Treatment of Paper Mill Effluent via Calcium-Alginate Immobilized Beads of Anatomical Components of Eichhornia Crassipes a Study on Phosphate and Nitrogen Adsorption Kinetics and Optimization Process

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***Abstract*—Treating Pulp and Paper mill effluent using Eichhornia crassipes proves to be an excellent way to remove total phosphate and total nitrogen due to its high nutrient adsorption ability and hence, rendering it in improving the quality of water. Also, it is economical, easily available, effective and efficient. Paper mill effluent was treated by using immobilized biosorbents: Leaf, Root and Petiole of Eichhornia crassipes. In the standard solutions around 99.57% of total inorganic phosphate, 96.02 % ammonia, 65.44 % nitrate and 85.33% of nitrite was removed under the optimized condition of 1% bead dosage, bead density of 15, 6 hours of time period, at pH 7 and at room temperature using sodium alginate-calcium chloride immobilized beads of Root, leaf and petiole of Eichhornia crassipes. In the paper mill effluent, about 81.60% of total inorganic phosphate, 93.46 % total organic phosphate, 100 % filterable phosphate, 79.75 % ammonia, 20.28 % nitrate and 91.66 % of nitrite was removed. This study has shown that the biosorbent has adsorbed the nutrients from the effluent onto its surface. Also, it reduces the hardness, TDS, BOD, COD and chloride from the waste water. Hence, it has shown that Eichhornia crassipes is an effective biosorbent in treating Paper mill effluent. Eichhornia crassipes has also reduced the microbial load gradually after its exposure. FTIR characterization of the treated effluent and the biosorbent inferred the total elimination of sulfur compounds and nitrogen compounds from the effluent.**

***Index Terms*—Adsorption, Biosorption, E.crassipes, Immobilization, Leaf, Nitrogen, Petiole, Phosphate, Root.**

I. INTRODUCTION

National economic growth heavily depending upon industrialization, which severely damages our ecological system [7]. As the 6^{th} largest polluting industry globally, pulp and paper mills extensively use resources like fresh water, energy and timber which are already in demand to sustain life on earth [7][9][14]. The industry also has detrimental influence on water, atmosphere, biodiversity, forest, agriculture and human health [7]. It releases highly toxic and recalcitrant such as dioxins and furans, chlorinated compounds, unsaturated fatty acids, sulfur compounds, resin acids, lignocellulosic compounds, hydrocarbons, tannins, etc[5][9][14].

The paper mill industry employs various treatment processes such as sedimentation, froth flotation, filtration, coagulation, electrolysis, precipitation, activated sludge process, composting, anaerobic process, ozonation, adsorption, chemical oxidation, catalysis, phytoremediation, etc[7][9][10][14]. Integration of these processes fetches higher efficiency in the treatment, but physicochemical treatments are expensive and leaves recalcitrant hazardous byproducts [4]. Despite being time consuming, biological methods go gentle on our environment, more natural and are cost effective [9]. Industrial water can be converted into usable water with the help of plants [10]. Heavy metals from soil and water can be phytoextracted by using specific plants [3][1]. Eichhornia crassipes is an excellent invasive free-floating plant used in phytoremediation of industrial waste water. Their capability of phytovolatization, rhizofiltration, Phyto assimilation, Phyto immobilization, Phyto restoration, phytoextraction, Phyto stimulation, phytodegradation, phytoaccumulation, phytohydroregulation makes them a wonderful broad-spectrum remediation tool for diversified contaminants [4][20][1]. Apart from the lab-scale study, E.crassipes is also used at large-scale in treating wastewaters [16]. The plant is used for heavy metal removal and in the reduction of COD, BOD, TDS, hardness, etc[11][20]. Depending on the innumerable functional abilities of its various plant parts, the study is focusing on evaluating the adsorption capacity of leaf, petiole and root part of the dried plant in treating paper mill effluent. The objective is to use pulverized E.crassipes as biosorbent to increase the surface area of adsorption. To enhance the application and recovery of the biosorbent during the effluent treatment, the biosorbents were immobilized using calcium-alginate.

II. MATERIALS AND METHODS

A. Collection of Pulp and Paper Mill Effluent Sample

Effluent samples from various Pulp and Paper mill were collected and transported to the lab. The samples were stored in the temperature between 3°C to 5°C in cold room to prevent biological activity. The collected samples were pooled together for further study.

