



# REMOVAL OF HEAVY METAL ZINC ( $Zn^{+2}$ ) AND COBALT ( $Co^{+2}$ ) USING MAIZE COB ANDBANANA PEEL AS BIOADSORBENT AND UTILIZATION OF ACQUIRED BIOMASS FOR BIOETHANOL PRODUCTION

K. Kadam<sup>1</sup>, S. Ambre<sup>2</sup>, S

Devadiga<sup>3</sup> Department of Biotechnology

Chikitsak Samuha's Sir Sitaram and Lady Shantabai Patkar College of Arts & Science and V.P. Varde  
College of Commerce & Economics, Goregaon (W), Mumbai, Maharashtra, India.

**Abstract:** Water plays a key role in diluting pollutants and because of that superiority as a solvent, it also implies that water-soluble wastes pollute water easily. The most significant environmental pollutants and those with the greatest economic value for industrial use are heavy metals. Due to the negative effects all over the world, heavy metal environmental pollution is a growing issue and a source of great concern. Aqueous solutions containing these heavy metals were prepared in the current study with the intention of removing specific heavy metals, such as zinc and cobalt, due to their recalcitrant nature. The current research focuses on the Adsorption of these heavy metals on natural sources such as maize cob and banana peel and examines the physicochemical parameters (initial concentration, temperature, and absorption capacity) involved in the optimization of this adsorption. Additionally, it aims to generate biofuel like alcohol from the waste generated post-treatment.

## 1. INTRODUCTION

A majority (71%) of the Earth's surface is covered by water, but freshwater constitutes a minuscule fraction (3%) of the total. Water fit for human consumption is obtained from freshwater bodies. Approximately, 70% of the freshwater goes to agriculture. This natural resource is becoming scarce in many places and its unavailability is a major social and economic concern. Human and industrial activities produce and discharge wastes containing heavy metals into the water resources making them unavailable and threatening human health and the ecosystem. Industrialization to a larger degree is responsible for environmental contamination, especially water where lakes and rivers are overwhelmed with many toxic substances. Environmental pollution by heavy metals has become a serious threat to living organisms in an ecosystem. (Azimi A, 2017). Their presence in aquatic ecosystems causes harmful effects on living organisms. The problem of removing pollutants from water is an important process and is becoming more important with the increase in industrial activities. (Paul B Tchounwou, 2012)

The heavy metal contamination in aqueous streams and other consumable water sources, emerging

from the release of untreated metal consisting of effluents discharged into water bodies, is one of the most critical environmental issues. Heavy metals are a group of metals and metalloids that are non-biodegradable, possess a relatively high density, and are toxic even at ug/L levels. They are released into the environment majorly via anthropogenic sources with a tendency to accumulate in human tissues at variable poisonous levels. Metal toxicity is of great environmental concern because of its bioaccumulation and non-biodegradability nature.

Heavy metals at higher concentrations are toxic in nature to higher life forms because of their recalcitrant nature which can lead to biomagnifications. Exposure to these metals at lower concentrations results in various disorders. Problems concerning pollution of water bodies can cause worse impacts on public health, ecology, and the economy of developing countries. Therefore, it is of prime importance for the study to determine the means of eliminating these pollutants via bioremediation. (Igiri BE, 2018)

Bioremediation is one of the most promising technological approaches to the problem of hazardous waste, which relies on microorganisms such as bacteria or fungi to transform hazardous chemicals into less toxic or nontoxic substances. Such biological transformation is more attractive than direct chemical or physical treatment. (Mohamed, 2020)

