

Feasibility Studies on the Removal of Chromium (VI) from Simulated Wastewater Using Banana Sheath Fibers (BSF)

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Abstract

The present study aims to assess the efficiency of Banana Sheath Fibers (BSF) in treating chromium (VI) from simulated wastewater. The batch studies were performed by studying different parameters such as concentration, pH, adsorbent dosage, time and the optimum concentration was found to be 200 mg/L which attained maximum efficiency of 85% at 1 hour for 1 g of adsorbent dosage and was found to be independent of pH range (3 to 9). The column studies were carried out for two different bed heights (10 cm, 20 cm) and flow rates (5 ml/min, 10 ml/min), from which it was found that the increase in bed height and decrease in flow rate gives good efficiency. The results were found to be well fitted in the Freundlich adsorption isotherm. These studies prove that the BSF could be an effective biosorbent for the removal of Chromium (VI) from aqueous solutions.

Keywords: Adsorption Isotherms, Banana Sheath Fibers, Chromium (VI), Simulated Wastewater, Biosorbent

1. Introduction

The presence of heavy metals in the environment specifically in various water resources is of major concern because of their toxicity, non-biodegradable nature and threat to human, animal and plant life [1]. Heavy metal contamination occurs in aqueous waste of many industries such as electroplating industries, paint industries, textile manufacturing industries, leather tanning industries, iron & steel industries, metal finishing industries etc. [2] and ultimately disposed to land or in to water courses. The water contamination by toxic metals through the discharge of industrial wastewaters is a worldwide environmental problem [3]. Industrial effluents which discharged from the textile and tannery contains a higher amount of metals especially chromium, copper and cadmium [4].

Chromium is widely used in electroplating, leather tanning, dye, cement and photography industries producing large quantities of effluents containing the toxic metal. The Cr(VI) is of particular concern because of its toxicity. The recommended limit of Cr(VI) in potable water is only 0.05 mg/L. But the industrial and mining effluents contain much higher concentrations compared to the permissible limit [5]. The presence of Cr(VI) and other heavy metals in the environment has become a major threat to plant, animal and human life due to their bio-accumulating tendency and

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toxicity and therefore must be removed from municipal and industrial effluents before discharge. Resultantly, it is necessary that there are technologies for controlling the concentrations of these metals in aqueous emissions [6]. Thus, treatment of the effluent to reduce/remove the pollutant before discharging into the environment becomes inevitable.

Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent [7]. Despite its extensive use in the water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon.

The low cost agricultural waste by-products such as sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shell, neem bark, etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [8]. Biosorbents which produced from agro-wastes may act as a significant material for heavy metals adsorption.

Our country being one of the major producers of banana in the world derives high quantity of waste during processing banana plant for edible purposes. A lot of components of banana plant like banana peel, pseudostem, pith, leaves and rind have found applications in heavy metals removal. However, one other component viz. Banana Sheath Fibers (BSF) hasn't been given the same level of attention as others. BSF, an agro waste is discarded all over the world as useless material. The sheath fibers was normally utilized as biodegradable binding ropes and can be a suitable feed for ruminant. It is causing waste management problems though it has some compost and adsorbent potentiality. It is an abandoned, readily available, low cost, cheap and environment friendly bio-material [9].

In the present study, an attempt has been made to adopt BSF as biosorbent in the remediation of chromium contamination. A sift through literature reveals virtually no evidence of the utilization of BSF in heavy metal removal. Hence, it may be worth to test the potential and adsorption capacity of this agro-waste in removal of chromium.

2. Materials and Methods

2.1 Biosorbent Preparation

The BSF used in this study was obtained locally. The sheaths were subjected to repeated washing with water to remove dust & soluble impurities and dried in sunlight for 1 or 2 weeks. The dried fibers were then cut into small pieces, grounded and sieved to a uniform size (Fig. 1) [6, 10].



Figure 1. Biosorbent Preparation

2.2 Characterization of Banana Sheath Fibers

In this study, the physical parameters such as porosity, bulk density, pH, particle size were analyzed [1, 11].

2.2.1 Particle Size

Particle size, also called grain size, refers to the diameter of individual grains of sediment. The term may also be applied to other granular materials.

2.2.2 Bulk Density

Bulk density is a property of powders, granules, and other "divided" solids, especially used in reference to mineral components (soil, gravel), chemical substances, (pharmaceutical) ingredients, foodstuff, or any other masses of corpuscular or particulate matter. It is defined as the mass of many particles of the material divided by the total volume they occupy. The total volume includes particle volume, inter-particle void volume and internal pore volume.