B. Analysis of physicochemical parameters of the effluent sample

The raw pulp and paper mill effluent sample was checked for its physicochemical properties like colour, pH, Hardness, Chloride, Biochemical Oxygen Demand (BOD), Dissolved oxygen (DO), Chemical oxygen demand (COD), Total dissolved solids (TDS), Total suspended solids (TSS), Total solids (TS), Ammonia, Nitrate, Nitrite, Organic phosphate, Inorganic phosphate and Filterable phosphate [2][6][18].

C. Collection of Eichhornia crassipes

Fresh and healthy samples of Eichhornia crassipes were collected from Valankulam, Coimbatore district. The samples were washed several times in running water to remove the dirt, small creatures and particulate matter bound to it. The samples were dissected and only petiole, lamina and roots were taken for further studies leaving the flowers and stalks. The separated samples were sun-dried for a period of 10 to 12 days and were powdered separately by mechanical shearing. The samples were then sieved using a mesh strainer (sift) with a particle size of 500-850µm and stored for further experiment.

D. Immobilization of powdered biomasses using Sodium Alginate-Calcium chloride method

About 1.8 grams of Sodium alginate (suitable for bead formation) powder was added to 50ml of agitated distilled water along with powdered biomass of roots, lamina and petiole separately in two different concentrations of 0.5% and 1.0%. 0.2M Calcium chloride was prepared and the sodium alginate-biosorbent solution was added drop by drop into it to immobilize the biosorbent beads separately. Only freshly prepared beads of the different biosorbent with different concentrations were used for all the experiments throughout the study [8].

E. Preparation of nitrogen and phosphorus solutions to evaluate the biosorption efficacy of the biosorbents

Stock solutions of phosphate, ammonia, nitrate and nitrite were prepared by dissolving known quantity of potassium dihydrogen phosphate, ammonium chloride, potassium nitrate and sodium nitrite in distilled water. Conical flasks were thoroughly cleaned and dried, stock solutions were diluted with known quantity of distilled water such that each working standard solution contains 10 mg PO_4^{3-} /ml, 10µg of NH_3/ml, 443 µg of NO_3^-/ml & 5µg of NO_2^- /ml respectively which is used for the adsorption study of the biosorbents. This has to be freshly prepared and used for each and every experiment [6][18].

F. Parameter optimization to improve the efficacy of the biosorbents

Immobilized biosorbents (lamina, petiole, root) were taken separately and introduced into the standard solutions under the following conditions: Bead dosage of 0.5% & 1.0%; Bead density of 5, 10 & 15; Time period of 2h, 4h & 6h; pH of 7 & 8 and Room temperature of 25-28˚C to optimize and identify the suitable parameter for effective removal of nutrients. 20 ml of working standard solutions were taken in a series of conical flasks and the optimization study was carried out. The reduction in phosphate, ammonia, nitrate and nitrite was observed.

G. Treatment of Pooled Pulp and Paper Effluent under Optimized Conditions

Under optimized conditions, 20ml of pooled pulp & paper effluent was taken in a series of conical flasks. All the three biosorbents of bead dosage 1% & bead density of 15 were taken separately and added to the effluent sample. The pH of the effluent was adjusted to 7 & 8 and the beads were exposed for a time period of 2h, 4h and 6h.

H. Bench-scale study to evaluate the biosorption efficacy in the treatment of paper mill effluent

About 500 ml of pooled effluent was taken. To it the most effective immobilized biosorbents - Leaf and Root were taken under optimized scale at a concentration of 1%, 7 pH, bead density of 375 counts, in room temperature and a time period of 6h in static condition and added. The beads were taken out immediately after 6h for further studies. The dry weight of the immobilized biosorbents before and after treatment of the effluent was estimated. The Physicochemical parameters of the biologically treated effluent were analyzed. Serial dilution of paper mill effluent was done at the 0h, 2h, 4h and 6h of bead treatment and the dilutions of 10^{-5} and 10^{-6} at each time interval were plated on nutrient agar media by using spread plate method and the reduction in colonies were observed in CFU/ml.

