Removal of Copper from Water Using Biosorbents

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Abstract - Banana peel and banana stem are agricultural wastes that are used for the adsorptive removal of copper from water. Both the adsorbents were cut, washed, dried and grinded into powder and sieved. Copper adsorption on both the adsorbents was determined by colorimetric method using spectrophotometer by varying parameters such as pH, adsorbent doses, particle sizes and copper concentration. Slightly acidic water (pH 5) was found to be suitable for banana peel and basic water (pH 9) was suitable for banana stem for the effective removal of copper. Maximum removal efficiency was found to be 75% for banana peel and 89% for banana stem. Waste water sample containing high copper content was also tested for removal efficiency they were 66% and 72% for banana peel and stem respectively. Equilibrium data were suitably fitted on freundlich adsorption isotherm.

Keywords - banana peel; banana stem; adsorption; colorimetric determination; adsorption isotherms.

I. INTRODUCTION

Water is an important requirement in our day to day life but in most places it is polluted by the industrial activities and increasing population. The increased population also increases the demand of pure water. So there is an urgent need for pure water. One of the predominant environmental issues today is the large scale waste water release from several industries. Wastewater that was not properly managed can cause several negative impacts on environment. Heavy metals in the environment become an important concern due to the toxicity and the bad effects on human health and other living organisms.

Copper contained water causes various health problems to living organisms so copper should be removed from water. There are several methods adopted for the removal of heavy metals but we need an economical and environmental friendly method and it should be efficient as well. In this thesis adsorption method is used for the removal of copper by using two types of bio-adsorbents such as banana peel and banana stem, their removal efficiencies were compared using this investigation. Banana peel and banana stem are easily available discarded agricultural wastes that are used as bio adsorbents. The efficiency of removal of copper was determined by using colorimetric method.

The adsorption isotherms such as freundlich and Langmuir were plotted using the equilibrium data. From the graphical data obtained, the process of adsorption has to be studied. Waste water samples containing high copper content was collected and tested the characteristics and the efficiency of copper removal using both the adsorbents. The efficiencies of both the adsorbents were compared in this investigation.

II. MATERIALS AND METHODS

2.1 Materials

Stock solution of copper were prepared using analytical grade Copper sulphate from Merck. Neocuproine was purchased from Loba Chemie, Sodium citrate, Hydroxylamine and chloroform were also obtained from local suppliers. Banana stem was obtained from a plantation nearby, they were cut, washed, dried, ground to powder and sieves such as 125µm and 275µm. waste water sample collected from the plywood factory located in Perumbavur, Ernakulam, Kerala.
2.2 Methods
Colorimetric method was used to find out the removal of copper by using spectrophotometer. Transfer 50 ml of the filtrate into separating funnel. Add 5ml hydroxylamine hydrochloride, 10 ml each of neocuproine and sodium citrate solutions and shake well. Add 20 ml of chloroform and shake for 1 minute. Allow the chloroform and aqueous layer to separate. Collect the chloroform layer in a dry flask. Dilute the extract to 50 ml with isopropyl alcohol. Prepare a reagent blank by treating 50 ml of distilled water in the same way as described above.

Measure the optical density of the sample solution at 457 nm against the reagent blank. Treat 50 ml portions of standard solutions containing 0.05, 0.1, 0.5,1.0,5.0,10 mg/l of copper as above. Plot absorbance versus copper concentration (mg/l) for the standards to get the calibration graph.

2.2.1 Study of pH
The effect of pH on the adsorption of copper onto banana peel and banana stem was investigated. 0.5 g of adsorbent having particle size of 125 µm added in 10 ppm copper containing 100 ml solution. Stir the solution for 1 hour and filtered using whatmann filter paper 1 and find out the absorbance using the above method for the filtered sample. Repeat the experiment for various pH values. Find out the equilibrium values for banana stem and banana peel. The other parameters are made constant in each experiment.

2.2.2 Study of adsorbent doses
The effect of adsorbent doses on the adsorption of copper onto banana peel and banana stem was investigated. The maximum adsorption value obtained from the study of pH was noted and that pH was kept constant. Various adsorbent doses having particle size of 125 µm were added in 10 ppm copper containing 100 ml solution. Stir the solution for 1 hour and filtered using whatmann filter paper 1 and find out the absorbance using colorimetric method for the filtered sample. Repeat the experiment for various adsorbent doses using banana peel and stem. The experiments were executed in batches and the maximum adsorption values were found.

2.2.3 Study of particle size
The effect of particle size on the adsorption of copper onto banana peel and banana stem was investigated. The maximum adsorption values obtained from the study of pH and adsorbent dose were noted and that values were kept constant. Various particle sizes of adsorbents were added in 10 ppm copper containing 100 ml solution. Stir the solution for 1 hour and filtered using whatmann filter paper 1 and find out the absorbance using colorimetric method for the filtered sample. Repeat the experiment for various particle sizes in batches using banana peel and stem. The experiments were executed in batches and the maximum adsorption values were found.

