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Biosorption of Cr (VI) using different types of husks (*Oryza sativa*, *Pennisetum typhoides* and *Vigna mungo*)

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Abstract

Different cereal husks of paddy (*Oryza sativa*), Indian millet (*Pennisetum typhoides*) and Black gram (*Vigna mungo*) were investigated as new biosorbent for the removal of Cr (VI) ions from aqueous solutions in laboratory condition. Adsorbent capacity of different concentrations of husks was determined by spectrophotometrically the paddy husk has more capacity to absorb the chromium than the Indian millet and black gram proved as a good candidate biosorption for treating waste waters containing low concentration of chromium.

Keywords: biosorption, husks, *Oryza sativa*, *Pennisetum typhoides*, *Vigna mungo*

INTRODUCTION

Mobilization of heavy metals in the environment is due to industrial activities of serious concern as these metals are toxic to all forms of life including human beings. The presence of heavy metals in the environment is of major concern because of their toxicity, accumulating tendency, threat to human life and the environment (Igwe and Abia, 2003 ; Horsfall and Spiff, 2005). Some metals are more toxic even at very low levels (Forstner and Wittman, 1979). Chromium has both beneficial and detrimental properties. Two stable oxidation states of chromium Cr (III) and Cr (IV) which have contrasting toxicities, mobility and bioavailability present in the environment, (Saiffudin and Kumaran, 2004). Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin (Park and Jung, 2001). Chromium is a transition metal and is a ubiquitous element, not only because of its occurrence in nature, but also due to the many anthropogenic sources resulting from its wide spread industrial applications. Very recently Ahalya *et al* (2007) have studied the Cr (VI) removal using *Cajanus Cajan* husk. Earlier unmodified rice husk has been evaluated for their ability to bind metal ions (Marshall *et al*., 1993; Roy *et al*., 1993; Munaf and Zein, 1997).

Biosorbents are naturally available biological materials prepared from naturally abundant and/or waste biomass. Due to the high uptake capacity and very cost-effective source of the raw material, biosorption is a progression towards a perspective method. The biosorption or biological metal removal has distinct advantages over conventional methods. These techniques are non-polluting, highly selective, more efficient, easy to operate and hence cost effective for treatment of large quantities of waste water containing low concentration of heavy metals. Adsorption is the ability of the adsorbate to adhere or attach to the adsorbent. It is a well established separation technique to remove dilute pollutants as well as to recover valuable products from aqueous streams.

The aim of this research was to know their efficiency of different husk materials removing Cr (VI) from the artificially chromium mixed water. Rice husk is a cellulose based fibre. The outer surface of rice husk is relatively rougher than the inner surface that houses the rice grain, which can be utilized in the manufacture of composite panels (Low *et al*., 2000). Like all vegetable biomass, rice husks are composed of cellulose, hemi-cellulose and lignin (Juliano, 1985). Biosorption of Cr (VI) by using husks of paddy (*Oryza sativa*), Indian millet (*Pennisetum typhoides*) and Black gram (*Vigna mungo*) in the laboratory condition is presented in this paper.

MATERIALS AND METHODS

Preparation of Reagents for experiment

Standard chromium (VI) Solution

Analytical grade chromium (VI) (0.535g) was taken and dissolved in water and made up to 100 ml distilled water. Then 5 ml of this solution was pipette out in to distilled water and made it up to 250 ml. This diluted solution contained 0.001 mg Cr (VI) per ml.

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2, 4, 6, 8, 10 ml of the standard Cr (VI) solution were added into five Nessler tubes each. Five ml of 1:1 H_2So_4 and 5ml Diphenylcarbazide solution were added in each tube. This was diluted up to the 50ml mark with distilled water and was stirred. OD value of the each standard solutions were taken at 540 nm using spectrophotometer.

Preparation of biosorbent (Different types of husks)

Different types of husks viz., Paddy (*Oryza sativa*), Indian Millet (*Pennisetum typhoides*) and Black gram (*Vigna mungo*) were selected as biological materials for removing the heavy metal of Cr (VI). All types of husks were thoroughly washed in running tap water to remove dirt and other particulate matter. This was later subjected to colour removal through washing and boiling in distilled water repeatedly. Subsequently the husks were oven dried at 105ºC for 24 hours, stored in a desiccator and used for biosorption studies in the original piece size (Ahalya *et al.*, 2007).

Laboratory Chromium effluent preparation

0.0001% Concentration

100 ml of distilled water was taken in a conical flask and added 0.1 mg of $K_2Cr_2O_7$ crystal and in to it 1 gm of paddy husk was added and shacked well for two hours constantly.