I. Characterization of immobilized biosorbents of water hyacinth and its subsequent nutrient removal from Pooled pulp and paper effluent-Fourier - Transform Infrared Spectroscopic Analysis (FTIR)

FTIR characterization of the untreated and treated effluent was done along with the characterization of potent biosorbent. In order to determine the changes in the functional groups after the effluent was treated and to determine the functional groups responsible for the nutrient uptake by the biosorbent FTIR was used. It was done for the effluent before and after treatment and also for the immobilized beads of Root before and after treatment. FTIR was done at wave number of 4000-800 cm $^{-1}$.

III. RESULTS AND DISCUSSION

Immobilized beads of three biosorbents i.e., Lamina, Root and Petiole of Eichhornia crassipes were used to determine the adsorption efficiency of each in reducing the mineral content. The initial parameters of pooled effluent were analyzed every time before the experiments. Optimization of the biosorbent to improve the adsorption efficiency were done under pH (7 and 8), bead density (5, 10, 15), time of action (2hours, 4hours and 6 hours), bead concentration (0.5% and 1%) and temperature of room (25℃ - 28℃) in working standard solutions and pooled effluent. By comparing the results of both working standard solutions and pooled effluent, the optimized condition with higher efficiency and biosorbent with higher adsorbing potential were determined and bench-scale study was done.

A. Effect of Time:

The nutrient removal efficiency was analyzed at different time intervals of 2h, 4h and 6h. As the time period increases, the reduction in nutrient level increases, but only up to a certain limit. This is because saturation level is attained and no more nutrient can be adsorbed to the functional groups present on the surface of the biosorbent. Maximum nutrient reduction was obtained when the immobilized beads were exposed to the time period of 6 hours, although only a gradual increase in the removal of nutrients occurred from 4 hours to 6 hours. Retention time or contact period is a significant parameter as it determines the saturation time at which the rate of adsorption equals the rate of desorption. This is beneficial in industrial scale where the achievement of maximum adsorption in minimal contact period is expected [17].

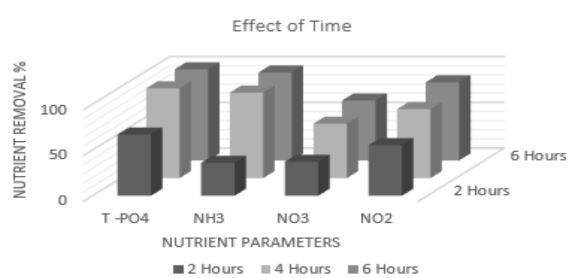

Figure I: Bar graph showing the effect of Time in Nutrient Removal Activity

In effect of time, after 6 hours of treatment the reduction in nutrients was found to be 99.57 % of total inorganic phosphate, 96.02% ammonia, 65.44% nitrate and 85.33% of nitrite.

B. Effect of pH:

The reduction efficiency of the biosorbents varied with the change in pH. Nutrient reduction was found to be maximum in the pH of 8 when estimated using standard solution, but maximum reduction occurred in the pH of 7 when estimation was done using the pooled effluent sample itself, only nitrate and nitrite showed higher reduction at 8 pH than at 7 pH. This is attributed to the interference factors present and variations in the composition of the raw effluent compared to the standard solution. The adsorption efficiency is a pH and functional group dependent process [22].

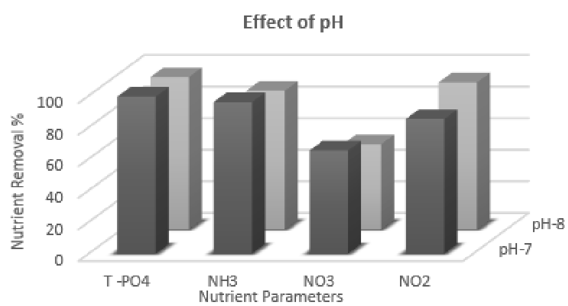

Figure II: Bar graph showing the effect of pH in Nutrient Removal (Root) Activity

In effect of pH, the reduction in nutrient level obtained was 99.5% of total inorganic phosphate, 96.02 % ammonia, 65.44 % nitrate and 85.33% of nitrite at pH 7.

C. Effect of Temperature:

Eichhornia crassipes, being a free-floating aquatic plant lives in the surface of water bodies in the temperature range of 25-28˚C. So, its biomolecule functional groups and their structure remain stable at such temperature. So, it is better to use them in that particular temperature range for a stable adsorption of minerals to the biosorbents throughout the process [19].

