

A

PROJECT (IDP) REPORT ON

**A COMPARATIVE STUDY: REMOVAL OF HEAVY
METALS FROM LEACHATE BY PHYSICAL AND
BIOLOGICAL TREATMENT**

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TABLE OF CONTENT

Contents	Page No.
CERTIFICATE	ii
ACKNOWLEDGEMENT	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	viii
ABSTRACT	ix
Chapter: 1. INTRODUCTION	
1.1 Background	1
1.2 Need of Study	3
1.3 Aim of Study	4
1.4 Scope of Study	
	13
Chapter: 2. TREATMENT METHODS FOR HEAVY METALS	
2.1 Sources of heavy metals contaminated waste water	16
2.2 Concentration of heavy metals in Leachate	17
2.3 Removal of heavy metals by orange peels	18
2.4 Removal of heavy metals by micro-organisms	19
Chapter: 3. REMOVAL BY USING BIO-SORPTION	
3.1 Bio-sorption	20
3.2 Bio-sorption Mechanism	20
3.3 Procedure	21
3.4 Physical Treatment	22
3.5 Biological Treatment	22

Chapter 4 OBSERVATIONS

4.1 Physical Treatment Observations	24
4.2 Biological Treatment Observations	25
4.3 Result	26
4.4 Conclusion	26

REFERENCES

LIST OF TABLES

Table No.	Page No.
Table 1	17
Table 2	19
Table 3	24
Table 4	25
Table 5	26

LIST OF FIGURES

Figure No.	Page No.
Figure 1	16
Figure 2	18
Figure 3	21
Figure 4	22

LIST OF ABBREVIATIONS

Symbol	Abbreviations
BOD	Bio-chemical Oxygen Demand
COD	Chemical Oxygen Demand
TSS	Total Suspended Solids
TDS	Total Dissolved Solids
DO	Dissolved Oxygen
AAS	Atomic Absorption Spectroscopy
TLC	Thin Layer Chromatography

ABSTRACT

Heavy metal pollution is one of the major pollution in today's world. The aim of the study is to remove heavy metals based on the treatment method applied to leachate from a municipal waste landfill i.e. BEIL situated in Ankleshwar. As there were many issues related to presence of heavy metals in this industry, we have decided to take IDP based project to remove heavy metals from leachate. The sources of heavy metals in leachate are industrial waste, municipal waste and many other waste. The highest concentrations of heavy metals found in leachate are from young landfills in the acid fermentation phase and at very low pH. pH becomes neutral and there is decrease in concentration of heavy metals due to solubility at both maturation and stabilization phases. Heavy metals such as zinc, lead, cadmium and nickel are present in relatively high concentration at landfill site. This treatment includes two processes: (i) Physical (ii) Biological. The physical treatment includes removal of heavy metals by filtration mechanism using low cost orange and banana peels. The biological treatment includes various bacteria for removal of heavy metals. It is a comparative study of both the processes and can conclude the result.

CHAPTER 1

Introduction

1.1 Background

In recent years pollution of aquatic environment by heavy metal has increased. Toxic pollutants such as heavy metal originating from various sources are deposited in the aquatic environment. The continuously mixing of industrial effluents containing heavy metals to the river water causes several adverse effects. Water is essential to all forms of life and makes up 50-96 % of the weight of all plants and animals. Due to their potential toxic effect and ability to bioaccumulate it is very difficult to remove from wastewater stream. The potential sources of the heavy metal are industries, mining, and agriculture. Due to rapid increase in the concentration of heavy metal there is a necessity of efficient methods for the removal of heavy metal from industrial wastewater stream before discharge so as to eliminate the risk on the human life as well as on the aquatic environment. Amongst all the sources of heavy metal effluent one of the potential source is leachate from landfill site of BEIL. Landfill site generates wastewater containing heavy metal such as Mercury, Nickel and Cadmium. In order to reduce environmental pollution due to heavy metal a number of studies are being considered to minimize the problem. Though conventional methods such as membrane process, chemical precipitation, electrochemical process, ion exchange etc. are adopted still number of studies are being carried on the development of other processes such as biological treatment, treatment based on the biosorption process etc. to supplement the conventional process so as to increase removal efficiency.