2.2.3 Porosity

Porosity or void fraction is a measure of the void (empty) spaces in a material, and is a fraction of the volume of voids over the total volume Eq. (1, 2).

$$\text{Void Ratio (e)} = V_v / V_s \quad (1)$$

$$\text{Porosity} = 1 / e \quad (2)$$

2.2.4 pH

pH is a measure of the activity of the (solvated) hydrogen ion. Pure water has a pH very close to 7

at 25°C. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline.

2.3 Adsorbate Preparation

The simulated stock solution of Cr(VI) (1000 mg/L) was prepared using potassium chromate by dissolving in the distilled water. The stock solution was then diluted with distilled water to obtain the desired concentration.



Figure 2. Desired Concentration of Chromium Solution in Conical Flasks

2.4 Batch Studies

2.4.1 Treatment Using Unmodified Banana Sheath Fibers

The batch studies were done by studying different parameters. In this study, the parameters [1, 2, 3, 6, 9, 11, 12] such as concentration, pH, adsorbent dosage, time were studied (Table 1).

Table 1. Controlling Parameters of Chromium Adsorption

Concentration(mg/L)	50, 100, 200
pH	3, 5, 7, 9
Adsorbent Dosage (g)	1, 2, 3, 4, 5
Time (hr)	1, 2, 3, 4

The simulated stock solution was diluted using distilled water to obtain the desired concentration. The desired concentration was selected and a required amount was prepared (Fig. 2). 100 ml of chromium solution was taken in different conical flasks and the appropriate pH was set. The pH was adjusted using concentrated HCl and NaOH solutions.

The appropriate amount of adsorbent was then added to the conical flasks containing the simulated chromium solution. The conical flasks were then placed in the shaker to achieve uniform mixing for 135 rpm, at room temperature. The samples were collected at the appropriate intervals (Fig. 3). The

collected samples were then analyzed using Atomic Absorption Spectroscopy (AAS) at 357 nm.



Figure 3. Samples Collected at Different Time Intervals

The observed values from AAS were then tabulated and the efficiencies were found by using the following formula Eq. (3, 4), after calculating the efficiencies the optimum results were found from the observed values.

$$\text{Metal Uptake Capacity} = \text{Initial Cr Conc} - \text{Final Cr Conc} \quad (3)$$

$$\text{Adsorption Capacity (\%)} = (\text{Metal Uptake Capacity} * 100) / \text{Initial Cr Conc} \quad (4)$$

2.4.2 Treatment Using Modified Banana Sheath Fibers

The natural BSF powder was chemically modified to check the efficiency increase in the chromium removal. The BSF was modified according to the methods reported in literature [10, 13, 19].

Formaldehyde Treatment

The treatment is done using 1 % formaldehyde in the weight to volume ratio of 1:5 at 50°C for 4 hours. The resulting fibers were washed with sample amount of water till a pH close to neutral was obtained.

Alkali Treatment (NaOH)

The fibers immersed in 5% NaOH aqueous solution (w/v) for 1 hour at room temperature ((1:15) fiber to solution weight ratio). The treated fiber was then washed thoroughly with the distilled water to remove excess NaOH from the surface and oven dried at 110°C.

2.5 Column Studies

The column studies were carried out using a glass column which is of 70 cm long, 2.5 cm internal

diameter as shown in Fig. 4. The parameters such as bed height and flow rate [14, 15, 16] were studied. To enable a uniform inlet flow of the solution into the column 2 cm of cotton was placed and the gravel stones were provided at the bottom of the column to support the packing. A known quantity of biomass was placed in the column to yield the desired biosorbent bed height.

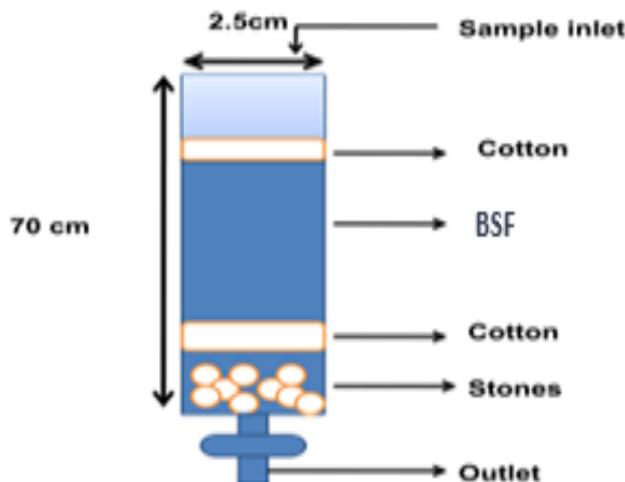


Figure 4. Sktech of the Column Model

Chromium (VI) solution of optimum concentration was fed upward inside the column after adjusting to the desired flow rates. Chromium solution of relatively lower concentrations are used to obtain gentle breakthrough curve. Chromium concentrations of the sample at the column exit collected at different time intervals were analyzed and the column was operated till the effluent metal concentration reaches the initial concentration or nearer.