D. Effect of Biosorbent concentration:

The biosorbent concentration under study were 0.5% and 1%. The increase in bead dosage may increase the nutrient reduction efficacy, but after a level, saturation may occur. By analyzing the biosorbent concentration, the optimum bead dosage for effective nutrient removal was found to be 1%. Reference [17] implies the same that adsorption efficiency increases with the increase in dosage.

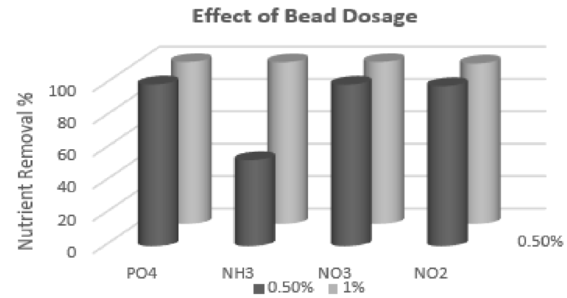

Figure III: Bar graph showing the effect of Bead Dosage in Nutrient Removal (Root) Activity

In effect of bead dosage, the maximum reduction in nutrients occurred at 1% bead concentration and was found to be 99.57% of total inorganic phosphate, 96.02 % ammonia, 65.44 % nitrate and 85.33% of nitrite.

E. Effect of Bead density:

Bead density is the number of beads incorporated in the fixed amount (20 ml) of sample. Maximum reduction in nutrient level occurred when the number of beads increased. Therefore, bead density of 15 showed maximum reduction in mineral level. This is due to the increase in the attachment sites as the number of beads have increased.

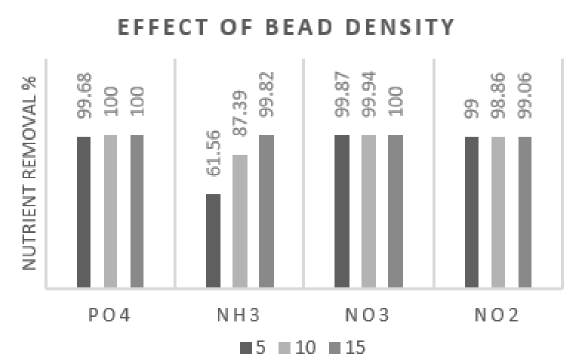

Figure IV: Bar graph showing the effect of Bead Density in Nutrient Removal (Root) Activity

In effect of bead density of 15, the nutrient reduction was found to be 99.57% of total inorganic phosphate, 96.02 % ammonia, 65.44 % nitrate and 85.33% of nitrite.

F. Effect of Lamina, Root and Petiole biosorbent:
The different plant parts have varied functions such as carrying out photosynthesis, anchoring, adsorbing nutrients and water, acting as storage organs, transpiration, transportation etc. Depending on their functions, the chemical composition of the plant parts varies. This variation in plant parts showed varied nutrient adsorption capacity.

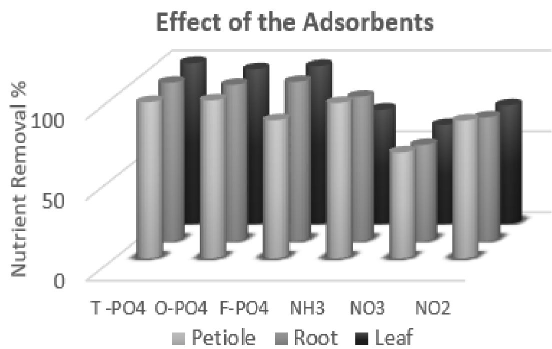

Figure V: Bar graph showing the effect of Different biosorbents on Removal of Nutrients

The capacity of the biosorbents - Lamina, Root and Petiole were determined under appropriate conditions. Maximum reduction of minerals was found in the effluent when it was treated with that of the biosorbents- Root and Leaf. Leaf showed maximum nutrient adsorption of phosphate source (Total inorganic phosphate, total organic phosphate and filterable phosphate) while Root showed maximum nutrient adsorption of nitrogen source (Ammonia, Nitrate, Nitrite). And Petiole showed moderate adsorption of both nitrogen and phosphate sources.