Levels of zinc beyond permissible limits can lead to flu-like symptoms, stomach/intestinal disorders, and liver dysfunction. The maximum permitted limit of zinc in water is 5 ppm. Beyond these levels, can be consequential for the aquatic ecosystem and other living beings. Therefore, it is necessary to reduce the menace of these heavy metals by effective removal methods. Thus, biosorption is a cost-effective and rapid mechanism for the remediation of metals. (J.C Igwe, 2007). Toxic concentrations of Co inhibit active transport in plants. Relatively higher concentrations of Co have toxic effects, including leaf fall, inhibition of greening, discoloured veins, premature leaf closure, and reduced shoot weight. Thus, there is a strong need to remediate Co accumulated sites. The maximum permissible limit of cobalt in water is 0.5 ppm (Mahey, 2020) Bio sorption is a process of rapid and reversible binding of ions from aqueous solutions onto functional groups that are present on the surface of biomass. This process is independent of cellular metabolism (Mohamed, 2020) Corn cob blast can be used to remove paint from metal, fiberglass, and wood surfaces and clean log homes, electrical insulators, transformer substations, barns, boat hauls, and wooden decks, and remove smoke damage. Banana peels can be used as a good adsorbent for heavy metal adsorption. (Deviant, 2021) These plant materials consist of anionic cell wall function groups which bind to cationic metal ions by electrostatic attraction. Therefore, to estimate the practical adsorption capacity of food waste such as maize cob and banana peel as an effective adsorbent for the removal of cobalt and zinc metal from contaminated waters, the study is been carried out. Also, the effect of treated biomass on the production of bioethanol is being investigated Also, the global warming effect, depletion in fossil fuel reserves, and higher petroleum prices are the main issues driving worldwide interest in the development of alternative renewable, biodegradable, and sustainable biofuels. Biofuels produced from waste are considered to be a potential candidate to replace conventional fossil fuels. (Bhattacharya, 2010) Ethanol production is generally achieved by the chemical synthesis of petrochemical substrates and microbial transformation of sugars present in horticultural items and oil can be utilized as biodiesel. Ethanol production is usually accomplished by chemical synthesis of petrochemical substrates and microbial conversion of carbohydrates present in agricultural products and oil can be used as biodiesel. (Arpan Das, 2016) Biofuel functions similarly to nonrenewable fossil fuels. The main difference between them is that biofuel can be grown indefinitely and generally cause less damage to the planet. The simple and complex polysaccharide plant food reserves are broken down into simple sugars and fermented to produce bioalcohol. (Bušić, 2018) Photosynthetic processes in plants produce simple and complex sugars, which can be decomposed by fermentation in the presence of microorganisms such as *Escherichia coli*, *Klebsiella oxytoca*, *Saccharomyces cerevisiae*, and *Zymomonas mobilis* to produce bioethanol. It is highly soluble in water and is hygroscopic, thus requiring an energy-intensive distillation process to separate it from the mixture during the extraction process (Das, 2016)

## 2. MATERIALS AND METHODS

### 2.1 Sample preparation:

The maize cobs (*Zea mays*), were procured from the local vegetable market vendors in Mumbai, India. The peels of banana (*Musa paradisiaca*) were sourced from the local market and domestic household waste, Mumbai, India

### 2.2 Pretreatment:

#### 2.2.1. Maize cob

The maize cob wastes were washed, chopped and sundried. The dried samples were ground into powder and sieved using a 40- 80nm sieve. The sample was weighed to determine the mass of procured sample and stored in air-tight containers. The sample was activated by subjecting to 14.8 M  $H_3PO_4$ . Blended in a ratio of 3:1 for 24 hours followed by washing. The acidity of the sample was monitored and maintained at a pH of 6- 7 . The sample is to be dried again and used for the analysis

#### 2.2.2. Banana peels

15-20 bananas peels are cut and washed. Then sample was activated using KOH i.e 20 g of banana peel was added into 25 ml of solution (50 % W/V for 40 g and 25% W/V for 20 g) and soaked at 60<sup>0</sup>C for 3 days .Wash repeatedly with distil water till the alkalinity of the sample was within the pH range of 6-7. The peels were dried at 60<sup>0</sup>C and grind to powder.

### 2.3. Biosorption

#### 2.3.1 Batch Biosorption

Standard concentration solution of Zn metal was prepared as control for analysis. For each run, weighed amount of 1g adsorbent was placed in the flask and agitated on a rotary shaker at an agitation rate of 110 r/min for 2 hours. The optimization of parameters was done by studying the effect of adsorbent dosage (0.5 ,0.75 ,1.0, 1.25g of sample) agitated mechanically at R. T, effect of initial Zn metal concentration (50, 100, 150, 200 ppm and finally Effect of temperature at (2<sup>0</sup>C, Room temperature, 40<sup>0</sup>C and 60<sup>0</sup>C) were analyzed by keeping biosorbent amount constant. The flask containing samples was withdrawn from the shaker, filtered and the final concentrations of metal ions in the supernatant solutions was examined by complexometric titration. After optimization, suitable parameters were chosen and a separate set was run.