2.6 Adsorption Isotherms

Laboratory batch studies are useful in obtaining and providing fundamental kinetic and equilibrium adsorption data for potential adsorbents. The quantity of adsorbate that can be taken up by a particular adsorbent at equilibrium is a function of both adsorbate concentration and temperature. When experiments are conducted at constant temperature, the resulting function is commonly referred to as an adsorption isotherm. Theoretically, the adsorption capacity of an adsorbent is achieved at equilibrium when the rate of adsorption equals the rate of desorption. Different adsorbents and adsorbate combinations require different time intervals to reach equilibrium [1, 3, 6, 10, 17, 18, 20].

Fundamental adsorption properties and capacities of different adsorbents, which are a function of the amount of adsorbate sorbed onto the adsorbent and the liquid concentration, are often described using isotherm models. Models that are commonly employed to describe isotherms in adsorption studies are the Freundlich and Langmuir isotherm models. Both Freundlich and Langmuir isotherms are developed from the equilibrium adsorbate capacity Eq. (5) as,

$$q_e = \frac{(C_o - C_e)V}{m} \quad (5)$$

where q_e is adsorbent phase capacity for the adsorbate at equilibrium (mg adsorbate/g adsorbent), C_o is initial concentration of adsorbate (mg/L), C_e is final equilibrium concentration of adsorbate after adsorption has occurred (mg/L), V is volume of liquid in the reactor (L), and m is mass of

adsorbent (g).

Based on adsorbate capacity Eq. (5), Freundlich and Langmuir isotherms can be developed as shown in Eq. (6) for the Freundlich isotherm model:

$$q_e = \frac{x}{m} = K_f C_e^{1/n} \quad (6)$$

where x is the mass of adsorbate adsorbed onto the adsorbent at equilibrium (mg), m is the adsorbent used for adsorption (g), K_f is the Freundlich capacity factor and C_e is the equilibrium concentration of adsorbate in solution at equilibrium adsorption (mg/L), and $1/n$ is the Freundlich intensity parameter.

In order to get the Freundlich capacity factor and the intensity parameter Eq. (7), the isotherm relationship presented in the Eq. (6) can be linearized by,

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where in plotting $\log(x/m)$ versus $\log C_e$, the slope ($1/n$) and the intercept ($\log K_f$) can be obtained.

The Langmuir isotherm model is expressed as (8):

$$q_e = \frac{x}{m} = \frac{abC_e}{1+bC_e} \quad (8)$$

where x is the mass of adsorbate adsorbed at equilibrium (mg), m is the adsorbent used for adsorption (g), C_e is the equilibrium concentration of adsorbate in solution at equilibrium adsorption (mg/L), and a and b are empirical constants.

Similar to the Freundlich equation, the empirical constants of the Langmuir isotherm Eq. (9) can also be determined by linearizing the Eq. (8), and plotting $\frac{C_e}{\left(\frac{x}{m}\right)}$ versus C_e .

$$\frac{C_e}{\left(\frac{x}{m}\right)} = \frac{1}{ab} + \frac{1}{a} C_e \quad (9)$$

3. Results and Discussion

3.1 Adsorbent Characterization

The physical properties of the adsorbent such as the particle size was analyzed by sieve analysis, the bulk density was measured using the volumeter, using this the porosity of the adsorbent was found and the pH was measured by pH meter. The results are tabulated as follows (Table 2):

Table 2. Physical Characterization of Adsorbent

Physical Property	Observed Value
Particle size (mm)	<0.425

Porosity	0.362
Bulk density (g/cc)	0.256
pH	7.5

3.2 Batch Studies

3.2.1 Treatment Using Unmodified Banana Sheath Fibers

Effect of Concentration

To evaluate the sorption characteristics of BSF for Cr ions, the change of sorption capacity with time for different initial concentrations have been studied. A trial was carried out using 10 mg/L & <10 mg/L but the reduction efficiency for 10 & <10 mg/L of Cr was found to be very less. So, a series of experiments were undertaken by varying the initial Cr concentration in the range of 50 mg/L, 100 mg/L, 200 mg/L on the removal of Cr from the simulated solution. It has been found that as the concentration increases the adsorption capacity also increases. The optimum concentration was found to be 200 mg/L (Fig. 5). So, the BSF can be used in the industry effluent samples for higher concentrations of chromium.