G. Removal Percentage of Phosphate and Nitrogen in working standards

The removal of Phosphate and Nitrogen content by the resultant biosorbent in both working standard solution under optimized parameter is shown in table below.

H. Removal of Phosphates in paper mill effluent
Phosphate level was found to be reduced in the effluent sample on treating it with immobilized biosorbents. Maximum reduction in phosphate was found to occur when treated with immobilized beads of concentration 1%, with bead density of 15 at pH 7 and after 6 hours of its exposure at room temperature. The phosphate level was estimated in three forms, i.e., Total inorganic phosphate, total organic phosphate and filterable phosphate. Its estimation was done before and after treatment. The level of nutrient reduction in case of phosphate was found to be 99.5% of total inorganic phosphate.

I. Removal of Nitrogen in paper mill effluent
The level of Ammoniacal nitrogen, Nitrate nitrogen and nitrite nitrogen was estimated before and after treatment. Maximum reduction in nitrogen was found to occur when treated with immobilized beads of concentration 1% with bead density of 15 at pH 7 & 8 and after 6 hours of its exposure at room temperature. The level of nutrient reduction in case of nitrogen was found to be 96.02% ammonia, 65.44 % nitrate and 85.33% of nitrite.

J. Analysis of physicochemical parameters of the Pooled Pulp and Paper Effluent-Bench-Scale study
The pooled effluent was found to possess the pH of 7.3. After the treatment the pH was found to be 7.45, this could be due to the reduction in the nutrient content or due to the change in the other parameters. This result falls within the TNPCB and CPCB standard requirements. Similar increase in pH from 6.25 to 6.63 was observed on treating kitchen wastewater with Eichhornia crassipes [15]

Table I: Maximum Reduction in Nutrient Levels on treatment under optimum conditions

S.No	Parameter	Value before treatment	Value after treatment	Removal percentage
1.	Total Inorganic Phosphate	32.89 (mg/ml)	0.14 (mg/ml) (leaf)	99.57 %
2.	Ammonical Nitrogen	201.67 (µg/ml)	8.01 (µg/ml) (petiole)	96.02 %
3.	Nitrate-Nitrogen	153.11 (µg/ml)	52.91 (µg/ml) (petiole)	65.44 %
4.	Nitrite-Nitrogen	1.5 (µg/ml)	0.22 (µg/ml) (petiole)	85.33 %

Table II: Effect of Immobilized Biosorbents in Treatment of Pooled Pulp and Paper mill effluent [Removal of Phosphate (7 & 8 pH)]

Adsorbent	T -PO_4 (mg/ml)		O-PO_4 (mg/ml)		F-PO_4 (mg/ml)		Time of Action
	7	8	7	8	7	8	
Petiole	14.81	10.90	10.90	25.56	7.23	4.54	2 Hours
Root	10.90	20.67	7.96	10.90	1.12	5.52	
Leaf	13.34	21.89	6.50	20.67	0.14	9.18	
Petiole	2.10	3.56	5.76	15.78	5.27	0.87	4 Hours
Root	1.61	13.34	2.59	8.45	1.85	2.1	
Leaf	0.63	15.78	2.10	8.45	1.61	7.96	
Petiole	1.12	1.12	0.63	13.34	4.05	0.14	6 Hours
Root	0.63	10.90	0.87	3.56	0.39	1.61	
Leaf	0.14	6.01	1.12	1.12	0.63	6.50	

* T-PO_4 = Total Inorganic phosphate; O-PO_4 = Organic phosphate; F-PO_4 = Filterable phosphate

Table III: Effect of Immobilized Biosorbents in Treatment of Pooled Pulp and Paper mill effluent [Removal of Nitrogen- Comparison table (7&8 pH)]

Adsorbent	NH_3 (µg/ml)		NO_3 (µg/ml)		NO_2 (µg/ml)		Time of Action
	7	8	7	8	7	8	
Petiole	164.02	104.84	113.26	101.87	0.85	0.65	2 Hours
Root	129.05	83.32	107.56	118.95	0.81	0.63	
Leaf	137.12	94.08	96.18	141.72	0.67	0.69	
Petiole	13.39	53.74	73.40	65.43	0.68	0.12	4 Hours
Root	26.84	48.36	67.71	62.02	0.37	0.10	
Leaf	59.11	64.49	62.02	96.18	0.42	0.40	
Petiole	8.01	51.05	153.006	54.05	0.22	0.10	6 Hours
Root	21.46	24.15	152.99	56.32	0.35	0.10	
Leaf	59.11	61.80	152.995	92.19	0.4	0.30	

