Adsorption of Heavy Metals from Waste Waters using Waste Biomass

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Abstract- **The organic compounds and various kinds of heavy metals present in waste water are harmful for environment and aquatic life. Now days much attention is being given to remove these contaminants and a lot of work is being done in this direction .many physico-chemical method are being used to remove and recover the metals from waste water. Adsorption is one of the alternatives and is an effective separation technique used to treat waste waters. Cost is an important parameter and the aim of this work is to study the removal of Chromium and Zinc from aqueous solution using low cost adsorbent. The effect of variation in different parameters like metal concentration, contact time, pH value and dose of adsorbent was investigated. The biomass adsorbent is effective in dilute solutions. The metal removal percentage is high and the data fits well in Lanmuir and Freundlich isotherm.**

Keywords- Adsorbent; Heavy metals; Biomass; Langmuir isotherm; Freundlich isotherm.

I. INTRODUCTION

Rapid industrialization has led to increase disposal of heavy metals into the environment. Their presence creates environmental inequality and serious health hazards. Heavy metals in particular are a group of pollutants of major concern in the aquatic environment due to their toxicity [1,2].

In order to reduce pollution, contaminated waters need to be cleaned. To minimize this problem, biosorption can be a part of the solution. Biosorption of heavy metals by bacterial fungal or algae biomass (live or dead cells) or agricultural waste biomass [3-18] has been recognized as a potential alternative to existing technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for the removal of heavy metals from industrial wastewater because all these processes have the limitations of technical or economic viability.

The literature reveals two distinct approaches to use of living organisms or dead biomass [19, 20]. There are significant practical limitations to systems which use living microorganisms, like the microbial growth is inhibited when the concentrations of metal ions are too high or when significant amount of metal ions are adsorbed by microorganisms [21]. Dead cells or agricultural wastes accumulate heavy metal ions to the same or to a greater extent than living cells, because the changes which occur in the cell structure after the cells are dry killed, affect adsorption in a positive manner [22,23].. The main sources of biomass include seaweeds, microorganisms (bacteria, fungi, yeast, molds), activated sludge, fermentation waste and other specially propagated biomasses [24-26] or some agricultural wastes such as sugarcane, bagasse, straw, wool fiber, leaves, jute coir, rice husk, saw dust, cotton seed hulls, coconut shell, saw dust, and crop milling waste [27-32] etc. Coal and straw are inexpensive but ineffective. Peat moss has been found effective in adsorbing heavy metals [33], also gave good results.

For metal removal applications, the use of dead biomass or agricultural waste [34-37] may be preferable as large quantities are readily and cheaply available as a byproduct of various industries. This paper deals with the removal of Chromium and Zinc metals, which are among the major contaminants in industrial effluents. The sources of Chromium in waste waters include the industries such as chrome plating, petroleum refining, leather, tanning, wood preserving, textile manufacturing and pulp processing industries and zinc sources include effluents from paint, rubber, dye, wood preservatives, ointments and electroplating industries.

There are major health risks due to heavy metal ingestion for eg. chromium causes irritation, nausea and vomiting at low level exposure, kidney, liver, circulatory and nerve tissue damage at long term exposure and zinc causes nausea and vomiting.

The aim of this work was to study the biosorption of metal ions (Cr6+ and Zn2+) from single ion solutions using waste biomass, a by product of pharmaceutical fermentation industry. The influence of initial concentration of heavy metals, pH and contact time in the aqueous solutions on biosorption of metal ions was studied. The biosorption data were evaluated in terms of equilibrium isotherms using the Langmuir and Freundlich adsorption isotherm models.

II. MATERIALS AND METHODS

A. Adsorbent preparation

Waste biomass was collected from a pharmaceutical company. It was dried and pulverized in a blender . Then it was sieved to obtain an uniform particle size of 2 mm. This biomass was then washed several times with distilled water and then placed in an oven at 80^0C for two days. This dried biomass was used for the sorption experiments.

B. Preparation of solution

Aqueous stock solution (1000mg/l) of Cr^{6+} and Zn^{2+} was prepared using salts of $K_2Cr_2O_7$ and $ZnSO_4$ respectively. The concentration range was varied between

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5-50mg/l for metal aqueous solution. The solution pH was adjusted with 0.1 N HCl or 0.1 NaOH.