#### 2.3.2 Estimation of metal concentration by Complexometric titration

Prepare 100 ml of 0.01M EDTA. Pipette out 10 ml of sample. Add 2ml of ammonia buffer pH 10 solution and a pinch of 2% Eriochrome Black T indicator. Shake well and titrate against 0.01 M EDTA. The end point will be from purple/wine red to blue.

#### 2.3.3 Desorption

Desorption of metal ions from treated biomass was accomplished by submerging the treated biomass in 100 cm<sup>3</sup> distilled water and agitating on a mechanical shaker at 110 rpm for a period of 24 hrs. The biomass was filtered and the removal of zinc ions was determined by titration of the filtered solution obtained.

## 2.4 Bioethanol Production

### 2.4.1 Preparation of maize cob and banana peel media

Table .1- Composition of maize cob and banana peel media

Ingredients	Gram/litre
Biomass	30g
Yeast extract	0.1g
KH <sub>2</sub> PO <sub>4</sub>	0.05g
MgSO <sub>4</sub> .7H <sub>2</sub> O	0.05g
NaCl	0.01g
CaCl <sub>2</sub>	0.01g
Distil water	100ml
pH	6.5-7.0

Inoculation Of *Saccharomyces cerevisiae* in Sterile Media Broth- Overnight grown culture of *Saccharomyces cerevisiae* were, incubated on a rotary shaker at 37<sup>0</sup>C for a period of 10 days.

### 2.4.2 Bioreactor

To produce bio-ethanol a bioreactor was designed consisting of a glass jar, shaft, metal propellers, AC motor, Speed regulator and heat control unit. A speed regulator control the speed of rotation of the shaft and the heat control unit avoids overheating of the motor, preventing damage.

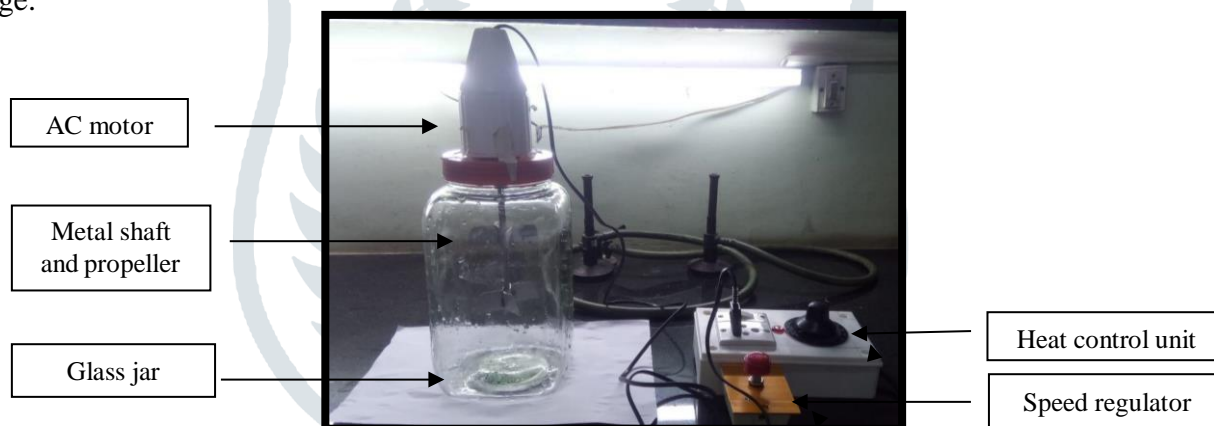


Figure 1. Bioreactor unit

### 2.4.3 Estimation of alcohol

- To quantify the reduction of sugar concentration in the media, the broths were subjected to Cole's Ferricyanide method which involves titrating an alkaline solution of ferricyanide ions with reducing sugars under boiling conditions

### 2.4.4. Extraction of produced bioethanol in the media

Distillation was used to separate the alcoholic ethanol produced from fermented materials. Remove 50 ml fermented to that a pinch of phenol red indicator is added and the pH of the sample is adjusted between 7.0 to

8.0. To this add 2 ml of 25% ZnSO<sub>4</sub>. Add 2 ml of 1N NaOH. Adjust the mixture to a definite volume (twice) using D/W. Centrifuge the content to remove the precipitate. Carry out distillation at 82°C. Collect the distillate in a flask.