Leachate is referring to rain waters migrating through a landfill and leaching dissolved organic and inorganic compounds. Leachate occurs when the water content in landfill exceeds its storage volume, i.e. the maximum water amount which can be retained in the porous material of the landfill. A leachate is any liquid that, in the course of passing through matter, extracts soluble or suspended solids, or any other component of the material through which it has passed. Leachate is a widely used term in the environmental sciences where it has the specific meaning of a liquid that has dissolved or entrained environmentally harmful substances that may then enter the environment. It is most commonly used in the context of land filling of putrescible or industrial waste. The

conventional methods for metal removal from leachate include reduction, precipitation, ion exchange, electrochemical reduction and reverse osmosis. Most of them involve high capital costs with recurring expenses, which are not suitable for small scale industries.

This project reports the potential of banana and orange peels as adsorbents for removal of heavy metals. The residues of banana and orange peels can be processed and converted to be adsorbent because they have large surface areas, high swelling capacities, excellent mechanical strengths and are convenient to use and have great potential to adsorb harmful contaminants such as heavy metals.

1.2 Need of Study

Heavy metals are discharge by number of industrial processes and this can lead in turn to the contamination of the freshwater and marine water.

The release of large quantities of hazardous materials into the natural environment results into the number of environmental problems and due to their non-biodegradability and persistence can cause danger to the human beings.

The heavy metals hazardous to human include lead, cadmium, arsenic, copper, zinc, and chromium.

Continuous discharge of the industrial and agricultural wastewater in the rivers, lakes and any other natural body causes deposit of pollutants in sediment.

The problem of heavy metal pollution in water and aquatic organisms including fish needs the continuous monitoring and surveillance as these heavy metals do not degrade and tend to bio magnify in man through food chain.

Hence there is the need to remove heavy metal from the effluent.

Research and development therefore focuses on sector specific methods and technologies to remove heavy metal from wastewater stream.

1.3 Aim of the Study

A Comparative Study: Removal heavy metals from leachate by physical and biological treatment.

1.4 Scope of the Study

The scope of our project is removal of the heavy metal removal using bio-sorbents followed by biological treatment using families of the different species of microorganisms. This can be used in various industries bearing the heavy metals. The industries include: chemical, dyes and pigments, paint industry, textile industry, etc.

1.5 Literature Review

In this Section, we have referred various research papers. Some of them are listed below:

1. *“Adsorption of Heavy Metals from Water Using Banana and Orange Peels”* by G. Annadurai, R.S. Juang and D.J. Lee from ‘Research Gate’.

Findings: In this paper, Liquid-phase adsorption removal of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} in the concentration range of 5–25 mg/L using low-cost banana and orange peel wastes was examined at 30 °C. Under comparable conditions, the amount of adsorption decreased in the order $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ for both adsorbents. The adsorption isotherms could be better described by the Freundlich equation. The amount of adsorption increased with increasing pH and reached a plateau at $\text{pH} > 7$, which was confirmed by the variations of zeta potentials. The application potential of such cellulose-based wastes for metal removal (up to 7.97 mg Pb^{2+} per gram of banana peel at pH 5.5) at trace levels appeared to be promising.

2 *“Application of Citrullus lanatus rind as biosorbent for removal of trivalent chromium from aqueous solution”* by Nimmala Anvesh Reddy, R. Lakshmi pathy, N.C. Sarada from ‘Elsevier’.

Findings: In this paper, Watermelon rind (WR) an agro waste was evaluated as an adsorbent for the removal of Cr^{3+} ions from aqueous solution. Batch mode adsorption studies were performed by varying parameters such as pH, contact time, adsorbent dose and initial metal ion concentration. Maximum loading capacity of WR was found to be 172.6 mg/g for Cr^{3+} ions at pH 3. Kinetic studies show that removal of Cr^{3+} ions is

rapid and follows a pseudo second order model. Equilibrium data fit better with the Langmuir isotherm than the Freundlich isotherm..

3. “*A Study on the Potential of Moringa Leaf and Bark Extract in Bioremediation of Heavy Metals from Water Collected from Various Lakes in Bangalore*” by Shinomol George K, BhanuRevathi K, Deepa N, PoojaSheregar C, Ashwini T.S., Suchandrima Das from ‘Elsevier’.