C. Batch sorption studies

(a) For the effect of initial metal concentration

Experiments were performed using 1g of biomass adsorbent in 100ml of metal solution. Four sets of 10 flasks each ,were used with the metal Cr concentration of 5,15,25 and 50 mg/l per set. These flasks were kept on a shaker at 120 rpm for 24 hrs. At regular time intervals (0-24 hrs.). The samples were filtered with Whatman filter paper and the filterate was analyzed by using AAS for the metal concentration. Similar procedure was repeated for Zn solution and the data is reported as the percentage mof metal removal.

(b) *For the effect of pH*

Four sets of 10 flasks each ,were used having pH 2, 3, 4 and 5 with the metal Cr^{6+} concentration of 25 mg/l and 1g of the adsorbent. These flasks were replaced on the shaker ar 120 rpm and at regular time intervals. The samples for different pH were filtered and analyzed for the amount of metal removed by adsorption. same procedure was repeated with Zn solution. The data is reported in terms of the % metal removal.

Similar batch experiments were conducted for known metal concentration with varying dose of adsorbent to see the effects of amount of adsorbent on the metal removal efficiency.

D. Adsorption Isotherms

1) Langmuir Adsorption Isotherm

Langmuir developed an adsorption model, which is valid for a single layer adsorption with the assumptions that the molecules are adsorbed on the surface of the adsorbent and each site can accommodate only one molecule (monolayer) and that the adsorbed energy is the same at all sites. The area of site is fixed and its magnitude is determined solely by geometry of the surface.

The mathematical form of Langmuir isotherms is given as

$$qe = q_{max}\, bC_e/(1+ bC_e) \text{ -----------------(1a)}$$

Where

q_{max} and b are Langmuir constants related to adsorption capacity and the enrgy of adsorption respectively. The equation can also be written in the following form as-

$$(Ce/qe) = 1/(q_{max}.b) + Ce/q_{max} \text{ ---------------------------(1b)}$$

q_{max} and b can be determined from the linear plot of Ce/qe versus Ce. The adsorbed molecules cannot migrate across the surface or integrate with the neighboring molecules, where q_e is the mass of solute adsorbed per unit mass of adsorbent at the concentration Ce.

2) Freundlich Adsorption Isotherm

Freundlich (1962) developed an empirical equation for the adsorption isotherm, which encompasses the heterogeneity of the surface and the experimental distribution of the sites and their energies. This equation can also be explaining the variation of adsorption with concentration over a limited range at constant temperature. The freundlich adsorption isotherm equation, on taking logarithmic on both side, can be expressed as

$$\log qe = \log K + (1/n) \log Ce$$

K(mg/g)- an indicator of the adsorption capacity and 1/n(mg/lit)-adsorption intensity, can be calculated by plotting (log qe) Vs (log Ce).

III. RESULTS

The effect of pH on the adsorption of metals was studied by performing batch adsorption experiments. The results are plotted in the Fig.1. The sorption experiments were repeated for the different metal solutions, having different initial concentrations ranging from 5-50 mg/L at room temperature and pH 4. The concentrations of solutions were measured at various time intervals. The result data obtained, showing the effect of contact time on the removal of metal is plotted in Fig.2. The effect of initial metal concentration on the removal percentage of metal is shown in Fig. 3.

The effect of the adsorbent dose used for adsorption was also studied and the results are plotted in Fig. 4

The adsorption data is fitted to the standard adsorption isotherm models. The Langmuir Isotherm model fitting is shown in Fig. 5 and Fig. 6, and the Freundlich Isotherm model fitting is shown in Fig. 7 and Fig. 8.

The Langmuir constants 'b' and 'q_{max}' were calculated from this isotherm and their values are given in the Table 1(a). Also the Freundlich constants (k_F and n) were calculated and recorded in the Table 1(b).