## 2.5. Qualitative Determination of Bio-ethanol

### 2.5.1. UV-Visible Spectroscopy:

To evaluate the presence of ethanol in the obtained distillate, a UV-Visible spectrophotometer was used, to determine the maximum absorption of ethanol. The Standard used was absolute alcohol with a blank as distilled water. A double-beam Shimadzu UV-1800 UV Vis Spectrophotometer was availed.

### 2.5.2. Acetylchloride test

1cm<sup>3</sup> of acetyl chloride, Add 2 drops of the sample, if there is strong effervescence indicates that alcohol is present.

## 3. RESULTS AND DISCUSSION

Activation of maize cob with 14.8M H<sub>3</sub>PO<sub>4</sub> and banana peel with 50 wt% KOH opened micro-pores on the surface of maize cob and banana peel and prepared them for adsorption.

Adsorption capacity – Optimization of parameters (initial metal concentration, temperature, adsorbent dosage) The results for the experimental trials for Zn (II & Co (II)) adsorption on maize cob and banana peel is been presented. The following values in the table represent residual metal concentration obtained after adsorption.

### 3.1. Initial Zn and Co Metal concentration

Complexometric titration was employed to determine the metal concentration adsorbed by the biosorbent. The effect of the primary parameters which is the initial concentration of Zn and Co metal was studied where standard solutions of variable concentration of Zn metal ranging from 50-200 ppm with a constant adsorbent dosage of 0.25 g kept at R.T. The pH maintained was 7.

Titrimetry was performed using EDTA and Zn and Co metal amount left behind in the solution was determined. The table provided below portrays the obtained calculations

Table no.2 Residual metal concentration obtained for initial concentration variation parameter

Control (in ppm)	Zinc		Cobalt	
	Maize (in ppm)	Banana (in ppm)	Maize (in ppm)	Banana (in ppm)
50	12.07	11.5	20	29
100	16.1	12.9	43	72
150	18.6	16.6	87	116
200	25.8	20.9	145	145

With the rise in metal concentration, the adsorption capacity declines slightly as the adsorbent amount is constant. The biosorption capacity of maize cob is less than the banana peel, as the metal amount left in the solution are found to be higher in contrast to maize cob. 150 ppm metal concentration shows better adsorption rate, for a high amount of metal present. The higher concentration of 200 ppm might be inhibitory

### 3.2. Temperature

Table 3: Residual metal concentration obtained for temperature parameter (At concentration 150 ppm)

Control (in °C)	Zinc		Cobalt	
	Maize (in ppm)	Banana (in ppm)	Maize (in ppm)	Banana (in ppm)
2	14.3	8.6	72	14
Room Temperature	20	14.9	58	58
40	20.1	21.28	75	23
60	20.9	23.29	75	17

Banana peel shows better biosorption rate than maize cob for zinc metal, while vice versa for cobalt. At lower temperatures of 2°C and R.T enhanced removal is observed, than at higher temperatures where the metal concentration reaches a steady amount.

### 3.3. Adsorption Dosage

Table 4 Residual metal concentration obtained in flask of Adsorption Dosage parameter (At concentration 150 ppm, Temperature : 2°C)

Adsorbent Weight (in grams) for zinc	Concentration OF Zn metal obtained for variable adsorbent dosage (ppm)		Concentration of Co metal obtained for variable adsorbent dosage (ppm)	
	Maize (ppm)	Banana peel (ppm)	Maize cob (ppm)	Banana peel (ppm)
0.5	17.5	12.9	11	13
0.75	11.5	9.4	52	5
1.0	11.2	7.47	46	26
1.25	8.05	5.4	5	29

As the amount of adsorbent increases, simultaneous increase in degree of sorption is been observed. The highest adsorbent dosage 1.25g shows best metal removal from the solution

