

Removal of Copper and Zinc from Aqueous Solutions by Using Low Cost Adsorbents

Mayur A. Chavan¹, Sachin Mane²

¹Student, D. Y. Patil College of Engineering, Akurdi.

²Assistant Professor, D. Y. Patil College of Engineering, Akurdi.

Abstract: As the current global trend towards more stringent environmental norms, technical application, and cost effectiveness became key factors in the selections of adsorbents for water and waste water treatment. Recently, various low cost adsorbents derived from agricultural material, industrial waste material and by products or natural materials, have been intensively investigated. So the development of value added by products from waste material is to be welcomed. In the present work, the potential of using papaya seeds and eggshell powder as a sorbent for removal of Copper and Zinc from aqueous solution is investigated. Calcium carbonate, magnesium carbonate and calcium phosphate are the main constituents of eggshell powder, which have good adsorption capacity. A batch scale experiment for different amount of adsorbents in different concentrations of both metals in mixed combination is carried out. The sorption characteristic of the sorbent will be studied under various experimental conditions, such as pH, contact time, adsorption dose and concentration of Copper and Zinc. The optimum pH for maximum uptake of Copper and Zinc was at pH 6. Results indicate that removal efficiency for Copper and Zinc is about 99% using eggshell powder and 95% using Papaya seeds powder.

Keywords: Adsorption, batch experiment, Copper, Eggshell powder, papaya seeds, Zinc.

1. Introduction

Waste water contamination is ever increasing problem which the whole world is now facing. Waste water comprises liquid waste discharged by domestic, industrial waste, agricultural activity and commercial properties. Industrial waste constitutes the major source of metal pollution in natural water. Toxic heavy metals (Cd, Zn, Pb and Ni) are major pollutant of waste water which is very hazardous. Various methods are used for the removal of these heavy metal like chemical oxidation and reductions, ion exchange, Electrodialysis, Electro precipitation, extraction of liquid, microfiltration etc. which are costly as well as not completely remove the metal[2]. Biosorption is potentially an attractive technology for treatment of waste water for retaining heavy metal form dilute solution. Biosorption has been suggested as cheaper, more effective and minimization of chemical and biological sludge[3]. There are many natural bisorbent are present in our environment which have the capacity to remove heavy metal from waste water [3].

In this study papaya seeds and eggshell are used as low cost adsorbent to absorb copper and zinc from water. The main characteristic of papaya seed that is useful in metal removal is due to its chemical composition. Papaya seed is made up of cellulose and lignin as major constituents and may also contain other polar functional groups of lignin, which include alcohol, ketone, aldehydes, phenol, carboxylic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution[7]. Due to the high production and consumption of papaya fruits, massive amounts of seeds are readily available to be used as biosorbents instead of being disposed and causing environmental problems

Chicken eggshell can be used to adsorb heavy metal in wastewater due to its calcium carbonate content which is responsible for metal adsorption[2]. This alternative method will not produce chemical sludge, hence there is no secondary or other pollution and it is more efficient and easy to operate compared to other methods.

2. Materials and Methods

2.1 Materials

Copper sulfate (CuSO₄) was used for the preparation of stock standard solutions of Cu(II) and Zinc Nitrate (Zn(NO₃)₂·6H₂O) was used for the preparation of stock standard solutions of Zinc in distilled water. For adjusting pH throughout the experiment, 1 N hydrochloric acid (HCl) and/or 1 N sodium hydroxide (NaOH) were used as necessary. A stock solution of 1000 mg/L was prepared and subsequently diluted when necessary.

All chemical used in the present study were of analytical Grade. Atomic adsorption spectrometer (AAS Model Thermo Fisher AAS 201) was used to measure the Cu(II) and Zn(II) concentration.

3. Preparation of Adsorbents

3.1 Papaya Seeds Powder

The Papaya seeds were collected from a local market and washed several times to remove impurities and other dirt material. Papaya seeds were washed with distilled water to get rid of transparent gelatinous material. The washed materials were dried in oven at 60°C for 48 hr. to ensure the removal of moisture content from the seeds. The dried Papaya seeds was then crushed into fine particles and then finally sieved to fine powder of less than 0.425mm particle

size. The powdered form of Papaya seeds was stored in a container in a cool dry place for further use. No other physical or chemical treatments were employed prior to sorption experiments.