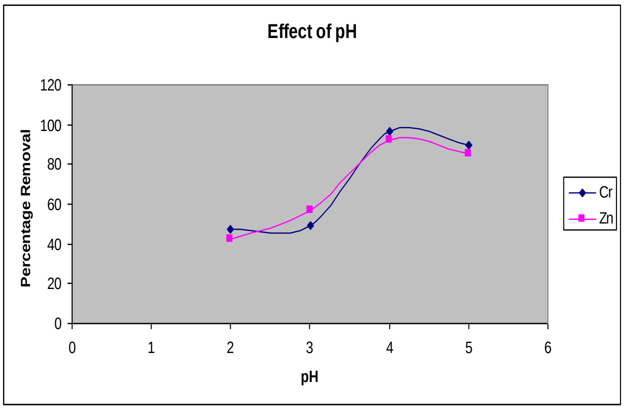

Fig. 1. Effect of pH on % removal of Metals by adsorption on biomass

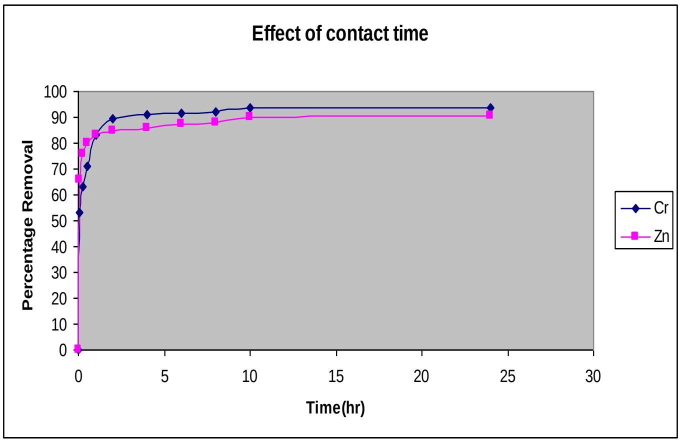

Fig. 2. Effect of contact time on % removal of Metals by adsorption on biomass

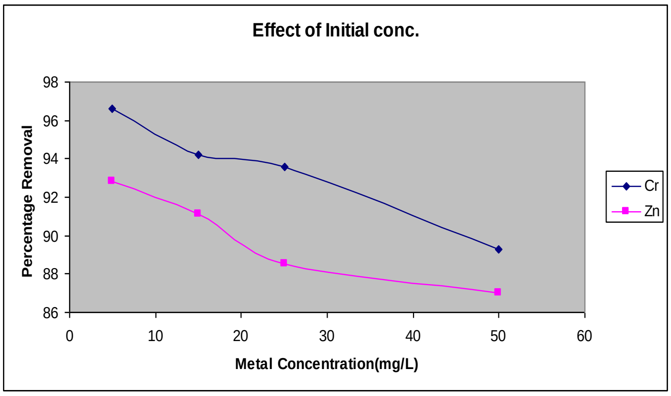

Fig. 3. Effect of initial conc. of dye on % removal of Metals by adsorption on biomass

