 g. The results of this study indicated that the maximum removal percentage of TDS, BOD and COD in a paper mill effluent was found to be 82.3 %, 88.6 % and 79.1 % respectively. The experimental values of paper mill effluent were simulated with the model for its reproducibility. This study concluded from the experimental and model studies that bioremediation by *Azolla Caroliniana* was effectively used for removing various parameters in a paper mill effluent.

KEY WORDS: *Azolla caroliniana*, contaminants, removal.

1. INTRODUCTION

The surface water and groundwater is contaminated due to various industrial effluent when it is not discharged properly (Sivakumar Durairaj, 2013c; Sivakumar, 2011), the contaminants in the paper mill effluent is affecting the environment highly, because it generates a considerable volume of wastewater containing high concentrations of organic matter, BOD, COD, TDS, TSS, phenols, sulphate, calcium, magnesium, sodium and colour. The quantity of paper mill effluent generation from various plants of paper mills in India place 20th rank in the world. The generated effluent from paper mill may not dispose on any medium with proper treatment leading to contamination on medium (Sivakumar, 2011). The soil medium particularly was affected more and in turn affects the growth of plants. Hence, the effluent characteristics must be controlled to an acceptable level before being discharged to the environment.

The suggested treatment methods for the removal of pollutants from various industries are adsorption (Sivakumar and Shankar, 2012; Sivakumar, 2013b; Sivakumar, 2014c; Sivakumar, 2014f; Sivakumar, 2014g; Sivakumar, 2014k; Shankar, 2014a), ion exchange, chemical precipitation, bioremediation (Shankar, 2014b; Sivakumar, 2014d; Sivakumar, 2014e; Sivakumar and Nouri, 2015), constructed wetland (Sivakumar, 2015; Sivakumar, 2013a; Sivakumar, 2014h; Ingole and Bhole, 2003; Soltan and Rashed, 2003) and electro-dialysis (Sivakumar, 2014i; Sivakumar, 2014j) etc. Presently bioremediation method using aquatic and terrestrial plants is consider more for treating various industrial wastewater, because of more advantages than any other conventional treatment methods include: low cost; high efficiency; minimization of chemical and biological sludge. There are several studies conducted on germination of plants stated that growth rate was diminished when used raw paper mill effluent, whereas the growth was improved when used paper mill effluent in diluted conditions.

In the present study, aquatic plant grown in constructed wetland is used for removing contaminants from paper mill effluent (Turker, 2014). Constructed wetlands are artificial wastewater treatment systems consisting of shallow ponds or containers, which have been planted with aquatic plants and which rely upon physical, chemical, microbial and biological processes to treat wastewater. The treatment systems of constructed wetlands are similar to that of ecological systems found in natural environment. In order to do the design and construction of treatment wetlands and the processes by which constructed wetlands can remove pollutants, it is necessary to have a basic understanding of how natural wetlands work. Thus, this study was conducted to remove contaminants from paper mill effluent using constructed wetland by aquatic macrophytes *Azolla Caroliniana*. Also, the experimental values of paper mill effluent were simulated with the model and the same were compared for reproducibility

2. MATERIALS AND METHODS

2.1. Collection of *Azolla Caroliniana*: The aquatic macrophytes *Azolla Caroliniana* were collected from the nearby pond, Chennai, which had no connection with any industry wastewater discharge points. The collected aquatic plants were washed with distilled water and weighed. Further, the aquatic macrophytes were initially subject to stabilization in small plastic tanks containing well water and the same were preserved for 15 days period. In addition, these plastic tanks were filled with gravel and wetland soil (collected from the local pond) up to five inches in height and maintained at normal temperature.

2.2. Collection of Waste water Sample: For the present study, the wastewater sample was collected from paper mill effluent, Karur, with the help of air tight sterilized bottles. Samples were taken to the Environmental Engineering Laboratory for analyzing the various contaminants from paper mill effluent. The analysis was carried out for different parameters as per the standard procedure stipulated by APHA, AWWA, and WEF (2005). The characteristics of paper mill effluent are presented in Table 1. The various parameters in the effluent from paper mill are varied in wide range depending on process details and working behaviors in the production step of industry.

