MITIGATION OF HAZARDOUS NATURE OF TREATED TANNERY EFFLUENT USING BIOADSORBENTS

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Abstract

Biosorption is an emerging eco-friendly and feasible technique for the utilization of available plant based waste materials to remediate contaminated industrial wastewater. In the present study, 50% (v/v) concentration (selected based on previous studies) of tannery effluent was bio-treated with shade dried, powdered leaves of Polyalthia longifolia cv pendula Sonn. and Azadirachta indica Linn. After the bio-treatment, the physico-chemical parameters were analysed and compared with the parameters of untreated tannery effluent. The result showed noticeable changes in the physico-chemical parameters of bio-treated effluent over the untreated tannery effluent and metal and non-metal ions of bio-treated tannery effluent improved much with Polyalthia leaf powder as bioadsorbent. Interestingly, the result showed that the leaves of Polyalthia recorded the highest mitigation of hazardous nature of untreated tannery effluent.

Keywords: *Tannery effluent, bio-adsorbents, mitigation, physico-chemical parameters.*

Introduction

Leather industry is one of the major foreign exchange earners of India, accounting for 2.5% of the global leather-related trade. This industry provides employment to 2.5 million people (CII report, 2006). Though tanneries are revenue and job generating sector, the objectionable constituents in large amounts in the effluents are suspended solids, chlorides, sulphides, chromium, tannins and organic wastes (Buljan *et al.*, UNIDO, 2000). Further both industrialization and urbanization have substantially enhanced the degradation of aquatic environments through the discharge of industrial wastewater in to the surrounding open environment. The tannery effluent contains higher amounts of total hardness, total dissolved solids, BOD, COD, calcium, magnesium, sodium, chloride, potassium and sulphate (Mariappan *et al.,* 2001). The danger associated with toxic ions present in the effluent, its phytotoxicity to crops and food chain contamination has become matters of environmental concern (Raniperumal and Singaram, 1995). Conventional methods of toxic ions removal from wastewater include chemical precipitation, ion exchange, coagulation and oxidation particularly adsorption. However, these methods are often cost prohibitive having inadequate efficiency at low metal concentrations (Kapoor and Viraraghavan, 1995). Some of these methods generate toxic sludge, the disposal of which is an additional burden. These constraints have caused the search for alternative methods that would efficient for metal sequestering. Metal sequestering properties of biomass provide a basis for a new approach to remove ions from industrial wastes (Volesky, 1990). The sorbents of biological origin help in the removal of toxic ions from dilute aqueous solutions (Nilanjana Das *et al.*,. 2008). This paper presents the findings of a study on the use of leaf powder of *Polyalthia longifolia* cv pendula Sonn and *Azadirachta indica* Linn for their mitigation efficiency of toxic ions present in the tannery effluent.

Materials and Methods

Effluent And its Physico-chemical Parameters

The untreated tannery effluent collected from Senkulam Lake, in the outskirt of Dindigul-Batlagundu highway, Dindigul, Dindigul District, where a Common Effluent Treatment Plant

(CETP) is functioning. From a pilot study, it was found that 50% (v/v) is the maximum optimal concentration of the effluent for irrigation of crop plants. Hence, the physico-chemical parameters of this concentration were analysed as per the standard procedures prescribed by APHA (1990) using ground water as control. The parameters like pH, Electrical Conductance, Total Solids, Total Dissolved Solids, Total Suspended Solids, Total Hardness, elements like Na, Ca_2, Mg_2^+, $So4^-$, K^- and $Cl,^-$ Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were analysed as per the standard methods (Table -1 and Table -2)

Table 1 Tannery Effluent Sample Preservation Technique as Recommended by APHA, 1990

S. No	Parameters	Minimum Sample Volume (mL)	Container	Preservation Technique
1	pH	100	Polythene	Measured within 4 hours
2	Dissolved Oxygen	100	Polythene	Measured within 4 hours
3	Chemical Oxygen Demand	500	Polythene	H_2SO_4 was added to adjust the pH to 2 and Refrigerated
4	Trace Inorganic	500	Polythene	2.5 mL concentrated HNO_3 was added and Refrigerated