### 3.4. Optimal parameters for temperature, initial metal concentration and adsorbent dosage

All the optimal parameters were assembled and studied for biosorption where experimental setup was prepared containing 150 ppm Zn metal concentration kept at 2°C and R.T with a constant adsorbent dosage of 1.25g. The pH maintained was 7. Titrimetry was performed using EDTA and the metal amount left behind in the solution was determined by the formula provided. The table provided below portrays the obtained calculations

Table 5. Residual metal concentration on assembly of optimal parameters

Optimal Parameter	Zinc		Cobalt	
	Maize	Banana	Maize	Banana
2°C; 150 ppm ; 1.25 g	13.5 ppm	10.35 ppm	81 ppm	43 ppm
20°C; 150 ppm; 1.25 g	7.7 ppm	6.03 ppm	23 ppm	35 ppm

### 3.5.Desorption

Table 6. Result of desorption

	Maize	Banana
Cobalt	58	14
Zinc	49.0	53.0

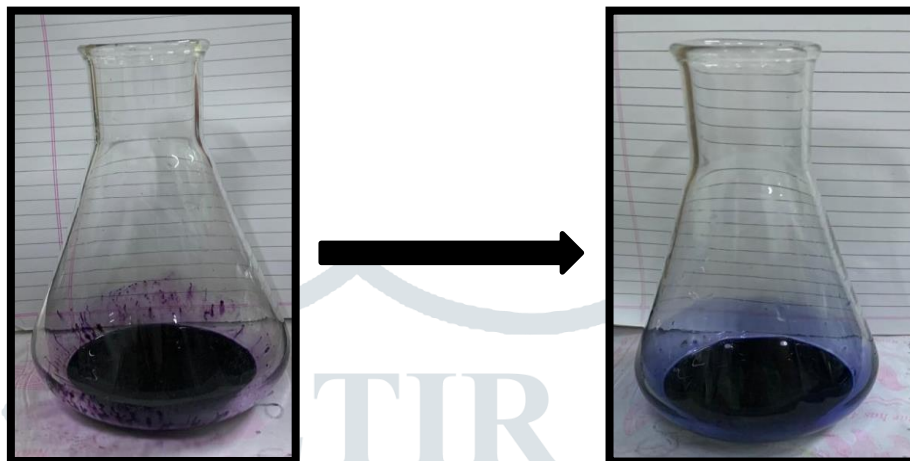
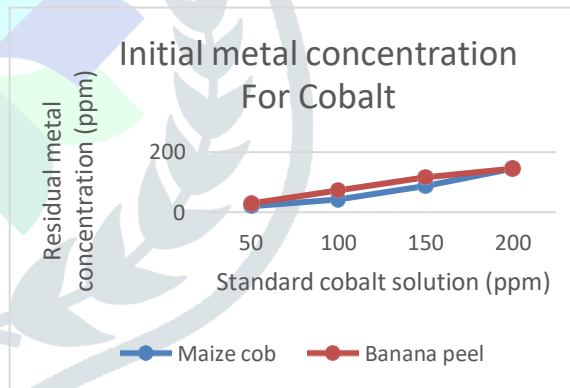
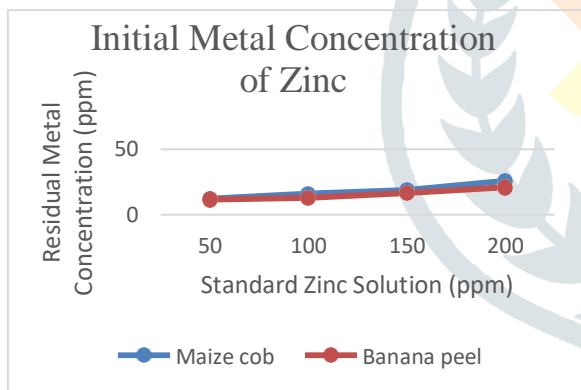