Table.1.Physico-Chemical characteristics of Paper Mill Effluent

Characteristics	Values
pH	8.4
EC	5.63µS/cm
TDS	2384 mg/l
BOD	1840 mg/l
COD	4560 mg/l
Calcium	358 mg/l
Chloride	542 mg/l
Alkalinity	356 mg/l
Sulphate	473 mg/l

2.3. Sorption Experiments: For the experiments, the *Azolla Caroliniana*, which maintained in the plastic tanks were collected, cleaned and introduced in the experimental tanks (constructed wetland). The experimental tanks also a plastic tank as similar to plastic tank for preserving the *Azolla Caroliniana*. These experimental tanks were filled with paper mill effleunt of 1000 ml. Triplicate of each experimental setup was maintained. In order to reduce the contaminant in a paper mill effluent, the experimental setup (constructed wetland) was examined for a period of 7 days by 1 day interval by using aquatic macrophytes *Azolla Caroliniana* and conducted the sorption study with various dilution ratio (2, 4, 6, 8, and 10), pH (3, 4, 5, 6, 7, 8 and 9) and biomass (200, 400, 600, 800 and 1000 g). The dilution ratio was used such that 1 part of wastewater with various numbers of part of well water, thus, the ratio of 2, 4, 6, 8, and 10 represents these parts of well water mixed with raw wastewater. The pH was adjusted by using 0.1 M of NaOH and 0.1 M of HCl. The concentrations of the various parameters in a paper mill effluent before and after treatment with *Azolla Caroliniana* were determined as per the standard procedure stipulated by APHA, AWWA, 2005. The percent removals of various parameters by *Azolla Caroliniana* were calculated by using the following formula:

$$\text{Percenrage Reduction} = \frac{(C_1 - C_2)}{C_1} x100 \qquad (1)$$

in which C_1 is concentration of the various parameters before treatment with *Azolla Caroliniana* and C_2 is concentration of the various parameters after treatment with *Azolla Caroliniana*.

3. RESULTS AND DISCUSSIONS

In this study, the different process parameters like dilution ratio, pH, biomass against the contact time were selected for removing TDS, BOD and COD in a paper mill effluent rather than other parameters using constructed wetland by an aquatic plant *Azolla Caroliniana*.

3.1. Effect of Dilution Ratio: Fig.1 indicates the experimental investigations conducted by changing the dilution ratio from 2 to 10 (wastewater 1: well water 2) with an increment of 2 using *Azolla Caroliniana.* The percentage reduction of TDS, BOD and COD in a paper mill effluent using *Azolla Caroliniana* against the different dilution ratios (Since, day 6 is the optimum contact time found from the study, the results obtained on the day 6 was presented and the results obtained by the day 1, 2, 3, 4, 5 and 7 were not presented in this study) with the contact time of 6 days, biomass of 200 g, and pH of 5 was presented in Fig.1.

The results revealed that the percentage removal for TDS, BOD and COD in a paper mill effluent is low at the beginning and then increases with dilution ratio. This is because; diluted concentration of various parameters in a paper mill effluent was sorbed easily by the *Azolla Caroliniana* than high concentration paper mill effluent. In other words, the active sites in the *Azolla Caroliniana* could not be sorbed the various parameters in a paper mill effluent, since, there is very strong bondage between the various parameters in a paper mill effluent at an elevated concentration and in later stage sorbent sites of *Azolla Caroliniana* could be effectively utilized. Up to dilution ratio of 6, the sorption of various parameters in a paper mill effluent by *Azolla Caroliniana* increased steadily. For the dilution ratio 8 and 10, the percentage removal results showed resembles of the results obtained for the dilution ratio 6. It is more likely that an even sufficient contact time available, the various parameters TDS, BOD and COD in a paper mill effluent was sorbed on the active sites of *Azolla Caroliniana* completely for the dilution ratio 6, and hence, there was no difference in sorption on dilution ratio 8 and 10.

Similarly, the sorption of TDS, BOD and COD in a paper mill effluent on day 7, was similar to that of day 6, indicated that the maximum removal of various parameters in a paper mill effluent was completed on day 6 itself. Hence, the optimum dilution ratio found in this study for the maximum removal of various parameters in a paper mill effluent is 6. Further, the maximum sorption removal percentage of TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* against dilution ratio of 6 was found to be 72.6 %, 76.6 % and 67.4 % respectively (Fig.1).

3.2. Effect of pH: Fig.2 represents the experimental investigations conducted by changing the pH from 3 to 9 with an increment of 1 using *Azolla Caroliniana.* The percentage reduction of TDS, BOD and COD in a paper mill effluent using *Azolla Caroliniana* against pH (Since, day 6 is the optimum contact time found from the study, the results obtained on the day 6 was presented and the results obtained by the day 1, 2, 3, 4, 5 and 7 were not presented in this study) with a contact time of 6 days, biomass of 200 g, and an optimum dilution ratio of 6 was presented in Fig.2.