3.2 Egg Shell Powder

The eggshell used in the experiment collected from different hotels located in Pune city, India. The samples were then washed with distilled water several times to remove impurities and dirt. The eggshells were then dried in oven at 40° C. The dried eggshells were ground into small particles and then finally sieved to fine powder of less than 0.425mm particle size and stored into small particles and stored in air tight container for future use.

4. Effect of pH on Cu(II) and Zn(II) adsorption

The effect of solution pH on adsorption of Cu(II) and Zn(II) was studied by mixing 2.5 g of individual adsorbent with 250 ml of mixed metal solution having concentration of 3.6mg/L, 4.2 mg/L, of Copper and 3.3 mg/L and 3.7 mg/L of Zinc concentration at different pH value (5 – 8) at room temperature. The pH was adjusted with 1 N NaOH or 1 N HCl solutions and pH meter was used to pH. Agitation rate was kept at a constant stirring speed of 170 rpm for 180 minutes. The remaining concentration of Cu(II) and Zn(II) after adsorption was measured using AAS.

The percentage uptake of Cu(II) and Zn(II) was calculated according to the following equation:

$$\text{Percentage uptake (\%)} = \frac{C_{ini} - C_{fin}}{C_{ini}} \times 100$$

Where C_{ini} is the initial concentration and C_{fin} is the concentration at time t .

5. Effect of Contact time on Cu(II) and Zn(II) adsorption

The effect of solution Contact Time on adsorption of Cu(II) and Zn(II) was studied by mixing 1.25 g of both adsorbents with 250 ml of mixed metal solution having concentration of 4.2 mg/L, of Copper and 5mg/L of Zinc concentration at pH value of 6 at room temperature. Agitation was made at a constant stirring rate of 170 rpm. The concentration remaining of Cu(II) and Zn(II) after adsorption was measured at different time intervals of 30, 60 120 and 180 minutes using AAS.

The percentage uptake of Cu(II) and Zn(II) was calculated according to the following equation:

$$\text{Percentage removal (\%)} = \frac{C_{ini} - C_{fin}}{C_{ini}} \times 100$$

Where C_{ini} is the initial concentration and C_{fin} is the concentration at time t .

6. Effect of Adsorption dose on Cu(II) and Zn(II) Adsorption

The effect of adsorption dose on Cu(II) and Zn(II) adsorption was investigated by different amount of adsorbents 1.5 gm, 2

gm and 2.5 gm in 250 ml of mixed metal solution having initial concentration of 4.4 mg/l, 7.9 mg/l of Copper and 5 mg/l, 9.2 mg/l of Zinc. Agitation was made at a constant stirring speed of 170 rpm for 120 minutes. The remaining concentration of Cu(II) and Zn(II) after adsorption was measured using atomic adsorption spectrometer (AAS).

7. Results and Discussion

7.1 Effect of pH on Cu(II) and Zn(II) adsorption

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the ionization degree and adsorbate specification. The batch experiment studied of mixed metal solution having concentration of 3.6mg/L, 4.2 mg/L, of Copper and 3.3 mg/L and 3.7 mg/L of Zinc concentration at different pH value ranging from 5to 8 were carried at room temperature. Fig. 1 and Fig. 2 shows that maximum percentage of Cu(II) and Zn(II) adsorption on egg shell and papaya seed were observed at pH 6.

Table 1: Effect of pH on the adsorption of Cu(II) and Zn(II) by chicken eggshells

| Sr. no | Quantity of Eggshell powder(gm) | pH | Initial concentration of Cu (mg/L) | Initial concentration of Zn (mg/L) |
|---------------------------|---------------------------------|----|------------------------------------|------------------------------------|
| | | | 3.6 | 3.3 |
| Adsorption Efficiency (%) | | | | |
| 1 | 2.5 | 5 | 97 | 99 |
| 2 | 2.5 | 6 | 99.7 | 99 |
| 3 | 2.5 | 7 | 95.8 | 96.6 |
| 4 | 2.5 | 8 | 97 | 99 |