Table 2 Components of the Experimental Programme and Analytical Techniques as per APHA, 1990

S. No	Parameters	Analytical Method
1	pH	pH Meter
2	Electrical Conductivity (micromhos/cm)	Conductivity Bridge
3	Total Solids	Gravimetric
4	Total Dissolved Solids	Gravimetric
5	Total Suspended Solids	Gravimetric
6	Total Hardness	Titrimetric
7	Sodium	Flame Photometer
8	Potassium	Flame Photometer
9	Calcium	Flame Photometer
10	Magnesium	Flame Photometer
11	Sulphate	spectrophotometric
12	Chloride	Titrimetric
13	Dissolved Oxygen	Titrimetric
14	Biological Oxygen Demand	B.O.D Chamber at 20^oC
15	Chemical Oxygen Demand	C.O.D Mantle

Preparation of Bioadsorbents

Leaves of *Neem* and *Polyalthia* collected from the campus of G.T.N. Arts College, Dindigul District, and Tamil Nadu. The leaves washed under running tap water to remove any traces of soil particles and other dirt. Further leaves washed with distilled water, cut into small pieces and air-dried for 07 days in shade at room temperature. Finally, the leaves were ground and sieved using a mesh size of 0.25 to 0.5mm, to get fine powder.

Adsorption Experiments

The experiments carried out in the batch mode for the measurement of mitigation efficiency of the adsorbents. The bottles with 1.5L capacity filled with 1000ml of the 50% (v/v) concentration of tannery effluent and 20gm each of powdered leaves of *Neem* and *Polyalthia* added separately and given mechanical shaking for 06 hrs at room temperature in a reciprocating shaker at 500 rpm. Then the adsorbents separated from the effluent solution by filtration using Whatmann filter paper No.42. The filtrates were stored in 2L water cans in a refrigerator, prior to analysis of various Physico-chemical parameters, as per the standard preservation technique (APHA, 1990).

Statistical Analysis

Each treatment was analysed with at least 3 replicates. Further, the data observed in the experiment were statistically analysed for the calculation of Standard Error (±SE).

Results and Discussion

The physico-chemical parameters of the untreated tannery effluent of 50% (v/v) concentration and the ground water used for dilution, presented in the Table -3.

Table 3 The Physico-chemical Characteristics of Tannery Effluent and Ground water

Parameters	Untreated Tannery Effluent50% (v/v)	Ground Water	BIS* Permissible Limit
Colour	Brownish Red	Clear	-
Odour	Unpleasant	Pleasant	-
Temperature	27.5°C	25.3°C	-
pH	6.7	7.56	7.0 – 8.5
EC (micromhos/cm)	14569	1475	400
Total Solids	13121	1259	-
Total Dissolved Solids	9907	1003	500
Total Suspended Solids	3214	256	-
Total Hardness	760	320	300
Calcium	192	64	75
Magnesium	67	38	50
Sodium	2190	158	20
Potassium	550	36	20
Chloride	4373	180	250
Sulphate	174	80	200
Dissolved Oxygen	17.22	7	-
Biochemical Oxygen Demand	48	2	-
Chemical Oxygen Demand	135	5	-
Water Quality Index	80	55	-

All the Values expressed in mg/L, except pH and Electrical conductivity (m.mohs/cm) Bureau of Indian Standard.

The physico-chemical parameters of the Neem and Polyalthia treated tannery effluent of 50% (v/v) concentration is presented in the Table-4.