The results revealed that the percentage removal of TDS, BOD and COD in a paper mill effluent is low at the beginning and then high with pH increases. This is because, in a slight alkaline to alkaline condition, the TDS, BOD and COD in a paper mill effluent is coupled with various cations and anions present in the paper mill effluent, can be easily sorbed by *Azolla Caroliniana* than in acidic condition. Up to pH of 8, the absorption of TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* increased steadily and for the pH 9, the percentage removal results showed the resembles of the results obtained for the pH 8. Hence, the optimum pH found in this study for the maximum removal of TDS, BOD and COD in a paper mill effluent is 8.

The absorption of TDS, BOD and COD in a paper mill effluent on day 7 and for the pH 9, the removal percentage of TDS, BOD and COD in a paper mill effluent was not significant even the contact time and pH were higher, it is more likely that the sorption was completed for the contact time day 6 and for the pH 8, leading to lower specific uptake for the pH of 9 and for the contact time of 7 days. Thus, the maximum sorption removal percentage of TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* against the optimum pH of 8 was found to be 76.2 %, 83.2 % and 73.8 % respectively (Fig.2).

3.3. Effect of Azolla Caroliniana Biomass: Fig.3 indicates the experimental investigations conducted by changing the *Azolla Caroliniana* biomass from 200 g to 1000 g with an increment of 200 g. The percentage reduction of TDS, BOD and COD in a paper mill effluent using *Azolla Caroliniana* against biomass (Since, day 6 is the optimum contact time found from the study, the results obtained on the day 6 was presented and the results obtained by the day 1, 2, 3, 4, 5 and 7 were not presented in this study) with a contact time of 6 days, optimum dilution ratio of 6, and optimum pH of 8.

The results revealed that the percentage removal of TDS, BOD and COD in a paper mill effluent is low by *Azolla Caroliniana* at the low biomass, and then increases with increased biomass. This is because, the supplied low biomass is completely utilized for the removal of TDS, BOD and COD in a paper mill effluent, but still there was portion of TDS, BOD and COD in a paper mill effluent available for the less biomass condition, which may be sorbed by supplied higher *Azolla Caroliniana* biomass. Up to biomass of 800 g, the sorption of TDS, BOD and COD in a paper mill effluent increased steadily and for the biomass of 1000 g, the percentage removal results showed the resembles of the results obtained biomass of 800 g. It is because, the maximum removal could be achieved for the biomass of 800 g and hence, there was no change is difference of removal percentage for the *Azolla Caroliniana* biomass of 1000 g.

Similarly, there was no difference in removal of TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* for the day 7. Hence, the optimum biomass found in this study, for the maximum removal of TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* is 800 g. Further, the maximum sorption removal percentage of TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* against the biomass of 800 g was found to be 82.3 %, 88.6 % and 79.1 % respectively (Fig.4).

From the Figs. 1 to 3, it may be observed that the order of maximum removal of various parameters in a paper mill effluent is BOD > TDS > COD for all selected process parameters of dilution ratio, pH and biomass.

3.4. Model Development: In this study, the experimental data are fitted with first order kinetic model. The first order model is given by

$$-\frac{dC}{dt} = k_1 C \qquad (2)$$

on integration the Eqn.2 becomes

$$\ln\left(\frac{C}{C_0}\right) = -k_1 t \qquad (3)$$

where C_0 is the initial concentration of TDS, BOD and COD in mg/l, C is the concentration of TDS, BOD and COD in mg/l at time 't', 't' is degradation time, days and 'k_1' is the first order rate constant, days^{-1}. The negative sign indicates as time increases the rate constant decreases.

The first order rate constant was calculated from the slope of the straight line by least square fit (Fig.4). The rate constant k_1 and R^2 values for the parameters TDS, BOD and COD in a paper mill effluent (Fig.4) by *Azolla Caroliniana* were obtained at an optimum dilution ratio of 6, biomass of 800 g and pH of 8 are presented in Table 2.

Table.2.The kinetic parameter and the regression coefficient for the parameters TDS, BOD and COD in a paper mill effluent by *Azolla Caroliniana* at at an optimum dilution ratio of 6, biomass of 800 g and pH of 8

Parameters	Regression Equation	k_1	R^2
TDS, mg/l	y = -0.2656x	0.2656	0.9727
BOD, mg/l	y = -0.3173x	0.3173	0.9538
COD, mg/l	y = -0.2410x	0.2410	0.9624

From the Table 2, it may be observed that the R^2 value for TDS, BOD and COD respectively was 0.9727, 0.9538 and 0.9624. This R^2 value indicates that the ability of the first order kinetic model in describing the kinetics of the present work. In other words, the model is fitted well with the experimental data for TDS, BOD and COD parameters. Thus, from the kinetic studies, it was found that the reduction of TDS, BOD and COD parameters in a paper mill effluent by *Azolla Caroliniana* at an optimum dilution ratio of 6, biomass of 800 g and pH of 8 follows the first order kinetic model.