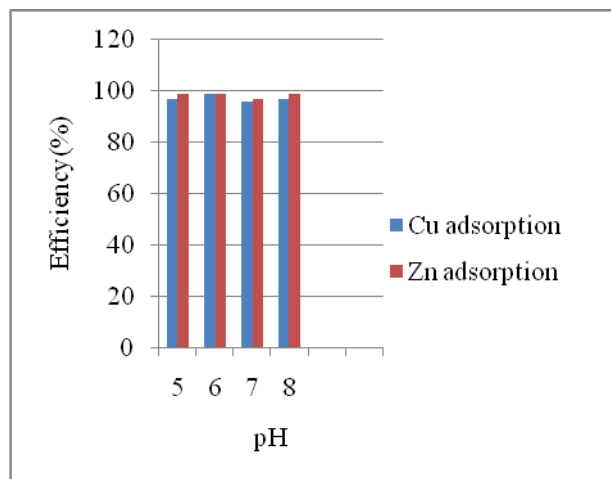


Figure 1: Effect of pH on the adsorption of Cu(II) and Zn(II) by chicken eggshells

Table 2 : Effect of pH on the adsorption of Cu(II) and Zn(II) by papaya seeds

| Sr. no | Quantity of Papaya seeds powder (gm) | pH | Initial concentration of Cu (mg/L) | Initial concentration of Zn (mg/L) |
|---------------------------|--------------------------------------|----|------------------------------------|------------------------------------|
| | | | 4.2 | 3.7 |
| Adsorption Efficiency (%) | | | | |
| 1 | 2.5 | 5 | 90 | 85 |
| 2 | 2.5 | 6 | 95.9 | 91 |
| 3 | 2.5 | 7 | 95.9 | 89 |
| 4 | 2.5 | 8 | 93 | 88 |

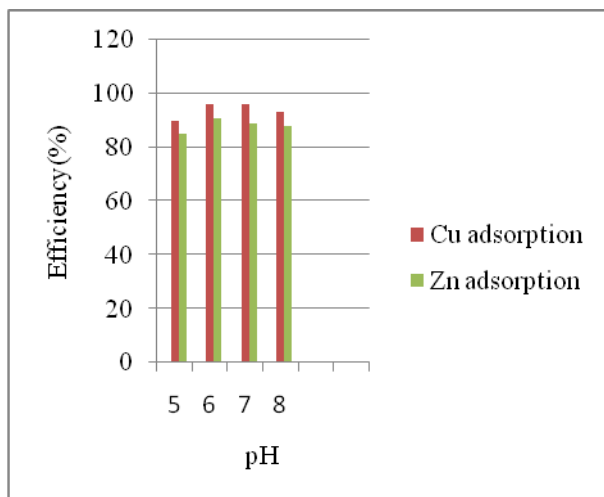


Figure 2: Effect of pH on the adsorption of Cu(II) and Zn(II) by papaya seeds

7.2 Effect of Contact Time on Cu(II) and Zn(II) Adsorption

Contact time plays an important role in adsorption process and the effect of contact time on adsorption capacity has been studied by varying the contact time from 30 to 180 minutes. The Copper and Zinc adsorption percentage at different contact time by chicken eggshell and papaya seeds is shown in Fig 3. Results indicated that the Cu(II) adsorption by chicken eggshell and papaya seeds reached almost 95% and Zn(II) adsorption by chicken eggshell and papaya seeds reached almost 86% at 2 hours contact time.

Table 3: Effect of contact time on the adsorption of Cu(II) and Zn(II) by chicken egg shells and papaya seeds

| Sr. no | Quantity of Papaya seeds powder (gm) | Quantity of Eggshell powder (gm) | Contact Time (minutes) | Initial concentration of Cu (mg/L) | Initial concentration of Zn(mg/L) |
|--------|--------------------------------------|----------------------------------|------------------------|------------------------------------|-----------------------------------|
| | | | | 4.2 | 5 |
| | | | | Adsorption Efficiency (%) | |
| 1 | 1.25 | 1.25 | 30 | 88.9 | 82 |
| 2 | 1.25 | 1.25 | 60 | 92.8 | 80 |
| 3 | 1.25 | 1.25 | 120 | 95.2 | 86 |
| 4 | 1.25 | 1.25 | 180 | 95.2 | 84 |

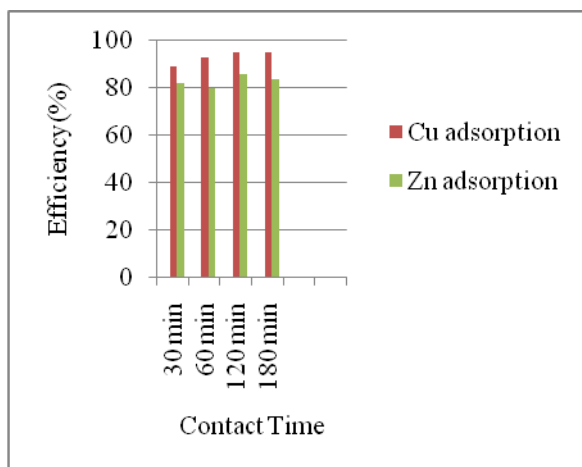


Figure 3: Effect of contact time on the adsorption of Cu(II) and Zn(II) by chicken egg shells and papaya seeds