Findings:In this paper, Bioremediation is a waste water management technique that facilitates removal or neutralization of pollutants from a contaminated site. Many plants and their extracts have been used for bioremediation of heavy metals in the process of phytoremediation. Moringaolifera, also known as drumstick is a fast growing, drought resistant plant that belongs to the family of Moringaceae. Its fruit and leaf are consumed as diet and the bark has healing properties as recorded in ancient medicine. Moringaolifera seeds have been reported to have bioremedial property which can be enhanced on chemical modification. The reduction in heavy metal content was observed by Thin Layer Chromatography (TLC) and Atomic Absorption Spectroscopy (AAS) methods. Other physico chemical parameters like turbidity, BOD, COD, DO, Nitrate and Phosphate content were examined to emphasize the bioremedial property of chemically modified Moringaolifera leaf and bark extracts. Biosorption of heavy metals was found for the bark and leaf treated water samples and also reduction in the BOD, COD, nitrate and phosphate content and turbidity were observed for both the biosorbents.

4. “*Water hyacinth (Eichhorniacrassipes) – An efficient and economic adsorbent for textile effluent treatment*” – A review by E. SanmugaPriya, P. SenthamilSelvan from ‘Arabian Journal of Chemistry’.

Findings:In this paper, the literatures related to the biosorption capacity of the water hyacinth in reducing the concentration of dyestuffs, heavy metals and minimising certain other physiochemical parameters like TSS, TDS, COD and BOD.

5. “*Uptake of Heavy Metals by Microorganisms: An Experimental Approach*” by Omar ChaalalAdulrazag Y. Zekri from ‘Taylor & Francis Inc.’

Findings:In this paper, bacteria were isolated and used in a reactor coupled with a membrane system. The bacteria, the stirrer and the membrane housed in the reactor are arranged in a distinctive way to form the novel bio-stabilization process proposed in this research. This proposed technique could be used at low cost and with great confidence in the purification of drinking water. The system was found to be adequate for concentrations of lead in the range of 5–40 ppm. The system was found to be adequate for concentrations of lead in the range of 5–40 ppm.

6. *“Biosorbents for heavy metals removal and their future”* by Jianlong Wang , Can Chen from ‘Elesiver’.

Findings: In this paper, the bio sorbents widely used for heavy metal removal were reviewed, mainly focusing on their cellular structure, bio sorption performance, their pre-treatment, modification, regeneration/reuse, modeling of bio sorption (isotherm and kinetic models), the development of novel bio sorbents, their evaluation, potential application and future. The pre-treatment and modification of biosorbents aiming to improve their sorption capacity was introduced and evaluated. The bio sorbent, unlike mono functional ion exchange resins, contains variety of functional sites including carboxyl, imidazole, sulphhydryl, amino, phosphate, sulfate, thioether, phenol, carbonyl, amide and hydroxyl moieties.

7. *“Isolation and characterization of heavy metal removing bacterial bio flocculants”* by J. Lin* and C. Harichund from ‘African Journal of Microbiology Research’.

Findings: In this paper, Thirteen metal-tolerant bacteria capable of producing metal-removing bio flocculants were isolated from an industrial effluent sample. The flocculating activity of bio flocculants produced by these microorganisms was assayed using the kaolin clay. The heavy-metal-removal efficiency was determined using atomic absorption spectrometer before and after mixing the bio flocculants with the heavy metal solutions.

8. *“Biological Methods for Heavy Metal Removal A Review”* by Sonali R. Dhokpande, Dr. Jayant P. Kaware from ‘International Journal of Engineering Science and Innovative Technology (IJESIT)’

Findings:In this paper, the key area of research in the heavy metal removal by biological methods is the recovery of heavy metals. The recovery and regeneration are the two important factors which can make the biological methods, a more attractive and economical alternative.

9. *“Treatment of Industrial Wastewater by using Banana Peels and Fish Scales”* by Aakanksha Darge, S. J. Manefrom ‘International Journal of Science and Research (IJSR)’.

Findings:In this paper, banana peels and fish scales were washed, dried and ground to 150- 200 μm and to 160 μm respectively. The combination of both these biosorbent was used for treatment of waste water with different proportion of adsorbents, variation of pH and contact time. It is found that the maximum efficiency of removal of heavy metal is 60% and 70% respectively.

10. *Removal of Heavy Metals from the Environment by Biosorption*” by M. Gavrilisceu from ‘Research Gate’.

Findings:In this paper, Studied about the unconventional removal method of heavy metals, i.e. Biosorption. It is presented as physio-chemical process for removal of heavy metals.

Result: Out of all the research paper we have referred, we have decided to use orange and banana peels as a bio-sorbent for removal of heavy metals from leachate followed by biological treatment with families of micro-organisms.