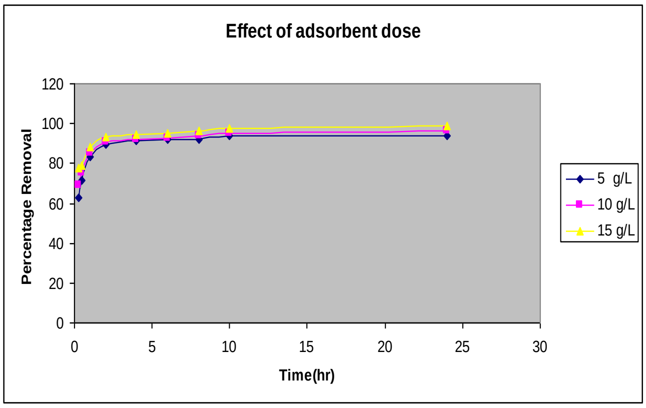

Fig. 4. Effect of adsorbent dose on % removal of Metals by adsorption on biomass

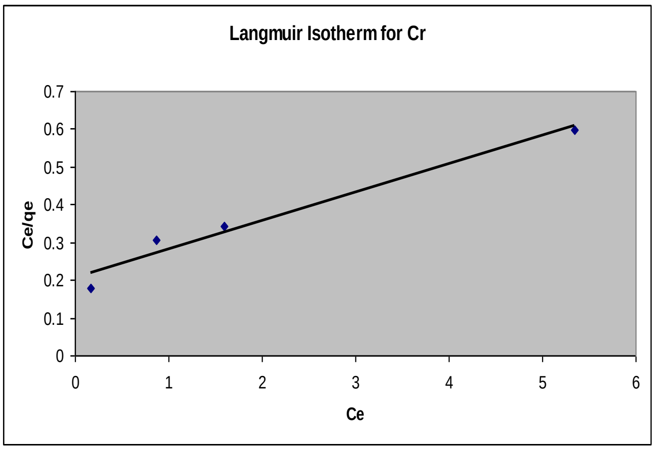

Fig. 5. Langmuir Isotherm for the adsorption of Chromium on biomass

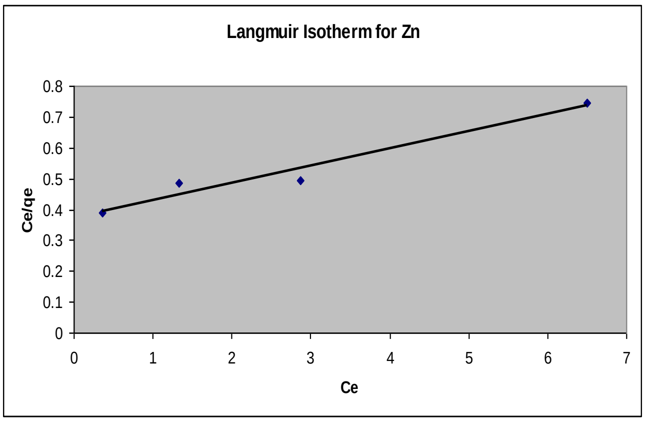

Fig. 6. Langmuir Isotherm for the adsorption of Zinc on biomass

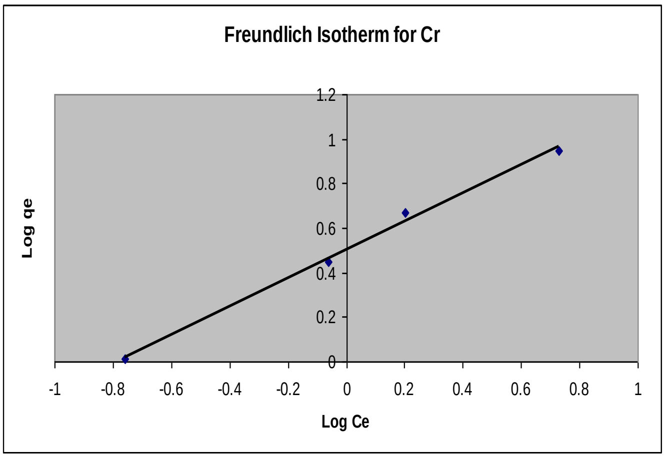

Fig. 7. Freundlich Isotherm for the adsorption of Chromium on biomass

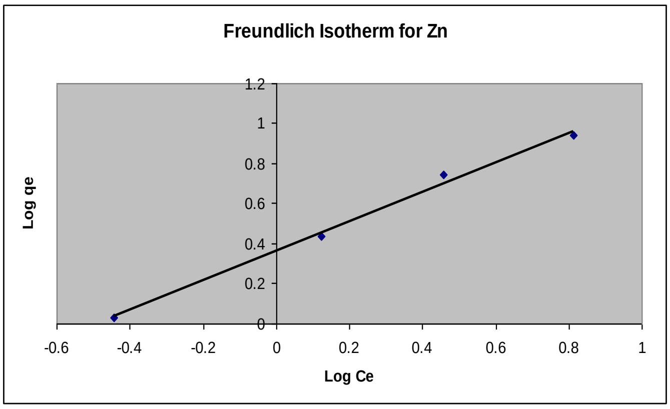

Fig. 8. Freundlich Isotherm for the adsorption of Zinc on biomass

TABLE 1(a). Langmuir Isotherm Constants

Constants	Cr	Zn
q_{max} , (mg/g)	13.3	17.9
b, (L/mg)	0.015	0.020
R^2	0.96	0.95

TABLE 1(b). Freundlich Isotherm Constants

Constants	Cr	Zn
K, (mg/g)	3.18	2.3
1/n, (L/mg)	0.64	0.74
R^2	0.99	0.99

IV. DISCUSSION

A. Effect of pH

Fig. 1. represents the pH effect on the adsorption of Cr^{6+} and Zn^{2+} .It is evident that the pH value has a significant effect on the adsorption of metals as it influences the electrostatic binding of ions . In the present study this pH effect is observed over the pH values 2, 3, 4 and 5 at initial concentration of metal of 25mg/l. The percent removal of metals is maximum at pH 4.The metal uptake was observed to be 42.3% for Zn and 43% for Cr at pH 2 and at pH 3 it was noted as 55.8% for Zn and 47% for Cr. It increased up to 92.24% for Zn and 97.8% for Cr at pH 4. But at pH 5 the percent removal of both metals again became low (86.5% for Zn ,90.2% for Cr). This trend change can be explained as , at lower pH the active sites are protonated , protons and metal ions compete for the adsorption sites and very high pH values may damage the structure of the biosorbent material and the decrease in the sorption capacity have been observed.