Table 4 The Physico-chemical Parameters of Bio-treated Tannery Effluent

Parameters	Polyalthia with Treated Tannery Effluent (50%)	Neem with Treated Tannery Effluent (50%)
Colour	Slightly Milky White	Turbid White
Odour	Slightly Acceptable	Slightly Acceptable
Temperature	26°C	26°C
pH	7.13	7.17
EC (micromhos/cm)	10577	12427
Total Solids	9521	10194
Total Dissolved Solids	5764	6904
Total Suspended Solids	3757	4280
Total Hardness	540	670
Calcium	140	179
Magnesium	40	59
Sodium	1586	1699
Potassium	375	425
Chloride	3175	3398
Sulphate	130	143
Dissolved Oxygen	12.01	10.07
Biochemical Oxygen Demand	37	41
Chemical Oxygen Demand	101	120
Water Quality Index	50	70

All the Values expressed in mg/L, except pH and Electrical Conductivit(m.mohs/cm).

The colour is usually the first contaminant, in wastewater, that affects the water transparency and gas solubility of water bodies (Yuxing and Jian, 1999). The raw (100%) effluent was reddish brown in colour and therefore did not fulfill criteria, Colourless, of BIS effluent discharge standard. However, after dilution up to 50% (v/v) (the optimal concentration found conducive for crop plants growth, from a pilot study), the colour was found slightly brown. Further, when 2% (w/v) bio-adsorbents of *Neem* and P*olyalthia* were added separately, the colour changed to pale white in both treatments.

Concentration of anions like Cl^- and So_4^{2-} before and after treatment with bio-adsorbents has been shown in Fig.1. The result clearly shows that there is an appreciable decrease in the concentration of these ions after treatment with *Neem* and *Polyalthia*. Singhal *et al.,* (2014) reported the appreciable decrease in the concentration of chloride after treatment of industrial wastewater using Banana peel as adsorbents.

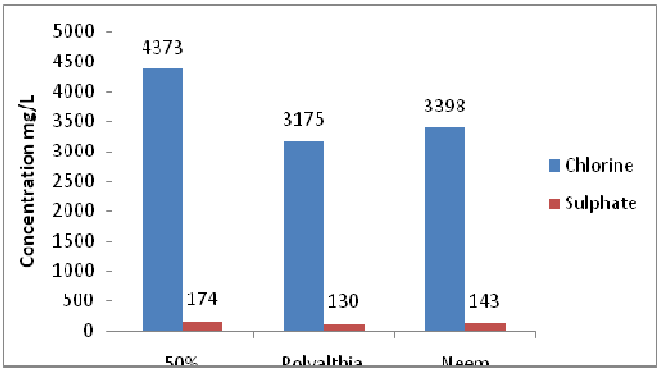

Fig.1 Anions concentration before and after treatment

The concentrations of cations like Ca2+, Mg2+, Na+, K+ have been found to decrease during treatment process. The result is shown in the Fig-2.

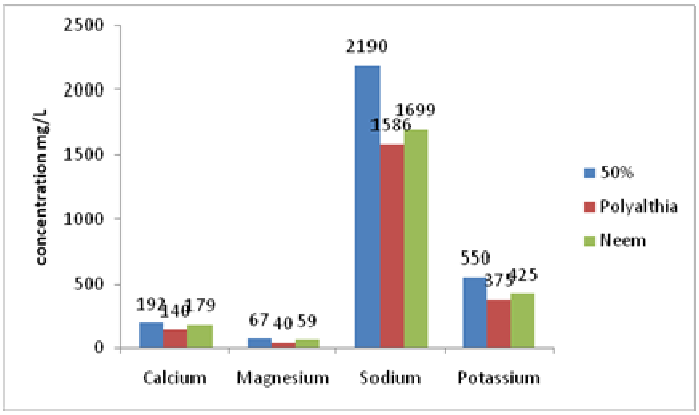

Fig.2 Cations concentration before and after treatment

The sorption of leaf powder of *Neem* bioadsorbent is mainly due to the presence of carboxyl, hydroxyl and amide groups at their surface (Kaewsarn *et al.*, 2008) and biologically active molecules like flavaniods, glycosides, tannin, phenolic compounds, saponins and terpenoids (Prashanth and Krishnaiah, 2014). Due to which, the bioadsorbents are able to chelate with various metal and non-metal ions and help in their removal.