CHAPTER 2

Treatment methods for heavy metals.

2.1 Sources of heavy metal contaminated wastewater

Various sources of heavy metals in waste water are as follows:

1. Mining and smelting of metalliferous
2. Surface fishing industry.
3. Energy and fuel production.
4. Fertilizer and pesticide industry
5. Leachate from landfill sites.

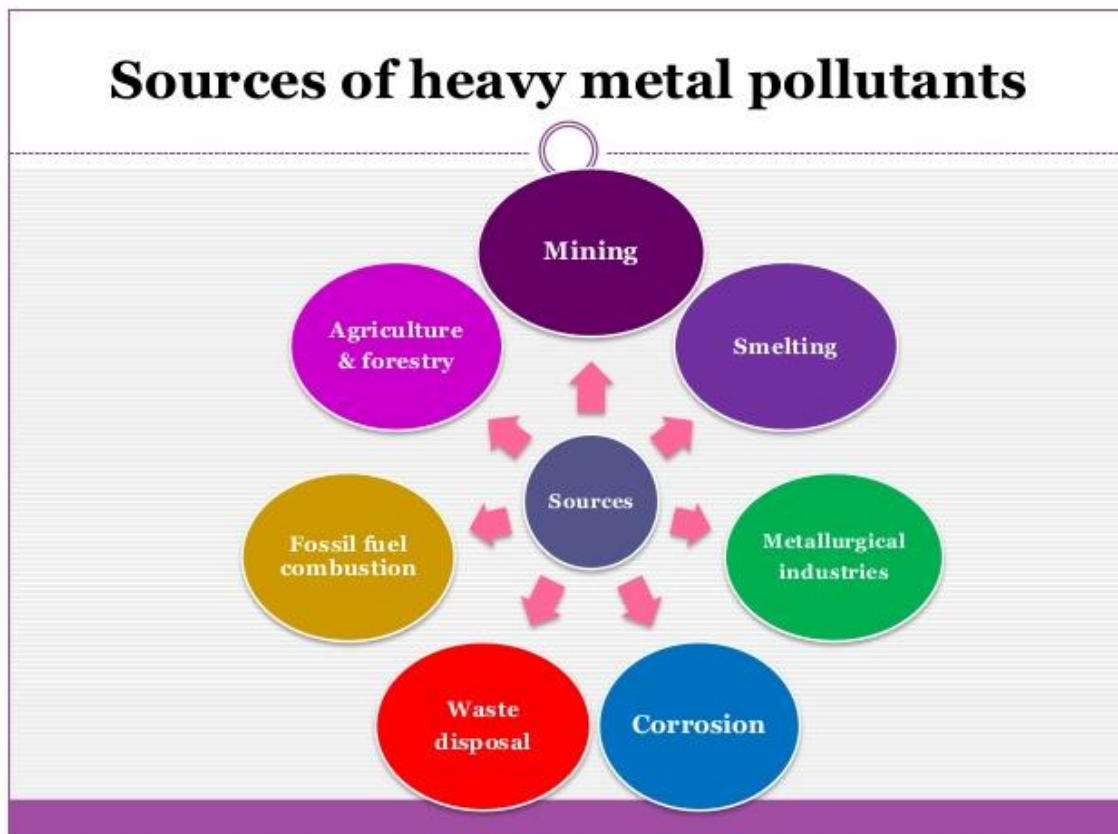


Fig 1. Sources of heavy metals

2.2 Concentration of heavy metals in Leachate

Sr No.	Heavy Metal Concentration	GL	IL	TL	HL
1	Arsenic(As)	BDL	BDL	<0.053	<0.053
2	Cadmium(Cd)	BDL	0.01	<0.002	<0.002
3	Chromium(Cr)	0.029	0.035	<0.007	<0.007
4	Lead(Pb)	BDL	BDL	<0.042	<0.042
5	Mercury(Hg)	BDL	BDL	<0.061	<0.061

Table 1 Concentration of heavy metals

2.3 Removal of heavy metals by orange peels

The physical treatment includes removal of heavy metals by adsorption followed by filtration mechanism using orange peels.

Orange peels were cut into small pieces, dried, crushed, and washed thoroughly with double distilled water to remove the adhering dirt. They were finally dried in an air oven at 100°C for 24 hrs. After drying, the adsorbents were sieved.