Adsorption also depends on the solubility of adsorbate. Sorption increases with decreasing solubility and solubility in most cases decrease with increasing pH, therefore the adsorption increases with increasing pH. But the further increase in pH may result in very low solubility of metal, so it may precipitate and does not get adsorbed on the adsorbent surface.

B. Effect of contact time

The results shown in Fig.2 reveal that the amount of the adsorbent metal onto the biomass increases with time and slowly reaches a value after some time, which is nearly constant and no significant change is observed beyond that.This time shows the value of equilibrium time which is about 24 hrs for these experiments. the rate of adsorption of metal is initially high but retards gradually as the concentration driving force decreases continuously.A large fraction of metal concentration is adsorbed in the first 30 minutes for an initial concentration of 25 mg/l of metal ions at room temperature.The uptake gradually reaches to a maximum indicating that the adsorbent is saturated at this level.

C. Effect of initial concentration

As shown in Fig. 3 the amount of metal adsorbed is depends on the initial concentration of metals. A series of experiments for Cr and Zn metal ions has been carried out at different initial concentration (5,15,25 and 50mg/l) at room temperature with pH 4.The amount of metal adsorb on the biomass increases with an increase in the initial metal concentration in the solution but the overall fraction remove the decreases with increasing metal concentration. The initial rate of adsorption is high for higher metal concentration , this may be explained as there is initially great amount of metal ions to be adsorbed on the adsorbent surface but with time the rate of adsorption decreases which may be due to reduced available surface of the adsorbent. At pH 4 the % of metal adsorbed at an initial concentration of 5mg/l of Cr and Zn are 96.58% and 92.8% respectively but for an initial concentration of 25 mg/l , the percent removal for Cr and Zn are 93.6% and 88.5 % respectively. The percentage removal of metals is greater for lower initial concentration of metal solutions.

D. Effect of adsorbent dose

The biomass quantity used for adsorption also affects the equilibrium adsorption of metal and the rate of adsorption also with time. The effect of the biomass dose on the adsorption of metals is shown in Fig. 4.

For the study of this effect, dose of biomass used for adsorption experiments was 5,10 and 15 g/L at an initial concentration of Cr metal solution equal to 25 mg/L and pH 4. It was observed that the percentage of metal removed increases on increasing the dose of adsorbent but the rate of increase of metal removal was not proportionate to the increase in biomass amount.

At 5 g/L adsorbent dose the maximum metal uptake was around 94% which inceased to 96.4% with 10 g adsorbent and for 15 g/L of biomass the percentage of Cr removed after 24hrs. was 99%.

E. Adsorption Isotherms

The experimental data fits well with the Langmuir and Freundlich adsorption isotherm models. When C_e/q_e was plotted against C_e, a straight line with slope of $1/q_{max}$ was obtained indicating that the adsorption on the biomass follows the Langmuir isotherm. The Langmuir model for Cr is shown in Fig. 5 and for Zn in Fig. 6. The Langmuir constants 'b' and ' q_{max} ' were calculated from these isotherms and their values are given in Table 1(a).

Conformation of the experimental data into the Langmuir isotherm model indicates the homogeneous nature of the adsorbent surface. The result also demonstrates the formation of monolayer coverage of metal molecule at the outer surface of the adsorbent.

The plot of log q_e versus log C_e gives straight lines with slope 1/n, which shows that the adsorption of the metals also follows the Freundlich isotherm. The Freundlich model for Cr is shown in Fig. 7 and for Zn in Fig .8. Accordingly, Freundlich constants (k_F and n) were calculated and recorded in Table 1(b).

The constant k_F can be defined as the adsorption or a distribution coefficient and represents the quantity of metal adsorbed onto the adsorbent for a unit equilibrium concentration. The slope 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

The plots show that the adsorption of these metals on the biomass follows Freundlich model better than the Langmuir model.

V. CONCLUSION

The present investigation shows that this biomass waste from a pharmaceutical industry can be effectively used as an adsorbent material for the removal of heavy metals from aqueous media over a wide range of concentration .Zn and Cr metal ions adsorb strongly on the surface of biomass and can be removed up to 90 % and above. The equilibrium time for this study is nearly 24hrs .It is found that the maximum adsorption of these metals occurs at pH 4 and at lower initial concentrations of metals. The experimental data fits well with the Langmuir and Freundlich adsorption isotherm models. The adsorbent used is cost effective and easily available so it can be employed conveniently for the treatment of industrial waste waters.

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