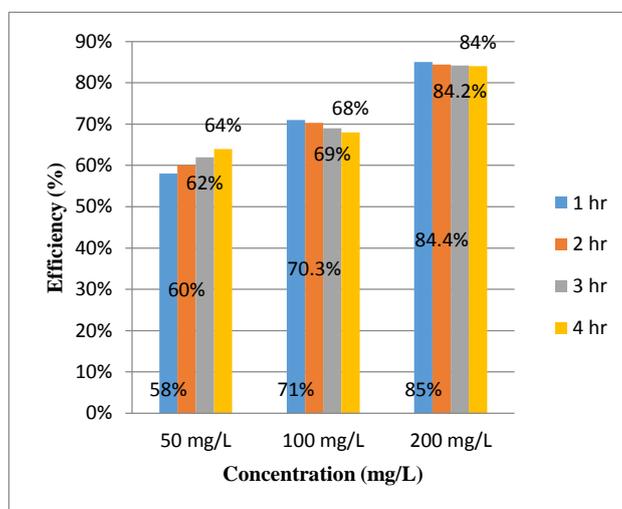


Figure 5. Effect of Concentration on Cr Adsorption

Effect of pH

pH of the solution is one of the most important controlling parameter for adsorption of heavy metals from aqueous solution. Adsorption of Cr was studied at various pH and the results are shown in Fig. 6. The surface properties of adsorbent, ionic state of functional groups and species of metals are dependent on pH condition. But in this study, it was found that the adsorption capacity was independent of the pH range 3 to 9.