Fig 2. Orange powder

2.4 Removal of heavy metals by microorganisms

Bacterial is mainly used for the removal of heavy metals from waste water contaminated with pollutants that are not biodegradable, like mercury, lead etc. However, their isolation, screening and harvesting on a larger scale may be complicated but still remain one of the efficient way of remediating pollutants. Different bacterial strains were used for the removal of different metal ions. Table 2 below shows the biosorption capacity of different metal ions by different bacterial biomass. Bacteria have evolved a number of efficient systems for detoxifying metals ions they develop these resistance mechanisms mostly for their survival.

Sr No.	Heavy metals	Sources
1.	Chromium	Electroplating industry, leather, chrome plating, petroleum refining , tanning, textile manufacturing and pulp processing units.
2.	Copper	Electroplating industries , metal refining, plastic industry and industrial emission.
3.	Cadmium	Metal smelting and refining , phosphate fertilizers , paint , pigment and copper refineries.
4.	Lead	Automobile batteries, petrol based materials .
5.	Nickel	Metal refining , galvanization , paint and powder , batteries processing.
6.	Zinc	Rubber industries , paint and dyes.
7.	Mercury	Emission from industries producing caustic soda .Thermometer , adhesives , paints etc.
8.	Iron	From metal refining , galvanization engine parts.
9.	Arsenic	Semiconductors , petroleum refining . Wood preservatives , animal feed additives , coal power plants.

Table 2 Some of the common industrial units releasing toxic heavy metals into environment are listed .

CHAPTER 3

REMOVAL BY USING BIO-SORPTION

3.1 Bio-sorption

The bio sorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bounded there by different mechanisms.

The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases.

3.2 Bio-sorption mechanism

The mechanism of biosorption is complex, mainly ion exchange, chelation, adsorption by physical forces, entrapment in inters and intrafibrillar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through cell walls and membranes.

There are several chemical groups that would act as sequester the metals in biomass: acetamido groups of chitin, structural polysaccharides of fungi, amino an phosphate groups in nucleic acids, amido, amino sulfhydryl and carboxyl groups in proteins, hydroxyls in polysaccharide and mainly carboxyls and Sulphates in polysaccharides of marine algae that belong to the divisions Phaeophyta, Rhodophyta and Chlorophyta.

The complex structure of microorganisms implies that there are many ways for the metal to be taken up by the microbial cell. The biosorption mechanisms are various and are not fully understood. They may be classified according to various criteria. According to the dependence on the cell's metabolism, biosorption mechanisms can be divided into: Metabolism dependent and Non –metabolism dependent.

3.3 Procedure

Orange peels were cut into small pieces, dried, crushed, and washed thoroughly with double distilled water to remove the adhering dirt. They were finally dried in an air oven at 100°C for 24 h. After drying, the adsorbents were sieved. The particle sizes were 1 to 5 mm. Synthetic solutions were prepared from analytical-reagent grade CuSO_4 , CoSO_4 , NiSO_4 , ZnSO_4 , and $\text{Pb}(\text{NO}_3)_2$. The sieved peels were treated separately with $0.4 \text{ mol L}^{-1} \text{NaOH}$, $0.4 \text{ mol L}^{-1} \text{HNO}_3$, and distilled water. A typical process of acid and alkali treatment was described as follows. Banana or orange peels (15 g) were soaked in 200 mL of $0.4 \text{ mol L}^{-1} \text{HNO}_3$ for 24 hrs. They were filtered and rinsed with distilled water until the filtrate was near neutral.

We have prepared bio-sorbent listed below in figure.



Fig3. Bio-sorbent preparations

Bio-adsorbent are prepared by solutions using acid, alkali and distilled water and adsorption takes place for removal of heavy metals.

3.4 Physical Treatment

The physical treatment includes removal of heavy metals by adsorption followed by filtration mechanism using orangepeels. Orange peels were cut into small pieces, dried, crushed, and washed thoroughly with double distilled water to remove the adhering dirt. They were finally dried in an air oven at 100°C for 24 hrs. After drying, the adsorbents were sieved.

Physical: Orange peels are dried and converted in powdered form and solutions of acid , alkali and distilled water are prepared by adding appropriate gm of powder. A sample of 100ml is taken and adsorbent of different quantity are added and placed in shaker for 48 hrs. Then after centrifuge was run for 5 minutes and treated sample was tested respectively.

3.5 Biological Treatment

Bacteria is mainly used for the removal of heavy metals from waste water contaminated with pollutants that are not biodegradable, like mercury, lead etc. However, their isolation, screening and harvesting on a larger scale may be complicated but still remain one of the efficient way of remediating pollutants.