Experiment

Fifty ml of sample solution was taken out and poured into a 250 ml conical flask. In it 5 ml of 1:1 H_2So_4 was added and the solution gently was boiled in a water bath for 15 minutes. To the boiling solution, the $KMnO_4$ solution was added drop by drop until very faint pink colour persisted. After the pink colour appeared, the sample was taken out from the water bath and the sodium azide was added drop by drop just to discharge the pink colour of the solution. This was kept in cool condition and the solution was made upto 100ml in standard flask. Twenty five ml of this solution was taken in a Nessler tube and 5ml of Diphenylcarbazide reagent was added. Stirred and added distilled water up to the 50ml mark. Like wise three sets of experiments were carried out for paddy husk. Similarly, three sets of same principle were carried out for the Indian millet husk and Black gram husk. The appropriate sample solution was analyzed in spectrophotometer at 540 nm. The absorbance measurement was completed within 15 minutes after the addition of diphenylcarbazide. The OD (Optical Density) values of all the samples were compared with the OD value of standard. The mean OD values of the samples were taken out and plotted in the map. The amount of absorptions were calculated using the formula.

OD of the sample X concentration of the standard / OD of the standard

0.0002% Concentration

In the same way 0.2 mg of $K_2Cr_2O_7$ crystal was added in 100 ml distilled water in the same procedure described above and three husk types were involved for the experiment. The OD values of all the samples were compared with the OD values of the standard. The mean OD values of the samples were taken out and plotted in the map.

Reaction of Chromium with chemical reagents

Principle:

Hexavalent chromium reacts with diphenylcarbazide $(C_6H_5NHNH)_2Co$ in acid condition to form a red-violet soluble complex. Therefore traces of chromium can be estimated either by visual colorimetry or by spectrophotometry using this reagent. Lower-valent Cr can be oxidized to Cr (IV) by $KMno_4$. Iron, copper and nickel, which may also be present in water, will interfere with this method. These metals should be removed from the sample by peroxidation treatment and filtration.

Table 1. Absorption of Cr (VI) in two different Concentrations by various types of husks

Concentration of Cr (VI)	Amount of absorption by husks in mg		
	Paddy (*Oryza sativa*)	Indian Millet (*Pennisetum typhoides*)	Black gram (*Vigna mungo*)
1 (0.0001%)	0.0072 ± 0.0032	0.0007 ± 0	0.0025 ± 0.0024
2 (0.0002%)	0.0202 ± 0.0032	0.0024 ± 0	0.0290 ± 0.0024

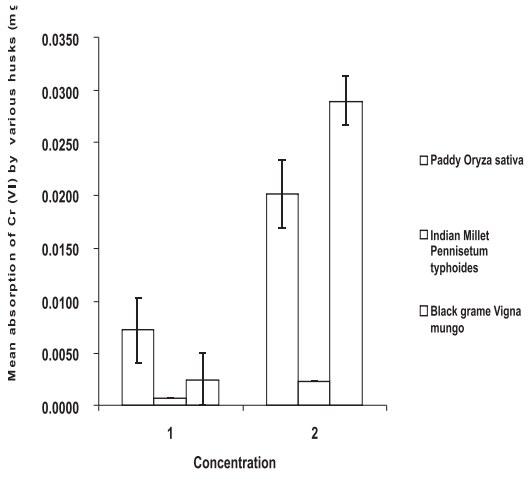

Figure 1. Absorption of heavy metal (Chromium VI) in two different Concentrations by various husks

Statistical analysis

Three set of results were brought down as mean by way of giving standard deviation. The different means of different husks in two concentrations were compared by one way ANOVA test.

OBSERVATIONS AND RESULT

In the present study, Chromium (VI) removal efficiency of different cereal husks was analyzed under laboratory condition. The absorption of Cr (VI) was done with the help of biological materials viz., Paddy (*Oryza sativa*) husk, Indian millet (*Pennisetum typhoides*) husk and Black gram (*Vigna mungo*) husk. It was attempted with two concentrations of Cr (VI) such as 0.1mg/100ml and 0.2 mg/100ml.

Concentration – 1 (0.0001%)

The result revealed that the Paddy husk showed maximum absorption of Cr (VI) (0.0072 ± 0.0032 mg). A minimum absorption of Cr (VI) was recorded in Indian millet husk (0.0007± 0 mg) (Table 1 and Fig. 1). From the results it is concluded that the paddy husk and black gram husk efficiently removed more Chromium (VI) in the water medium when compared to the Indian millet husk.