The presence of polar groups on the leaf powder surface of *Polyalthia* is likely to give considerable cation and anion exchange capacity. The irregular surfaces of the particles contain a number of small openings with wavy and highly broken edges. These may have resulted in high surface area and higher adsorption capacity (Mundhe et. al., 2012) than Neem leaf powder.

Conclusion

The present work aimed to find out the efficiency of bioadsorbents among *Neem* and *Polyalthia*. And it was found that *Polyalthia* leaf powder excel than *Neem* in removal of hazardous ions present in tannery effluent, which may hinder the growth of crop plants due to their excess amount than permissible limits of BIS in the tannery effluent. The P*olyalthia* leaf powder has been observed to change the physico-chemical properties of effluent towards the permissible range due to the presence of polar groups on the leaf powder surface is likely to give considerable cations and anion exchange capacity. The irregular surfaces of the particles contain a number of heterogenous holes and small openings with wavy and highly broken edges. These may have resulted in higher surface area and higher adsorption capacity. From the present study it has been concluded that among the two bioadsorbents that was capable of mitigating hazardous ions, *Polyalthia* leaf was superior to *Neem* leaf. However, a further study is needed; to find out optimum amount of bioadsorbent, the effect of time and temperature and the influence of pH on the adsorption of *Polyalthia* leaf powder to maximize its usage at industrial level.

References

1. APHA, 1990. Standard methods for the examination of water and wastewater. 18th Edition. American Public Health Association, Washington, New York.

2. Buljan, J., Bosnic, M and Daniel, R.P 2000. Pollution in tannery effluents. United Nations Industrial Development Organization (UNIDO). Regional programme for pollution control in the tanning Industry South East Asia. US / RAS / 92 / 120.
3. Confederation of Indian Industries, 2006 Report.
4. Kapoor, A and Viraraghavan T. 1995. Fungal biospoption – An alternative treatment option for heavy metal bearing waste waters: A Review, *Bioresour Technol*, 53, 195 – 206.
5. Kaewsarn, P., Saikaew, W and Wongcharee., S. 2008. Dried Biosorbent Derived from Banana Peel: A Potential Biosorbent for Removal of Cadmium Ions from Aqueous Solution. Presented at The 18th Thailand Chemical Engineering and Applied Chemistry Conference, October 20 – 2, Pattaya, Thailand.
6. Mariappan, V., Balamurugan, T and Rajan, M.R. 2001. A survey on the quality of three industrial effluents. *J. of Environ. Ecol.* 1992. 491-493.
7. Mundhe, K.S., Gaikwad, A.B., Kale, A.A., Deshpande, N.R and Kashalkar, R.V 2012. *Polyalthia longifolia* (Ashoka) seeds: An effective adsorbent for Methylene Blue removal. *Int. J. of Res. In Pharm. And Biomedical Sci*. Vol. 3 (1) Jan – March.
8. Nilanjana , D., Karthika, P., Vimala, R and Vinodhini, V. 2008. Use of natural products as biosorbent of heavy metals – An Overview. *Natural product Radiance*, Vol. 7(2), 133 – 138.
9. Prashanth, G.K. and Krisgnaiah, G.M 2014. Chemical composition of the leaves of *Azadirachta indica Linn* (Neem). *Int. J. of Adv. In Eng. Tech. Manage. & Applied Sci.* Vol.1 (5) October.
10. Raniperumal and Singaram, P 1995. Chemical pollution of soil and irrigation water by tannery effluent, Tamil Nadu Experience, Indian J. Agric. Chem. XXIV: 1-8.
11. Singhal, S., Agarwal, S., Bahukhandi, K., Sharma, R and Singhal, N.2014. Bio-adsorbent: A cost-effective method for effluent treatment. *Int. J. of Environmental Sciences and Research*. Vol.3, No.1: 151 – 156.
12. Yuxing, W and Y. Jian 1999. Decolorization of synthetic dyes and wastewater from textile. *Water Research* 33(16): 3512 – 3520.