* NH_3- Ammonia; NO_3 – Nitrate; NO_2 – Nitrite

The BOD value before the treatment was found to be 1888mg / L and after treatment was found to be 820mg/L. Wastewater on treatment using Eichhornia crassipes, the BOD gets reduced to 89% which was about 71% reduction in BOD in the constructed wetland [11]. The COD value before treatment was found to be 7424 mg/L and that after treatment and found to be 7480 mg/L.
The hardness value before treatment was found to be 3800 mg/L and that after treatment was found to be reduced to 3140 mg/L (17.36% reduction). Reference [15] says, about 50% of hardness was reduced in waste water on treating with Eichhornia crassipes. The chloride value before treatment was found to be 2399.26 mg/L and 2010 mg/L after treatment. Reference [16] implies, wastewater on treatment using Eichhornia crassipes percentage reduction in chloride was observed to be 12.24 %. Reference [10][20] also implies that live E.crassipes can also be able to reduce 75% of total nitrogen and 75% of total phosphorus and 39.1% of TDS.

K. Removal of Phosphate and Nitrogen:
The average phosphate and nitrogen reduction percentage of the pooled effluent during pilot scale study was found to be 91.68 % and 63.89 % respectively. Reference [20] infers, the total phosphate and total nitrogen reduction percentage was found to be 65 % for both on treating domestic wastewater with live Eichhornia crassipes.

L. Weight of the biosorbent before and after biosorption treatment:
The increase in dry weight of the beads after the treatment indicates that the beads have adsorbed the minerals from the effluent. That indicates that the

functional groups of minerals bound to the functional groups of the biosorbent.

Reference [12] goes hand-in hand with the results obtained by that the increase in dry weight is due to the presence of various recalcitrant like organochlorine, sulfonated and nitrogenous compounds, PO_4^{3-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe in the pulp and paper mill effluent needed to achieve the maximum vegetative. Reference [21] suggests these results are in the agreement of the phytoremediation experiment and yields maximum result when the effluent is diluted.

M. Difference in Microbial population during the biosorption process:

A gradual decrease in the number of colonies was observed from the initial plate till the 6th hour plate. The reduction in microbial population might be due to the entrapment of microbes in the immobilized bead or due to the antimicrobial effect of Eichhornia crassipes.

Table IV: Physicochemical Parameters of Paper mill effluent treatment by using biosorbents along with TNPCB & CPCB standard limits:

S.No	Parameters	Values before treatment	Values after treatment	TNPCB limits	CPCB limits
1.	pH value	7.0	7.45	5.5 to 9.0	5.5 - 9.0
2.	BOD (3 days at 27°C)- (mg/L)	1888	820	30	30
3.	COD (mg/L)	7424	7480	250	250
4.	TDS (inorganic) mg/L	5500	2280	2100	2100
5.	TSS, mg/L	3000	3000	100	100
6.	Ammoniacal Nitrogen (as N), (mg/L)	201.67	8.01	50	50
7.	Nitrate Nitrogen (mg/L)	153.11	54.05	10	10
8.	Dissolved Phosphates (as P) (mg/L)	28	0.39	5	5
9.	Hardness, mg/L	3800	3140	300	300
10.	Chloride (as Cl) (mg/L)	2399.26	2010	1000	1000

Table V: Removal of Phosphate and Nitrogen- Bench-Scale

S.No	Parameter	Value before treatment	Value after treatment	Removal percentage
1.	Total Inorganic Phosphate	96.44 (mg/ml)	17.74 (mg/ml)	81.60 %
2.	Total Organic Phosphate	35.82 (mg/ml)	2.34 (mg/ml)	93.46 %
3.	Filterable Phosphate	0.63 (mg/ml)	0.0 (mg/ml)	100 %
4.	Ammoniacal Nitrogen	68.80 (µg/ml)	13.93 (µg/ml)	79.75 %
5.	Nitrate-Nitrogen	42.09 (µg/ml)	33.55 (µg/ml)	20.28 %
6.	Nitrite-Nitrogen	0.6 (µg/ml)	0.05 (µg/ml)	91.66 %