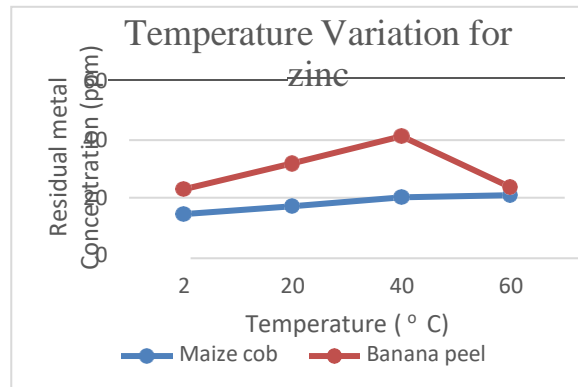
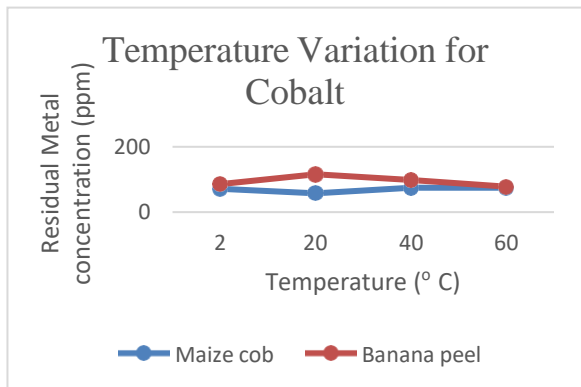
Fig 2 : Endpoint from purple to blue obtained for titration

### 3.6. Graphical Representation of Adsorption capacity of Zinc and Cobalt for each adsorbent :

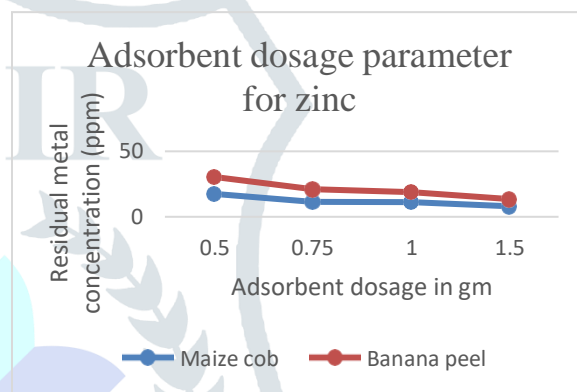
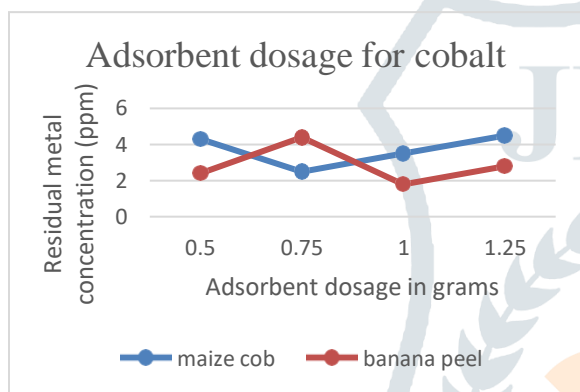
#### 3.6.1. INITIAL METAL CONCENTRATION