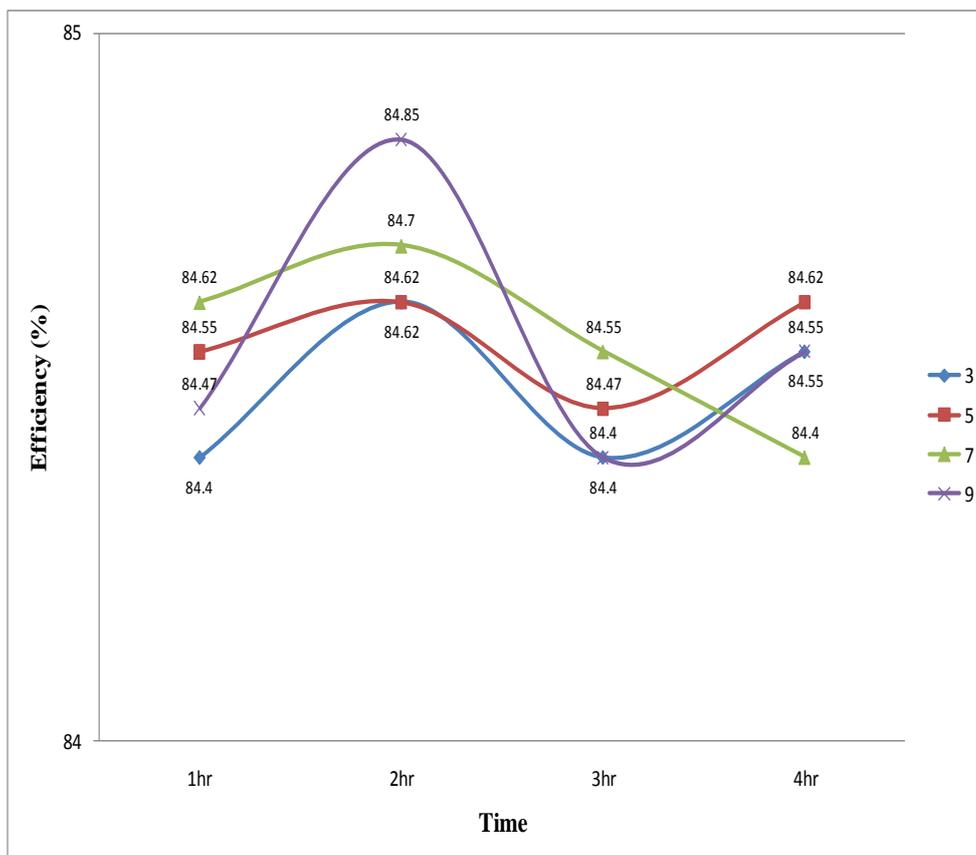


Figure 6. Effect of pH on Cr Adsorption

Effect of Adsorbent Dosage

The removal efficiency is generally increased as the concentration dose increases. This can be explained by the fact that more mass available, more the contact surface offered to the adsorption. The dependence of adsorbent dosage in the removal of Cr (VI) ions was studied at different dosages. The concentration of chromium was also varied and the results are represented in the Fig. 7. The amount of Cr (VI) adsorbed decreased from increased adsorbent dosage. This was due to metal shortage in solution at high dosage and also due to the availability of more surface area and adsorption sites which is the results of plenty of unadsorbed sites as dosage increased.

In this study, 1 g of adsorbent dosage was found to be effective. A trial was carried out by varying the dosages like 0.2 g, 0.5 g, 0.7 g, 1 g and it was found that as the adsorbent dosage increases the removal efficiency also increases. This was due to the increase in the total available area of the adsorbent particles. The dosage was increased even more like 2 g, 3 g, 4 g, 5 g to check whether the efficiency get increased or not. But as it was increased, the efficiency was found to be constant for each concentration and there was no more increase. Low dosage but good percentage of metal removal means less amount of adsorbent has to be used, thus treatment process will be economical.

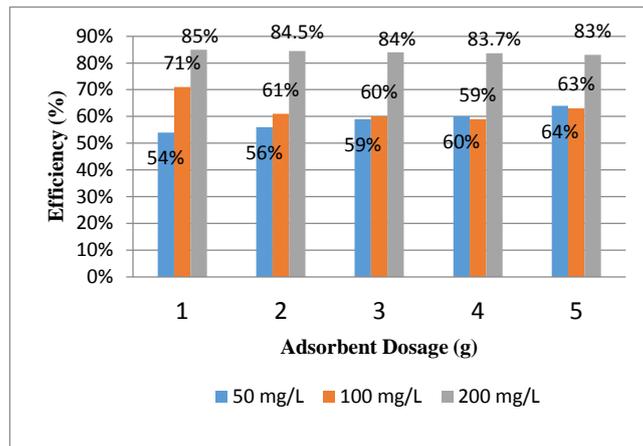


Figure 7. Effect of Adsorbent Dosage on Cr Adsorption

Effect of Contact Time

The longer residence time means the more complete the adsorption will be. Therefore, the required contact time for sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place, and also the possible diffusion control mechanism between the adsorbate. Experiments for contact time were conducted with various initial concentrations with different doses of BSF at 135 rpm and room temperature for 4 hours.

Fig. 8 shows the effect of contact time on adsorption of Cr ions by BSF. Adsorption rate of Cr on BSF was found to be relatively much faster. The rate of Cr removal was very rapid during the first 1 hour, and thereafter, the rate of Cr removal remained constant. There was no significant increase in adsorption after about 1 hour. The samples were taken at a time period of 1 to 4 hours (for every 1 hour). The optimum result was obtained at the 1st hour and as the time increases the efficiency was found to be constant for each concentration and there was no more increase.

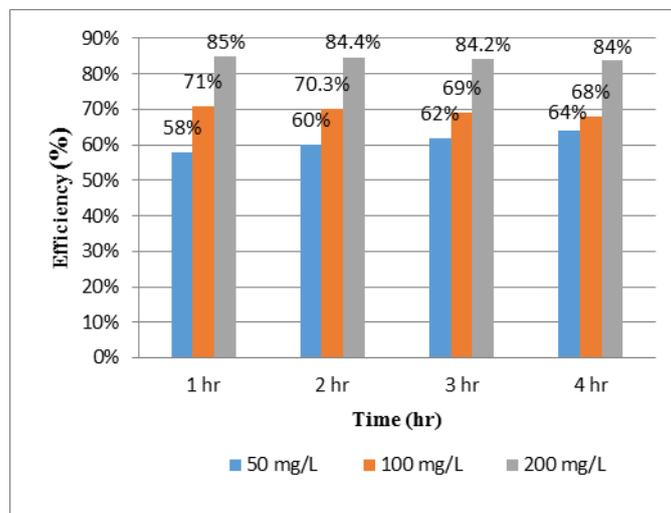


Figure 8. Effect of Contact Time on Cr Adsorption

Optimum Results

From the optimum results, it was found that the 200 mg/L of chromium concentration has shown good efficiency of 85% at 1 hour when compared to the other initial concentrations (50 mg/L, 100 mg/L) for 1 g of adsorbent dosage at room temperature for an agitation speed of 135 rpm (Table 3).