7.3 Effect of Adsorption Dose

The effect of adsorbent dosage was studied by varying the amount of adsorbent from 1.5 gm to 2.5 gm in 250 ml of mixed metal solution of copper and zinc. After equilibrium the solutions were analyzed for the amount of Cu(II) and Zn(II). The results indicate that adsorption increased with increase in adsorption dosage.

Table 4: Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by chicken egg shells and papaya seeds.

| Sr. no | Quantity of Papaya seeds powder(gm) | Quantity of Eggshell powder(gm) | Initial concentration of Cu (mg/L) | Initial concentration of Zn(mg/L) |
|--------|-------------------------------------|---------------------------------|------------------------------------|-----------------------------------|
| | | | 4.4 | 5.0 |
| | | | Adsorption Efficiency (%) | |
| 1 | 1.5 | 1.5 | 95 | 88 |
| 2 | 2.0 | 2.0 | 97 | 90 |

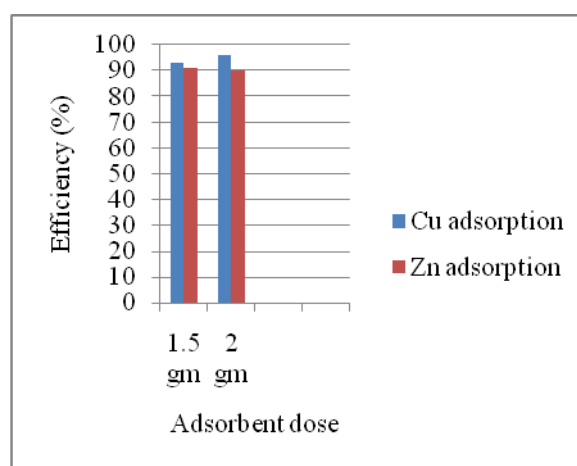


Figure 4: Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by chicken egg shells and papaya seeds

Table 5: Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by chicken egg shells and papaya seeds

| Sr. no | Quantity of Papaya seeds powder(gm) | Quantity of Eggshell powder(gm) | Initial concentration of Cu (mg/L) | Initial concentration of Zn(mg/L) |
|--------|-------------------------------------|---------------------------------|------------------------------------|-----------------------------------|
| | | | 7.9 | 9.2 |
| | | | Adsorption Efficiency (%) | |
| 1 | 1.5 | 1.5 | 93 | 91 |
| 2 | 2.0 | 2.0 | 97 | 93 |

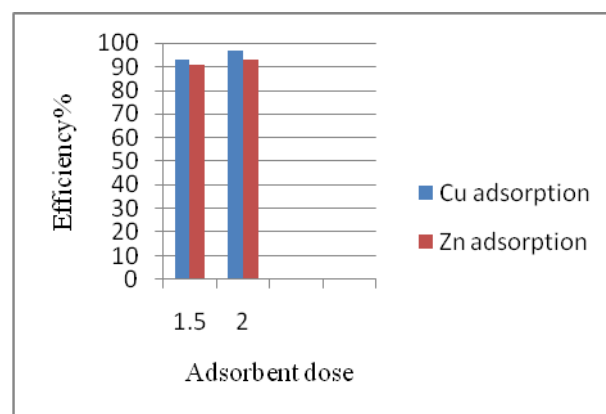


Figure 5: Effect of adsorption dose on the adsorption of Cu(II) and Zn(II) by chicken egg shells and papaya seeds

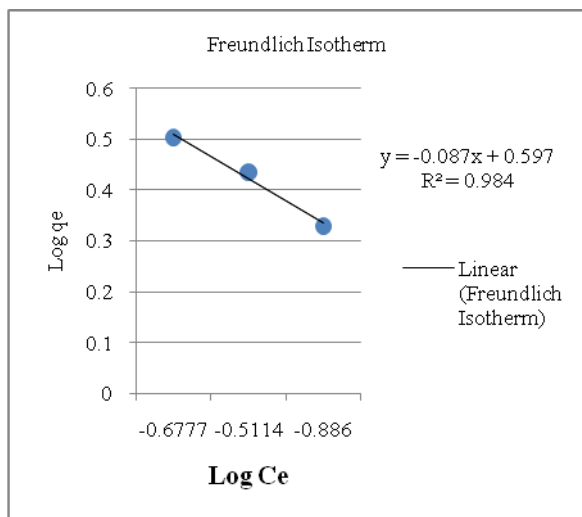


Figure 6: Freundlich Isotherm shown amount of copper adsorbed and equilibrium concentration