Table VI: Dried Weight of the biosorbent before and after biosorption treatment:

Biosorbent	Dried weight of beads before treatment (gm)	Dried weight of beads after treatment (gm)	Difference in Dry weight (gm)
Leaf	0.068	0.074	0.006
Root	0.069	0.079	0.010

Table VII: Enumeration of bacterial population during adsorption process

Biosorbents	Time Duration							
	Initial		2 Hours		4 Hours		6 Hours	
Effluent dilution factor	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}	10^{-5}	10^{-6}
Immobilized Root and Leaf beads	TNTC	TNTC	94	26	68	22	46	15

N. Characterization Using Fourier - Transform Infrared Spectroscopic Analysis (FTIR):

FTIR analysis of Raw Paper Mill Effluent:

In the untreated effluent, the peak 3387.00cm^{-1} is N-H stretch that indicates the presence of nitrogenous compounds and 1897.95cm^{-1} C-H bend indicates the presence of aromatic rings, which are predominant in paper mill effluent. Absorptions found at the peak of 2229.71cm^{-1} indicates the presence of Nitrile group that shows a weak C Ξ N bond. The strong peak at 2059.98cm^{-1} N=C=S stretching of isothiocyanates. Similarly, the absorptions at the peaks of 1975.11 cm $^{-1}$, 1365.60 cm $^{-1}$ and 1311.59 cm $^{-1}$ indicates the presence of allene which forms a medium C=C=C stretching, sulfonamide which forms a strong S=O stretching and sulfone which also forms a strong S=O stretching respectively.

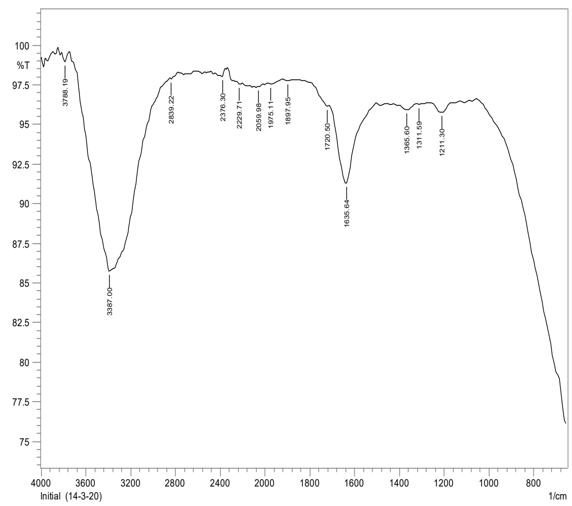

Figure VI: FTIR analysis Of Untreated Effluent

FTIR analysis of treated Paper Mill Effluent:

The post-treatment spectrum showed the change of peak from 3387.00cm^{-1} to 3379.29cm^{-1}. 2777.50cm^{-1} weak band shows the presence of O-H stretching alcohols and emergence of strong peak 1211.30cm^{-1} C-O stretching, vinyl ether might be indicating the leaching out of plant compound into the effluent which can be eliminated or minimized by reducing the biosorption retention time from 6h to 4h. The disappearance of nitrile and sulfur-oxygen peaks proves that the biosorbent removed such toxins out of the paper mill effluent [13].

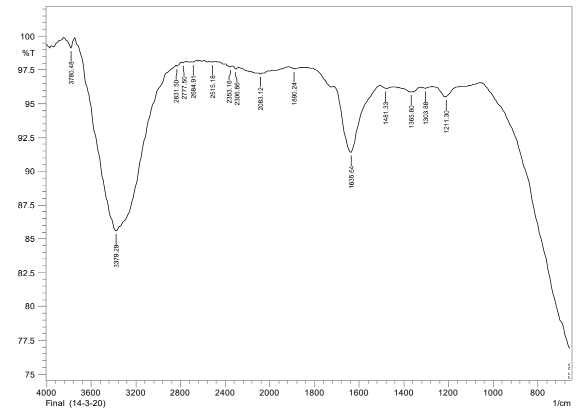

Figure VII: FTIR analysis of Treated Effluent

FTIR of unused Immobilized bead of Root biosorbent:

The absorptions found at the peaks of 3657cm-1 and 3000cm-1 shows the free active site of hydroxyl and carboxylic acid groups. The peak of 1797.66cm-1 and 1666.50cm-1 indicates the presence of strong carbonyl groups, 2245.14cm-1 indicating isocyanates and 2075.41cm-1 indicating isothiocyanates peak as active site on the surface before exposing it into the raw paper mill effluent.

