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Biosorption of chromium (VI) by *Tamarindus indica* pod shells

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Abstract
Chromium (VI) is a major pollutant released during several industrial operations. In this paper, we discuss how tamarind (*Tamarindus indica*) pod shells, otherwise discarded as a waste material is used in the biosorption of Cr (VI) from aqueous solutions. Parameters like agitation time, adsorbent dosage and pH were studied at different initial Cr (VI) concentrations. The adsorption data fit well with Langmuir and Freundlich isotherm models. Desorption studies were performed at different concentrations of sodium hydroxide. The infrared spectra of the biomass revealed that hydroxyl, carboxyl and amide groups are involved in the uptake of Cr (VI).

Key words: Heavy metals, chromium, biosorption, tamarind pod shells, infrared spectra

Introduction

Rapid industrialisation has led to increased disposal of heavy metals into the environment and hence effluent treatment is one of the most important targets for industry. Different alternatives for treating effluents are described in literature, including chemical precipitation, carbon adsorption, ion exchange and membrane separation process, among others (Juang and Shiau, 2000; Lacour et al., 2001; Yan and Viraraghavan, 2001). The most common of these alternatives is chemical precipitation However some limitations in the process can be pointed out, such as high cost, low efficiency, labour intensive operation, and lack of selectivity of the precipitation process (Lee et al., 1998). On the other hand, the use of other natural materials such as peanut shells, soybean hulls and corncobs, which are available in large quantities, may present high potential as inexpensive sorbents for effluent treatment (Marshall et al., 1999; Wafwoyo et al., 1999; Vaughan et al., 2001). Bailey et al., (1999) have reviewed the potential of a wide variety of low cost sorbents for heavy metals. A low cost sorbent is the one that requires less processing, is abundant in nature or is either a byproduct or waste material from another industry. These materials could be an alternative for expensive treatment processes.

In India, tamarind (*Tamarindus indica* L.) is an economically important tree which grows abundantly in the dry tracts of Central and South Indian States. Indian production of tamarind is about 3 lakh (0.3 million) tonnes per year. The hard pod shell is removed (deshelled) when the fruit is ripe and the fruit is the chief acidulant used in the preparation of foods. The shells are discarded as waste and since it is available free of cost, only the transport cost is involved for hauling it from the point of generation for wastewater treatment. Hence, recycling of this waste for wastewater treatment would not only be economical but also help to solve waste disposal problems.

Hexavalent chromium frequently encountered in electroplating effluent, is one of the most toxic heavy metal in the environment and is also a known carcinogen and mutagen in humans and animals (Zhao and Duncan 1998; Salunkhe et al., 1998). The possibility of using Tamarind shells, an agricultural waste for the removal of Cr (VI) from aqueous solutions has been examined in this paper.

2.0 Materials and Methods

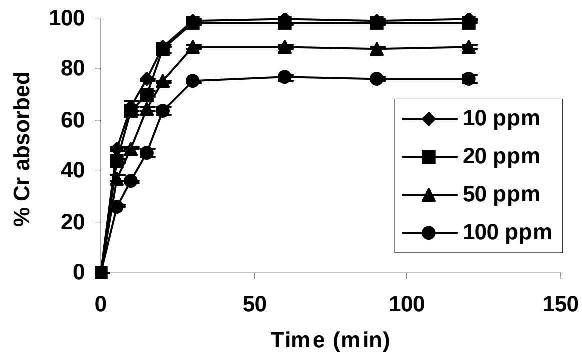
Tamarind pod shells were obtained from a de-hulling unit in Bangalore, Karnataka, India. The tamarind shells were washed thoroughly with distilled water and boiled to remove colour and impurities. They were dried in a hot air oven at 105°C and ground to a uniform size of 0.8 mm. So prepared tamarind pod shell particles were used for further studies. The stock solution (1000 mgl^{-1}) of Cr (VI) was prepared using potassium dichromate salt. Biosorption studies were performed in batch process. The processed tamarind shells equivalent to 1g dry weight were added to 100 ml of an aqueous solution of chromium (pH 2.0; adjusted with 0.1M H_2SO_4) of required concentration. The concentration of the unadsorbed chromium was determined spectrophotometrically at 540 nm using the diphenylcarbazide reagent. The effect of several parameters such as pH, metal concentration, contact time and quantity of biosorbent on adsorption is studied. The pH of the chromium aqueous solution was adjusted using 0.1 N HCl/NaOH. To study the functional groups responsible for the biosorption of Cr (VI), the biomass (tamarind pod shells) was analyzed using a Fourier transform infrared spectrometer (FTIR). Adsorption of Cr (VI) on the walls of the glassware is found to be negligible and is determined by running blank experiments.

Results and Discussion

Effect of agitation time and initial Cr (VI) concentration

The equilibrium time required for biosorption of Cr (VI) on tamarind shells is obtained by studying adsorption of Cr (VI) at various initial concentrations. The data is represented graphically in Fig. 1. The extent of adsorption efficiency increases sharply with time and attains equilibrium at about 60 minutes for all the concentration studied. According to the above results, the agitation/equilibrium time was fixed at 120 minutes for the rest of the experiments so that complete equilibrium is reached. The gradual increase in the rate of biosorption of Cr (VI) and plateau thereon after 60 minutes indicates that the adsorption occurs through a smooth continuous formation of adsorption layer till saturation.