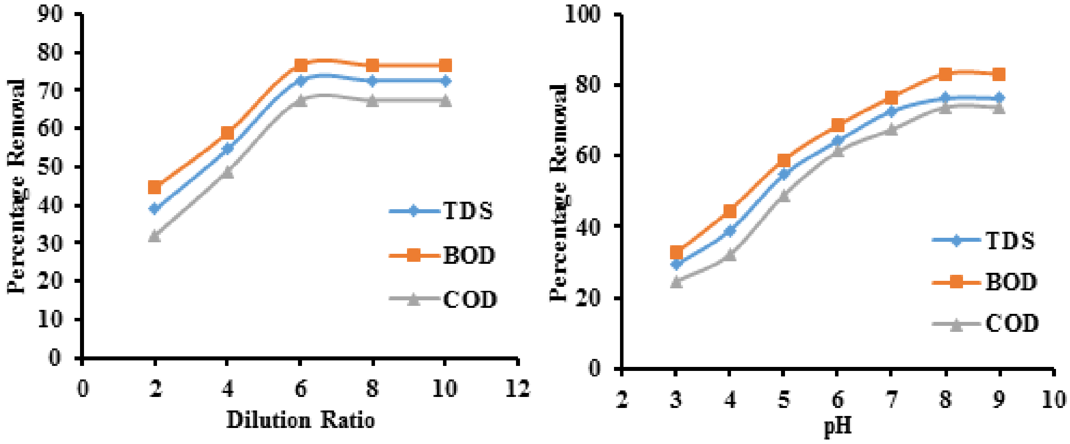

Fig. Effect of 1) Dilution Ratio 2) pH on Removal of TDS, BOD and COD from paper mill effluent

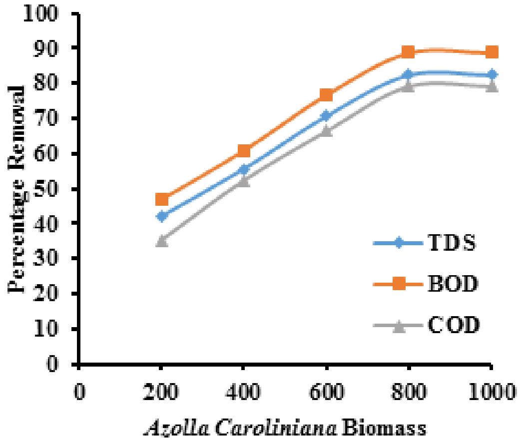

Fig.3.Effect of *Azolla Caroliniana* Biomass on Removal of TDS, BOD and COD from paper mill effluent

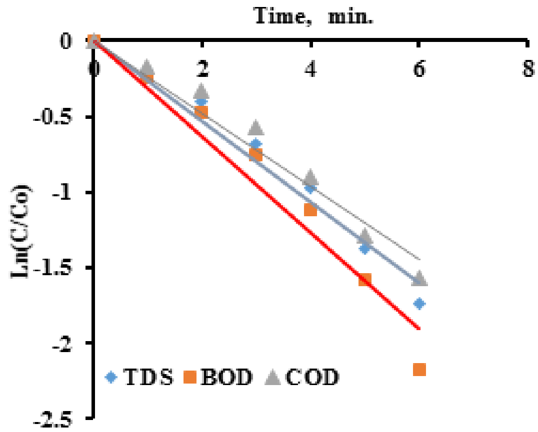

Fig.4.First order Kinetic Model for the parameters TDS, BOD and COD in a dairy industry effluent at an optimum dilution ratio of 6, biomass of 800g and Ph of 8

4. CONCLUSION

In the present study, the experiments were conducted to find out the suitability of *Azolla Caroliniana* for removing various parameters in a paper mill effluent. The ability of *Azolla Caroliniana* for removing TDS, BOD and COD in a paper mill effluent was done with various dilution ratio, biomass and pH against the optimum contact time of 6 days. The maximum percentage reduction of various parameters in a paper mill effluent by *Azolla Caroliniana* were obtained at an optimum dilution ratio of 6, biomass of 800 g and pH of 8. The results of this study indicated that the maximum removal percentage of TDS, BOD and COD in a paper mill effluent was found to be 82.3 %, 88.6 % and 79.1 % respectively. This study concluded that the aquatic macropyte *Azolla Caroliniana* might be used as sorbents for removing TDS, BOD and COD along with other parameters in a paper mill effluent. Also, the experimental values of paper mill effluent were validated with model and the model study concluded that the developed model is having reproducing capacity of the experimental data obtained from the paper mill effluent.

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