2.2.4 Study of copper concentration
The effect of copper concentration on the adsorption of copper onto banana peel and banana stem was investigated. The maximum adsorption values obtained from the study of pH, adsorbent doses and particle sizes were kept constant. 100ml solutions having various copper concentrations were prepared and the adsorbent dose which gave maximum adsorption added in it. Stir the solution for 1 hour and filtered using whatmann filter paper 1 and find out the absorbance is measured. The experiments were executed in batches and the maximum adsorption values were found.

2.2.5 Calculations
The maximum adsorption capacity ($q_e$) = \( \frac{(Ci-Ce)xV}{m} \)  

The percentage of adsorption was calculated by, 

Where, $C_i$ = initial copper concentration in mg/l
q_e = final copper concentration in mg/l
v = volume of sample taken in ml
m = mass of adsorbent in gram

2.2.6 Adsorption isotherms
Adsorption isotherms describe the equilibrium relationship between adsorbent and adsorbate. Langmuir and freundlich adsorption isotherms were used to represent the relationship. Its applicability was judged with the correlation coefficient (R^2). Correlation coefficient was found from the graph drawn between C_e and C_e/q_e for Langmuir adsorption isotherm and ln (q_e) Vs.ln (C_e) for freundlich adsorption isotherm.

III. RESULTS AND DISCUSSION

3.1 Standard calibration curve
Plot of absorbance versus copper concentration (mg/l) for the standards to get the calibration graph. The absorbance of various copper concentrations such as 0.05, 0.1, 0.5, 1, 5, 10 mg/l were determined using colorimetric method and the values were used to plot the graph. From the graph obtained, the values of final copper concentrations of batch experiments were found.

![Figure 1. Standard calibration graph](image)

3.2 Effect of pH
The effect of pH was investigated with four different pH such as 4, 5, 5.5, 6 for banana peel and 5 different pH such as 4, 6, 8, 9 and 10 for banana stem. The highest copper removal occurred at pH 5 (40.5%) for banana peel and at pH 9 (70.5%) for banana stem. Adsorbent dose of 0.5 mg/l, copper concentration of 10 ppm, particle size 125µm were kept constant and the experiment carried out by varying pH. The experiments were executed in batches.
### Table 1. Effect of pH

| Type of adsorbent | pH value | Optical density | Final copper concentration (mg/l) |
|-------------------|----------|-----------------|----------------------------------|
| Banana peel       | 4        | 0.632           | 7.95                             |
|                   | 5        | 0.483           | 5.95                             |
|                   | 5.5      | 0.651           | 8.25                             |
|                   | 6        | 0.698           | 8.75                             |
| Banana stem       | 4        | 0.602           | 7.55                             |
|                   | 6        | 0.491           | 6.1                              |
|                   | 8        | 0.474           | 5.9                              |
|                   | 9        | 0.246           | 2.95                             |
|                   | 10       | 0.296           | 3.55                             |

**Figure 2. Effect of pH using banana peel**

**Figure 3. Effect of pH using banana stem**

### 3.3 Effect of adsorbent doses

The effect of doses was investigated with six different adsorbent doses such as 0.3, 0.5, 0.7, 1, 1.3, 1.7 mg for banana peel as well as banana stem. The highest copper removal was observed at the adsorbent dose 1g for both the banana peel and the stem. For banana peel, pH 5 (maximum
adsorption attained pH) made constant and pH 9 for banana stem, copper concentration of 10ppm, particle size 125µm were kept constant and the experiment carried out by varying the pH. Experiments were executed in batches.

| Adsorbent used | Adsorbent dose (mg) | Optical density | Final copper concentration (mg/l) |
|----------------|---------------------|-----------------|----------------------------------|
| Banana peel    | 0.3                 | 0.444           | 5.4                              |
|                 | 0.5                 | 0.483           | 5.95                             |
|                 | 0.7                 | 0.388           | 4.8                              |
|                 | 1                   | 0.336           | 4.5                              |
|                 | 1.3                 | 0.359           | 4.8                              |
|                 | 1.5                 | 0.372           | 4.5                              |
| Banana stem    | 0.3                 | 0.431           | 5.25                             |
|                 | 0.5                 | 0.246           | 2.95                             |
|                 | 0.7                 | 0.276           | 3.3                              |
|                 | 1                   | 0.234           | 2.8                              |
|                 | 1.3                 | 0.239           | 2.95                             |
|                 | 1.5                 | 0.303           | 3.7                              |