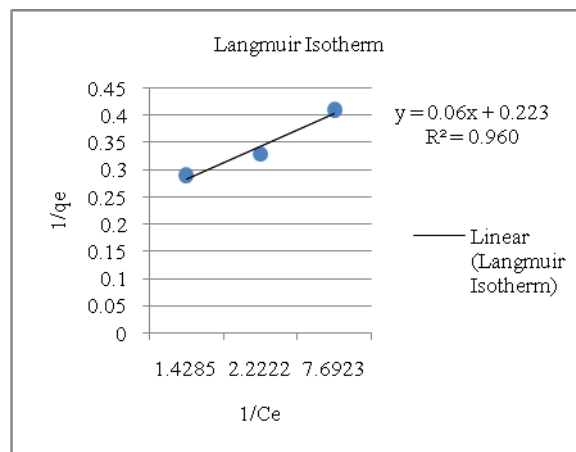


Figure 9: Langmuir Isotherm shown amount of zinc adsorbed and equilibrium concentration

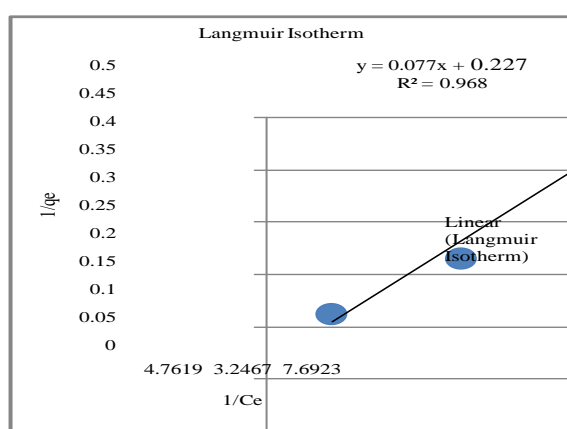


Figure 7: Langmuir Isotherm shown amount of copper adsorbed and equilibrium concentration

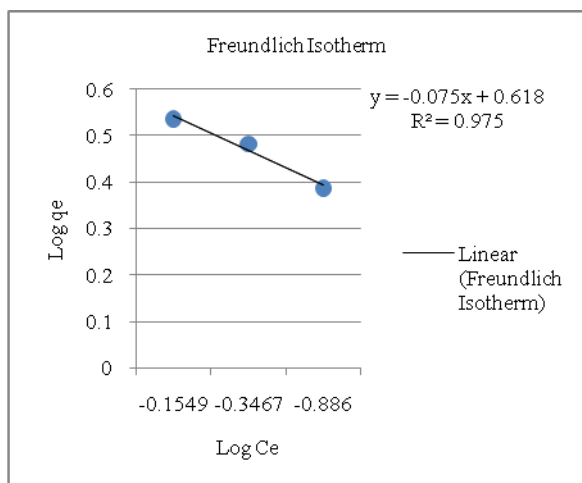


Figure 8: Langmuir Isotherm shown amount of zinc adsorbed and equilibrium concentration

8. Conclusion

The removal of Cu(II) and Zn(II) from water by using chicken eggshells and papaya seeds has been experimented under several conditions such as at different pH, contact time and adsorption dose. The optimum pH for copper and zinc adsorption was found at pH 6. The optimum contact time was found to be 120 minutes at an agitation speed of 170 rpm. Increase in adsorption dose increased the adsorption of metals. This study shows that chicken eggshells and papaya seeds have high potential to be used as low-cost adsorbent for the removal of copper and zinc from water.

Since the metals uptake by chicken eggshells is highly dependent on the number of active binding sites or functional groups on the adsorbents, further study can be attempted to enhance the existing results by modifying the chicken eggshell and papaya seeds adsorbents using bases or acids. Due to chemical modification, it is expected that the number of active binding sites or functional groups on the adsorbents might be increased which may result into increased adsorption capacity of the adsorbents.

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