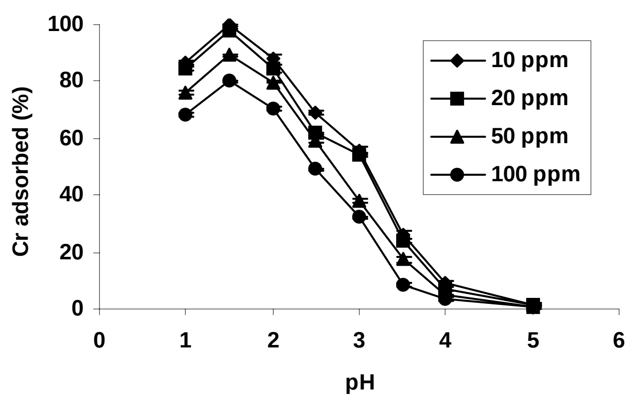
Fig 1: Percentage biosorption of chromium (VI) from solution of different concentration, pH 2.0, by $10gl^{-1}$ biomass as related to the time of contact at 120 rpm



Effect of pH

The biosorption of Cr (VI) was found to depend on the pH of the metal solution (Fig 2). Biosorption capacity was found to decrease with an increase in the pH, maximum adsorption being observed at a pH of 2. It is well known that the dominant form of Cr (VI) at this pH is $HCrO_4^-$. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$. It can be concluded that the active form of Cr (VI) that can be adsorbed by tamarind pod shell is $HCrO_4^-$.

Fig 2: Effect of pH on the biosorption of Chromium (VI) at different concentrations, by $10gl^{-1}$ at 120 rpm with equilibrium time of 120 minutes.



Adsorption Isotherms

Among various plots employed for analyzing the nature of adsorbate-adsorbent interaction, adsorption isotherm is the most significant. The results of adsorption studies of chromium (VI) at different concentrations ranging from 20 to 500 ppm on a fixed amount of adsorbent are expressed by two of the most popular isotherm theories viz., Freundlich and Langmuir isotherms. These isotherm equations are as follows:

Freundlich:

$$q = K_f \, C_{eq}^{\,1/n}$$

$$\ln q = \ln K_f + 1/n \ln C_{eq}$$

Langmuir

$$q = q_{max} \, b \, C_{eq} / 1 + b \, C_{eq}$$

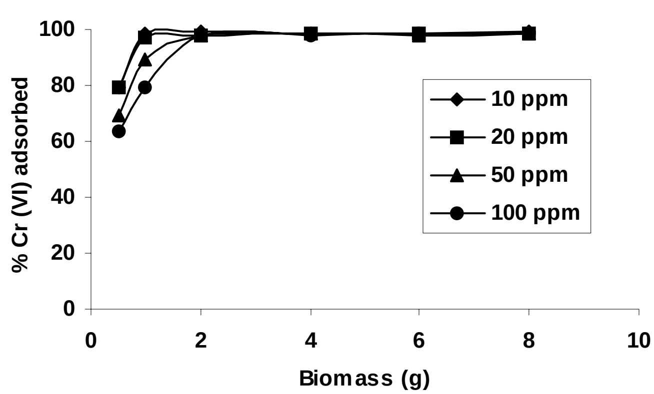
$$C_{eq}/q = 1/q_{max}.b + C_{eq}/ q_{max}.$$

In the above equations, K_f and n are Freundlich constants, which affect the adsorption process, such as adsorption capacity and intensity of adsorption, respectively. The values of these constants, obtained by least squares fitting of the data on ln q and ln C_{eq} are 1.17 and 1.80. q_{max} (mgg^{-1}) and b are Langmuir constants related to monolayer adsorption capacity and energy of adsorption respectively. The values of the parameters, evaluated by the least square fitting of the data on C_{eq} versus C_{eq}/q are 27.73 and 0.008.

Effect of adsorbent dose

The dependence of Cr(VI) adsorption on the amount of tamarind pod shells is studied at room temperature and at pH2.0 by varying the adsorbent amount from 0.5 to 8g, while keeping the volume constant and varying the initial Cr(VI) concentration (Fig 3) It is apparent that the percent removal of Cr (VI) increases with increase in the dose of adsorbent due to the greater availability of the biosorption binding sites.

Fig 3: Effect of quantity of biomass on biosorption of Cr (VI) from solutions of different concentrations, pH 2.0 for contact time 120 min at 120 rpm



Infrared spectroscopy

An un-reacted tamarind pod shell sample and pretreated with 100 mg/l Cr (VI) solution were analysed using FTIR, to determine the functional groups that play an important role in the biosorption of Cr(VI). The wavenumbers along with their corresponding functional groups are given in Table 1. The infrared spectroscopic studies show that several functional groups are available on the surface of the adsorbent for binding Cr (VI) ions.

Table: 1 IR absorption bands and the corresponding functional groups

Wavelength (cm^{-1})	**Functional group**
3425.30	-OH, -NH
2925	-CH
1745.50	-COO-
1621.98	C=C, -OH
1517	C=C
1461.42	C=C in carbon rings or CH from methyl
893.25	-CH

Desorption studies

The desorption of Cr(VI) from previously Cr(VI) loaded tamarind pod shells using distilled water was attempted. But Cr(VI) desorption was not observed. Hence, experiments were conducted with acid and alkali solutions to desorb Cr(VI) ions. The results obtained (not shown) indicate that the desorption of Cr(VI) ions with acid was not achieved even when 0.1 N HCl and 0.2 N HCl were used. However, there was little desorption with alkali solutions. It was found that Cr(VI) desorption was 27.8% with 0.2 N NaOH. The results of desorption studies indicate that either chemisorption or ion-exchange as the possible mechanism for Cr(VI) binding on the tamarind pod shells.

Conclusion

This is the first time in literature that tamarind pod shells have been used for the adsorption of Cr (VI). As the tamarind pod shells are easily available, its utility as biosorbent will be economical and be viewed as part of waste management strategy. Containing very less amount of protein (Nitrogen = 0.94%), tamarind pod shells is advantageous over the protein rich algal and fungal biomass projected as metal biosorbents, since proteinous materials are likely to putrefy under moist conditions.

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