Biological: A culture of ETL60 was prepared and mixed with the sample at different concentrations and were kept in the shaker for 48 hrs. Thereafter, the sample was kept in centrifuge for 5 minutes respectively. The treated effluent was then tested.



Fig 4. Samples in flask shaker

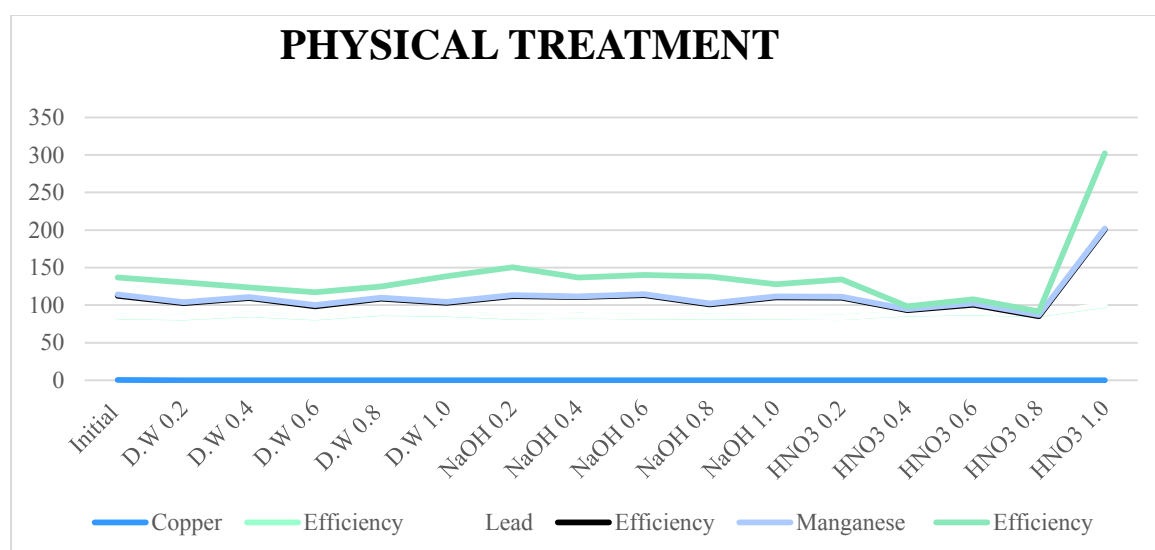
CHAPTER 4

OBSERVATION

4.1 Physical Treatment Observations:

Sample	Copper	Efficiency	Lead	Efficiency	Manganese	Efficiency
UNIT	mg/l	%	mg/l	%	mg/l	%
Initial	0.4355	84.3628	0.5129	27.3348	1.6239	22.5814
D.W 0.2	0.0681	83.44432	0.3727	18.6976	1.2572	26.7443
D.W 0.4	0.0721	87.50861	0.417	21.5832	1.1896	12.6424
D.W 0.6	0.0544	83.65098	0.4022	14.3888	1.4186	17.3471
D.W 0.8	0.0712	89.41447	0.4391	18.6976	1.3422	14.8839
D.W 1.0	0.0461	88.22044	0.417	14.3888	1.3822	33.8937
NaOH 0.2	0.0513	84.3628	0.4391	27.3348	1.0735	37.0589
NaOH 0.4	0.0681	85.80941	0.3727	24.4492	1.0221	25.1616
NaOH 0.6	0.0618	84.13318	0.3875	28.7775	1.2153	25.7159
NaOH 0.8	0.0691	84.61538	0.3653	15.8315	1.2063	36.1783
NaOH 1.0	0.067	84.13318	0.4317	25.892	1.0364	16.3187
HNO3 0.2	0.0691	83.65098	0.3801	25.892	1.3589	22.9509
HNO3 0.4	0.0712	88.70264	0.3801	4.30883	1.2512	3.71944
HNO3 0.6	0.0492	89.89667	0.4908	10.0604	1.5635	5.78238
HNO3 0.8	0.044	87.73823	0.4613	-2.8856	1.53	4.60619
HNO3 1.0	0.0534	100	0.5277	100	1.5491	100