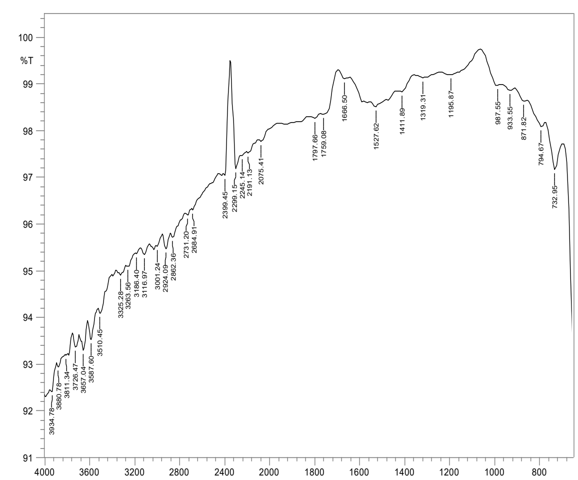

Figure VIII: FTIR analysis of Immobilized Root biosorbent before treatment:

FTIR of Spent Immobilized bead of Root biosorbent:

The absorbance peaks between 3649cm^{-1} and 3294cm^{-1} indicates broad spectrum of carboxylic acid groups.

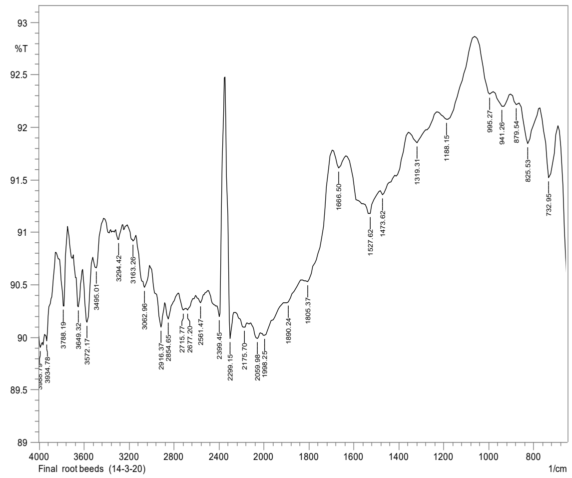

Figure IX: FTIR analysis of Immobilized Root biosorbent after treatment

In the case of biosorbent which was observed after the treatment, the absorbance peaks of 1998.25 cm^{-1}, 1890.24 cm^{-1}, 1805.37 cm^{-1} indicated the presence of an aromatic compound by a weak C-H bending and 1666.50 cm^{-1} signifies a conjugated carbonyl compound C=O respectively. The peaks 879.54 cm^{-1} and 825.53 cm^{-1} indicated the presence of a 1,2,4 trisubstituted compound and a 1,4 disubstituted (or) 1,2,3,4 tetrasubstituted compound respectively formed by a strong C-H bending. Similarly, the absorbance peak 732.95 cm^{-1} indicated the presence of mono-substituted compound formed by a strong C-H bending. These functional groups were not found in the biosorbents that were not subjected to treatment. This indicates that chemical changes have occurred in the immobilized root beads when used for treatment of effluent. The peaks 1527.62cm-1 and 1319.31cm-1 indicates the nitro compounds N-O stretch and sufones S=O stretch respectively which were seen in the effluent is now present in the root biosorbent proving the effective biosorption [13].

IV. CONCLUSION

This study hence proves the biosorbent of water hyacinth to be very efficient and faster in the removal of minerals from the pulp and paper mill effluent. It is cost effective and time saving. Instead of immobilization of the biosorbent, the biosorbent can be chopped and packed in a nylon mesh to treat the effluent in small scale mills. After treatment, they can be used as either soil amendment or fuel pellets depending on its toxicity assessment.

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