Table 3. Optimum Results of Batch Studies

Concentration (mg/L)	Adsorbent Dosage (g)	Time (hr)	Adsorption Capacity (%)
50	5	4	64
100	1	1	71
200	1	1	85

3.2.2 Treatment Using Modified Banana Sheath Fibers

In order to increase the adsorption capacities of adsorbent, the tested adsorbent was subjected to chemically modification using formaldehyde and alkali (NaOH). It was observed that, the modified BSF showed only a further slight increase in the sorption activity. The slight variation in the adsorption capacity of the chemically modified BSF as compared to that of the unmodified BSF suggests that the latter by its nature already an efficient biosorbent for the removal of Cr(VI). So, the column studies were performed with the unmodified BSF (Fig. 9).

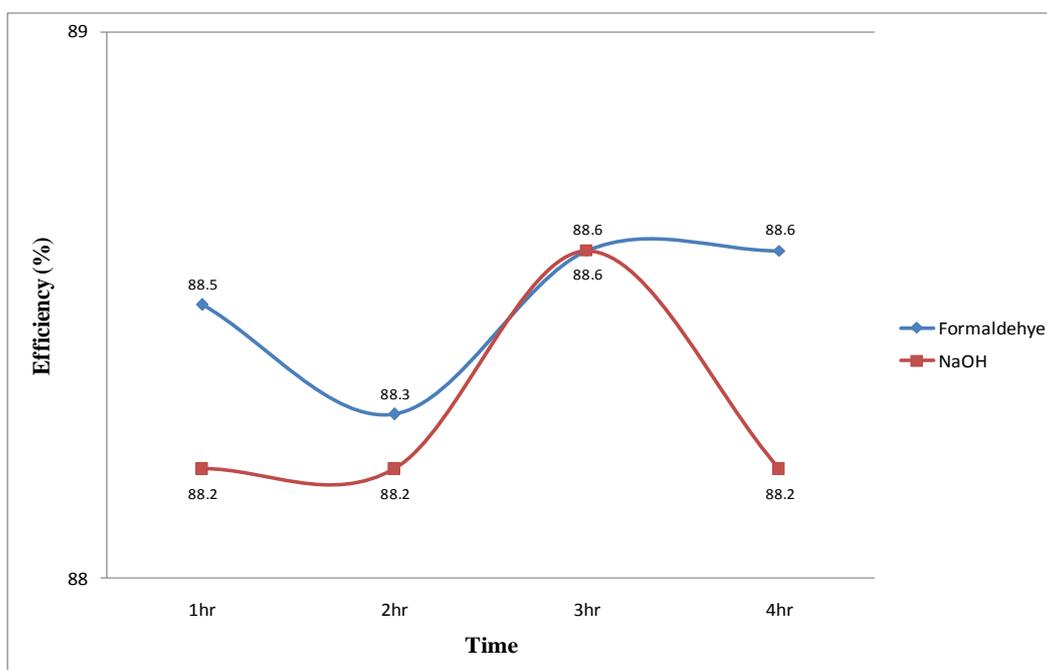


Figure 9. Effect of Modified BSF on Cr Adsorption

3.3 Column Studies

The column studies were performed using the optimum results found in the batch studies. In these studies, the parameters such as bed height and flow rate were studied (Fig. 10).



Figure 10. Column Model Used for Cr Adsorption

3.3.1 Effect of Bed Height

The amount of metal in the packed bed column is greatly influenced by the amount of biosorbent used. The study was conducted for two different bed heights 10 cm, 20 cm using 6 g and 12 g of biomass respectively. A flow rate of 5 ml/min or 10 ml/min of Cr solution with an initial concentration of 200 mg/L was fixed as the feed conditions for the column studies. Fig. 11 and Fig. 12 represents the breakthrough curves for the adsorption of Cr by BSF obtained for the various bed heights. It can be seen that the breakthrough time and exhaustion time increased with the increasing bed height. This is due to the reason that the adsorption regime available for mass transfer is increased and the quantum of binding sites is enhanced facilitating more sorption (Table 4).