3.4 Effect of particle size
The effect of particle size on the removal of copper was investigated with two different particle sizes such as 125µm and 275µm for both the banana peel and the stem. The highest copper removal was observed at 125µm (59.5% and 72% for banana peel and stem respectively) and indicates that the reduction in particle size increases the removal efficiency. For banana peel pH 5 (maximum adsorption attained pH) made constant and pH 9 for banana stem, copper concentration of 10ppm, adsorbent dose for banana peel and stem were kept as 1g (maximum efficiency of removal of copper). The experiments were carried out by varying particle size in batches.
### Table 3. Effect of particle size

| Adsorbent used | Particle size (µm) | Optical density | Final copper concentration (mg/l) |
|----------------|-------------------|-----------------|----------------------------------|
| Banana peel    | 125               | 0.336           | 4.5                              |
|                | 275               | 0.383           | 4.65                             |
| Banana stem    | 125               | 0.234           | 2.8                              |
|                | 275               | 0.319           | 3.9                              |

**Figure 5. Effect of particle size of banana peel**

**Figure 6. Effect of particle size of banana stem**

### 3.5 Effect of copper concentration

The effect of copper concentration was investigated with five different copper concentrations such as 1, 2.5, 5, 10, 15 mg/l. The highest removal of copper was observed at 1 mg/l (75%) and 5 mg/l (89%) for banana peel and banana stem respectively. For banana peel pH 5 (maximum adsorption attained pH) and pH 9 for banana stem, particle size 125µm (maximum adsorption obtained) were kept constant and the experiment is carried out by varying the copper concentration.
Table 4. Effect of copper concentration

| Adsorbent used | Initial copper concentration (mg/l) | Optical density | Final copper concentration (mg/l) |
|----------------|-------------------------------------|-----------------|----------------------------------|
| Banana peel    | 1                                   | 0.016           | 0.25                             |
|                | 2.5                                 | 0.055           | 0.65                             |
|                | 5                                   | 0.191           | 2.3                              |
|                | 10                                  | 0.336           | 4.05                             |
|                | 15                                  | 0.340           | 4.2                              |
| Banana stem    | 1                                   | 0.014           | 0.2                              |
|                | 2.5                                 | 0.029           | 0.3                              |
|                | 5                                   | 0.051           | 0.55                             |
|                | 10                                  | 0.234           | 2.75                             |
|                | 15                                  | 0.249           | 2.95                             |

Figure 3.6 Removal of copper from waste water sample
Waste water was collected from plywood factory having higher copper content and subjected to quality analysis. Initial copper content of the sample was previously determined. The removal of copper from waste water using banana peel and banana stem was determined using colorimetric method. The parameters like pH, adsorbent dose and particle size which produced maximum adsorption values applied in the analysis of the waste water sample. Initial copper concentration of waste water sample = 177.9 mg/l
After the addition of banana peel copper concentration = 60.15 mg/l
After the addition of banana stem copper concentration = 50 mg/l
Hence it shows that in waste water banana peel reduces 60.18% of copper content. By using banana stem the percentage of copper removal was found to be 71.89 %. The experimental result indicates that the banana stem has got more efficiency in copper removal compared to banana peel.

3.7 Adsorption isotherms
The equilibrium values were plotted using freundlich and Langmuir adsorption isotherms to find out the equilibrium relationship between adsorbent and adsorbate. Freundlich adsorption isotherm was suitably fitted and indicates chemical adsorption.

3.7.1 Langmuir adsorption isotherm
The values obtained from the experiments should not fit on Langmuir adsorption isotherm so there is no physical adsorption takes place.
3.7.2 Freundlich adsorption isotherm
The values obtained from the experiments fit on freundlich adsorption isotherm so there was chemical adsorption.

Figure 8. Langmuir adsorption isotherm for banana peel

Figure 9. Langmuir adsorption isotherm for banana stem
Banana peel and banana stem are highly efficient for the removal of copper from water. Banana stems having more adsorption capacity compared to banana peel. Maximum adsorption takes place at a pH 5 for peel and at pH 9 for stem. For adsorbent dose 1 g was the equilibrium value for both adsorbents. 125 µm particle sizes were found to be favorable for the effective adsorption. Maximum adsorption on concentration of copper was found to be 1 mg/l for banana peel and 5 mg/l for banana peel. The copper removal efficiency of banana peel in water found to be 75% and in the case of banana stem it would be 89%. Freundlich adsorption isotherm model was well fit in the equilibrium values of adsorption of copper by both banana peel and banana stem. The efficiency of removal of copper from waste water was found to be 60.18% for banana peel and 71.89% for banana stem. Hence we can conclude that both the adsorbents are efficient for the removal of copper from water and waste water and it is an economical as well as eco-friendly method for the removal of copper.

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