3.1.1. TEMPERATURE



3.1.2. ADSORBENT DOSAGE



3.8. Qualitative Determination of Bio-ethanol

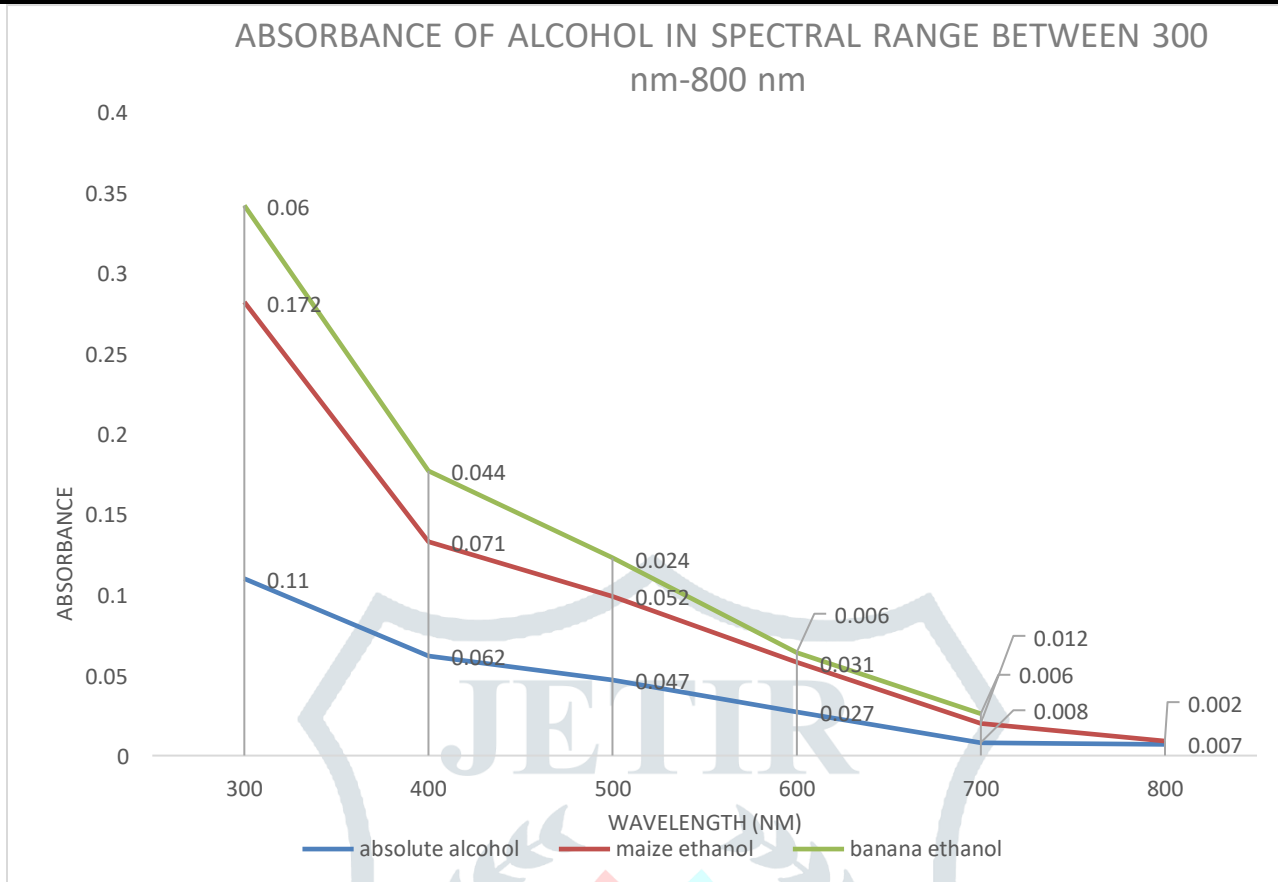
3.8.1. UV-Visible spectroscopy

UV-Vis spectroscopy analysis was done to detect the presence of ethanol in the obtained distillate of maize cob and banana peel. A graph was plotted of the sample distillate against standard absolute alcohol where the highest absorbance was obtained between the wavelength of 300 nm-500nm for standard ethanol. Maize cob distillate showed similar absorption spectra in comparison to standard absolute alcohol, denoting the occurrence of ethanol in the distillate. Banana peel distillate portrayed the highest absorbance and in the similar range as of standard 300nm- 500 nm, indicating excess alcohol concentration than that of standard and maize cob distillate. Absorption maxima were also determined where for standard alcohol it was **478 nm**, while maize cob distillate and banana peel distillate portrayed an absorption maxima of **477 nm** showing remarkable significance between standard and sample alcohol.

Table 8 : Absorbance of standard alcohol, maize cob distillate and banana peel distillate between spectral range of 300 nm- 800 nm

Wavelength (nm)	Absolute Alcohol	Maize Cob distillate	Banana Peel distillate
300	0.110	0.172	0.109
400	0.062	0.071	0.060
500	0.047	0.052	0.044
600	0.027	0.031	0.024
700	0.008	0.012	0.006
800	0.007	0.002	0.006





Graph of absorbance of maize cob ethanol and banana peel ethanol in comparison to standard ethanol between spectral range of 300nm-800nm

### 3.8.2. Acetylchloride test

Strong effervescence with bubble formation was observed for both distillate samples of maize cob and banana, indicating a positive result and presence of alcohol. Reaction product is hydrogen chloride which reacts with another products ammonium hydroxide to form fumes and bubbles.