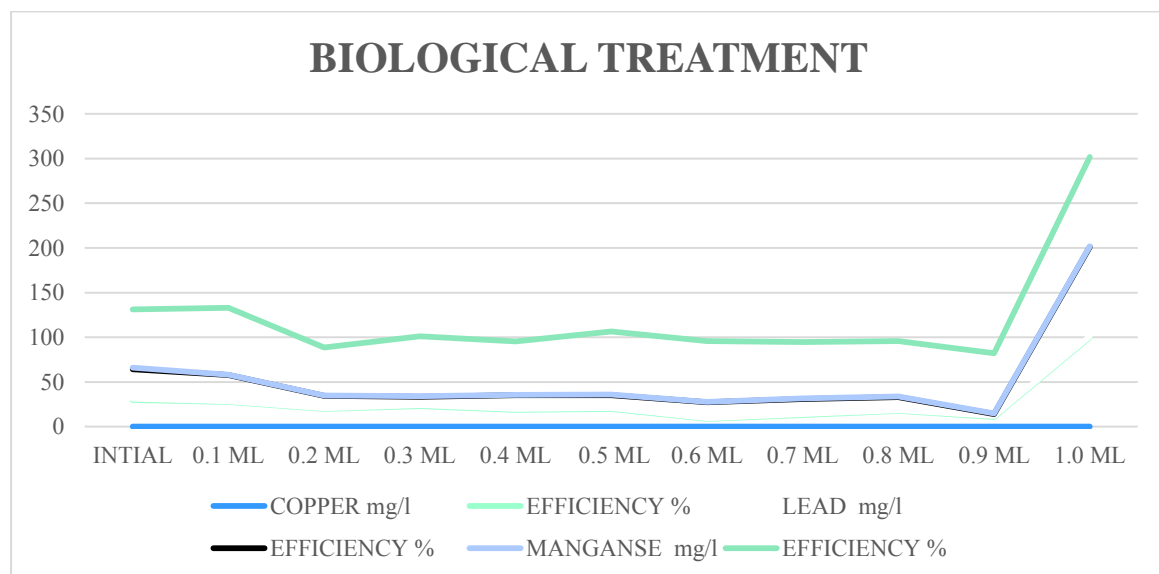
Table No.3 Observations of Physical Treatment



4.2 Biological Treatment Observations:

SAMPLE ID	COPPER	EFFICIENCY	LEAD	EFFICIENCY	MANGANSE	EFFICIENCY
UNIT	mg/l	%	mg/l	%	mg/l	%
INTIAL	0.0868	29.95391705	1.1834	33.08264323	1.6355	65.31947417
0.1 ML	0.0608	27.64976959	0.7919	29.22933919	0.5672	74.88229899
0.2 ML	0.0628	19.70046083	0.8375	13.84992395	0.4108	53.58605931
0.3 ML	0.0697	23.15668203	1.0195	9.236099375	0.7591	67.07428921
0.4 ML	0.0667	18.66359447	1.0741	15.38786547	0.5385	59.7431978
0.5 ML	0.0706	19.70046083	1.0013	14.61889471	0.6584	70.4738612
0.6 ML	0.0697	8.525345622	1.0104	17.69477776	0.4829	68.13818404
0.7 ML	0.0794	13.01843318	0.974	16.925807	0.5211	63.03882605
0.8 ML	0.0755	17.51152074	0.9831	14.61889471	0.6045	62.133904
0.9 ML	0.0716	10.71428571	1.0104	2.315362515	0.6193	67.44726383
1.0 ML	0.0775	100	1.156	100	0.5324	100

Table No.4 Observations on Biological Treatment



4.3 Results

After performing physical and biological treatments and analyzing the result, we have obtained positive results for both the treatment. But more reduction of heavy metals was found in biological treatment than physical treatment by using the microorganism i.e. bacteria named ETL60

Treatment	Concentration	Physical	Concentration	Biological
Unit	gm	%	ml	%
Copper	HNO ₃ 0.6	89.89	0.1	29.95
Lead	NaOH 0.6	28.77	0.1	33.08
Manganese	NaOH 0.2	37.05	0.2	74.88

Table No.5 Result Table

4.4 Conclusions

Biosorption is being an alternative to conventional methods for the removal of toxic heavy metals from industrial effluents. These Conventional methods are expensive, hence the use of low cost, abundant environmentally friendly bio sorbents have to be used. The advanced development of the bio sorption processes requires further improvement in the direction of modelling, regeneration of bio sorbent material and of testing immobilized raw biomasses with basic industrial effluents.

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