Table 4. Chromium Uptake Using Column Studies

Bed Height (cm)	Flow Rate (ml/min)	
	5	10
10	45.75 mg/g	42.6 mg/g
20	38.55 mg/g	36.3 mg/g

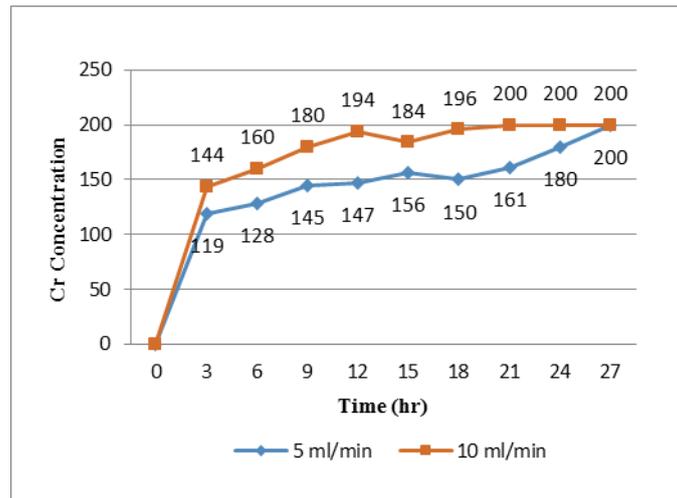


Figure 11. Breakthrough Curves of 20 cm Bed Height on Cr Adsorption

3.3.2 Effect of Flow Rate

Most of the industrial scale treatments of heavy metal removal from effluents are accomplished in continuous mode and hence the study on effect of flow rate on sorptive characters becomes an important criterion. In the present work, the sorption capacity of BSF was studied for two flow rates such as 5 ml/min & 10 ml/min for the initial concentration of 200 mg/L and bed heights of 10 cm & 20 cm. Fig. 11 and Fig. 12 represents the trend of the variation in the effluent Cr concentration against time for the flow rates 5 ml/min and 10 ml/min. Also it can be inferred that the Cr uptake dropped as the flow rate is increased. An earlier breakthrough and exhaustion time were observed for the flow rate of 10 ml/min respectively, which shows that the flow rate largely affects the sorption capacity. The reduction in the Cr uptake capacity at higher flow rates was due to the unavailability of sufficient retention time for solute to interact with the sorbent and the limited diffusivity of solute into the sorptive sites or pores of the biomass caused (Table 4).

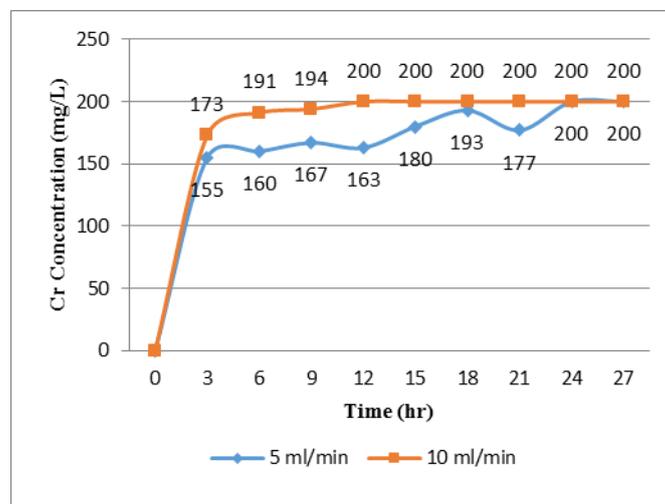


Figure 12. Breakthrough Curves of 10 cm Bed Height on Cr Adsorption

3.4 Adsorption Isotherms

To optimize the design of an adsorption system for the adsorption of wastewater, it is important to establish the most appropriate correlation for the equilibrium curves. Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. Two adsorption isotherms such as Langmuir and Freundlich models were used to describe the equilibrium characteristics of adsorption.

3.4.1 Langmuir Isotherm

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application for many sorption process of monolayer adsorption. The linear plot of Langmuir isotherm for Cr adsorption was shown in Fig. 13, this shows that the data has been fitted reasonably well.