Fig 3: Strong effervescence observed in banana peel distillate



Fig 4: Bubble and effervescence observed in maize cob distillate

Table 9. Results Of Organic Test Of Alcohol

## 4. CONCLUSION

With an ode of rising industrialization, the developing and developed nations are facing significant drawbacks which include the accumulation of heavy metals in soil and water sources. In developing countries like India, there is more industrialization taking place which leads to the problem related to wastewater containing heavy metals

constantly arising thus the challenge was to find a low-cost, low-tech, user-friendly method of wastewater treatment that would cause bioremediation of wastewater containing heavy metal. Along with this due to industrialization, the reserves of fossil fuels are also depleting causing scarcity of fossil fuel so new substrates for fuel need to be found which can give a utilizable fuel.

In this research, we target a heavy metal cobalt and zinc. The different varying parameter and after bioremediation maize sample and banana sample show more reduction at 20<sup>0</sup>C and 2<sup>0</sup>C and 1.25 g in maize and 0.75 g in banana .By observing this parameter best parameter was taken together and bioremediation was performed ie initial concentration 150 ppm;temperature was 2<sup>0</sup>C and 20<sup>0</sup>Cabsorption dosage 1.25 g for both the samples and thus temperature of 20 <sup>0</sup>C was efficient for both sample. When we compare both the sample maize cob show better reduction of Co than banana peel. The reduction was determined by titration by EDTA using EBT as indicator. During desorption, the recovery of metal was observed more in maize than banana from here also we can say that maize has adsorbed more metal ion..

The biosorption process is the ability of biological beings to adsorb heavy metals on their surface from aqueous solutions. It is an economical and effective method for the removal of heavy metals. Activation of adsorbent was done and experimental setups were prepared. The titrimetric method using EDTA as a chelating agent and EBT indicator was used to determine the metal concentration which involved an endpoint from wine red/purple to blue. Desorption of the metal ions was carried out using distilled water as the desorption agent.

The obtained distillate was utilized for qualitative estimation of alcohol using UV-spectroscopy and acetyl chloride test. Positive results were obtained for UV-Vis spectroscopy for both samples in contrast to standard absolute alcohol(ethanol), where all three solutions showed increased absorption in the 300 nm-500 nm spectral range. Also, strong effervescence obtained in acetyl chloride indicates the present of alcohol in both samples. The alcohol sample obtained was found to be diluted with water. However, the obtained ethanol may also consist of metal residues and other impurities, therefore, need to be subjected to distillation again for purification. Banana peel samples apparently throughout the study, showed better metal remediation capacity and good alcohol content. Bioreactor is also been designed which can be employed for the effective production of alcohol, by providing agitation and optimal growth conditions for fermentation. The ethanol obtained can further be exposed to confirmatory testing by HPLC analysis.

Therefore, an easy bioremediation experiment was carried out using natural resources available in our local material. This technique showed a reduction of heavy metal in controlling the physical parameters. This bioremediation-treated biomass can also be used to produce biofuel because the yeast was used to turn the sugar in the biomass into fuel. Using materials on hand, a bioreactor model was created and prepared. ethanol It may be possible to produce an effective fuel that can be used for daily purposes if this experiment is conducted using high-class technology. Thus, the adsorbents maize cob and banana peel may be employed for various water-cleaning protocols. For precise knowledge of remediated metal concentration. Also, the adsorbents can be used for alcohol production provided that metal removal is been done efficiently and appropriate purification methods are applied to remove other impurities.

## 5. FUTURE PROSPECTS

The present study is aimed to apply a simple and reliable process for the bioconversion of domestic waste for bioremediation and turn it into ethanol. The role of remediation using plant products is advantageous over microbial remediation keeping in consideration the economic feasibility, widespread pollution degradation capacity, public acceptance is higher, and low rate of contamination. The proposed approach futile complex operations that are currently essential and as such, are expected to provide cost-efficiency allowing the technology implementation throughout developed and developing countries. As there are chances of heavy metal contamination in water in near future; as India is a developing country so biosorption and biofuel production from domestic waste can be used as a renewable source and its availability is also throughout the year. If this bioremediation and biofuel extraction is been opted it can create a greater impact on the security and conservation of the environment.

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