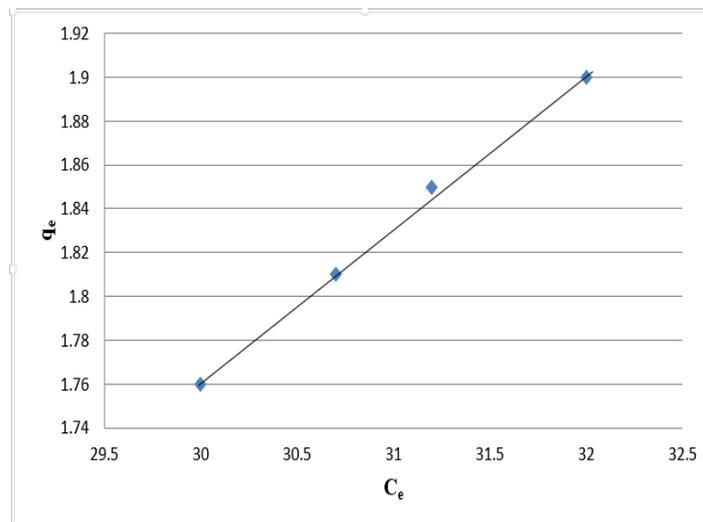


Figure 13. Langmuir Isotherm for Cr Adsorption

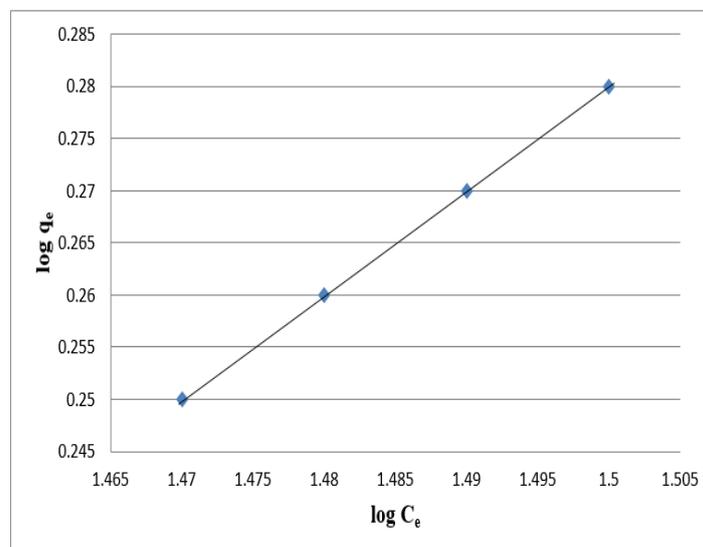


Figure 14. Freundlich Isotherm for Cr Adsorption

3.4.2 Freundlich Isotherm

The Freundlich isotherm is used most commonly to describe the adsorption characteristics of the adsorbent used in the water and wastewater treatment. The linear plot of Freundlich isotherm for Cr adsorption was shown in Fig.14. In this study, the Freundlich isotherm model was found best fitted with the experimental data when compared to the Langmuir adsorption isotherm.

4. Summary and Conclusions

This study showed that the BSF could be used as an efficient biosorbent for the removal of chromium (VI) ions. The adsorbent should possess certain features to become commercially acceptable and widely used. It should be potential to overcome any disadvantages and should be applicable for the process in which it is used. The conventional method of adsorption needs activated charcoal as adsorbent which is of high cost and hence not suitable for developing countries. This leads to the development of alternative low cost adsorbents.

From the batch studies, it was found that the 200 mg/L of chromium concentration has shown good efficiency of 85% at 1 hour when compared to the other initial concentrations (50 mg/L, 100 mg/L) for 1 g of adsorbent dosage at room temperature for an agitation speed of 135 rpm. The column studies were carried out for two different bed heights (10 cm, 20 cm) and flow rates (5 ml/min, 10 ml/min). It can be seen that the breakthrough time and exhaustion time increased with the increased bed height. Also it can be inferred that the chromium uptake dropped as the flow rate was increased. The reduction efficiency for 10 & <10 mg/L of Cr is very less, which required further research.

Low dosage but good percentage of metal removal means less amount of adsorbent has to be used, thus treatment process will be economical. In this study, high concentration of chromium is treated with 1 g of adsorbent and yielded 85% of efficiency which was found to be economical when compared to other cost effective methods like using activated carbon. So, this type of treatment method can be used in the industries in which chromium concentration is more.

The results of present investigations revealed that BSF is a potential adsorbent for the removal of Cr (VI) from aqueous solution. The Freundlich adsorption isotherm model fits very well with the adsorption behavior of Cr. The sorption showed that the adsorption is independent of pH range (3 to 9). The amount of Cr uptake at equilibrium increases with increasing solution concentrations and sorbent mass. The findings of the study show that BSF has excellent potential for use in the removal of Cr(VI) from wastewater, however further work may need to increase the adsorption capacity of BSF.

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