Concentration – 2 (0.0002%)

It is surprising to observe that Black gram husk showed the maximum absorption of Cr (VI) (*i.e.*,0.0290 ± 0.0024 mg) followed by Paddy husk (0.0202 ± 0.0032mg) when the concentration was increased in the water medium. On the other hand, the Indian millet showed the lowest absorption of Chromium (VI) (0.0024 ± 0.00 mg) (Table 1 and Fig. 1). However the differences among the Chromium (VI) absorption by different husks were not statistically significant (F=0.661 and p=0.533).

On the basis of the results obtained, it can be safely concluded that the Chromium (VI) uptake by the biological materials increased when the concentration was increased in the laboratory condition. However, in the concentration of 0.1mg/100ml the paddy husk showed highest percentage of uptake of Chromium (VI) (69.23%) and in concentration 0.2mg/100ml the Black gram husk showed highest uptake of Cr (VI) (56.2%) (Table2. Fig.2 and 3).

DISCUSSION

In the present investigation different kinds of husks were used for removal of Cr (VI) from the water medium. The present result revealed, if the concentration increased the absorption of Cr (VI) increased in a particular husk type that means it differed from species to species. For example in the concentration of 0.1mg/100ml the paddy husk showed higher absorption power. On the other hand, in the concentration of 0.2mg/100ml the black gram husk showed higher absorption power. According to Ahalya *et al*. (2007) the uptake of chromium (VI) was rapid and the equilibrium was attained within 15 minutes of contact between the biosorbents and the metal solution. The present study revealed that the biological materials such as the husks of Paddy (*Oryza sativa)* Indian millet (*Pennisetum typhoides*) Black gram (*Vigna mungo*) absorb the Chromium (VI). These results are in accordance with the results of Ahalya *et al.* (2007).

Commonly, the husks are considered to be a potentially useful material for the removal of metals from any medium. The present study emphasized that the Paddy husk, Indian millet husk, Black gram husk which are agro milling substances and are available in plenty at low cost are efficient in the removal of Cr (VI). These adsorbed heavy metal can be easily desorbed and the biomass be incinerated for final disposal. Since these biosorbent same of low cost, its utility will be economical and can be viewed as a part of a feasible waste management strategy. Tamilnadu is producing high yields of Paddy, Indian millet and Black gram.

Table 2. Percentage of absorption of Cr (VI) in two different Concentrations by various types of husks

Concentration of Cr (VI)	Percentage of amount of absorption by husks		
	Paddy (*Oryza sativa*)	Indian Millet (*Pennisetum typhoides*)	Black gram (*Vigna mungo*)
1 (0.0001%)	69.23	6.73	24.04
2 (0.0002%)	39.15	4.65	56.2

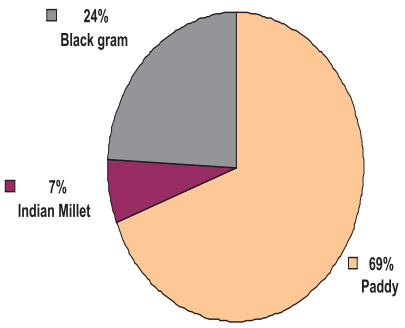

Figure 2. Percentage of absorption of Cr (VI) in Concentration 1 (0.0001%) by various husks.

The availability of these husks is plenty and at low cost. People can apply such bioabsorption technique in large scale in highly polluted areas. Khalid *et al*. (1999) have already described the ion exchange reactions that take place on the surface of these materials. Puranik and Paknikar (1997) have also observed Pb (II) and Zn (II) removal by *Streptoverticillum cinnamoneum* waste biomass.

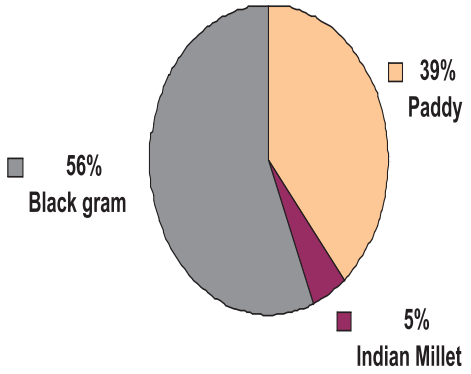

Figure 3. Percentage of absorption of Cr (VI) in Concentration 2 (0.0002%) by various husks.

Conventional methods of removal are expensive; hence the use of low cost, abundant environmentally friendly biosorbents is good source for the removal of Cr (VI). The adsorption is highly dependent on particle size distribution and on metal ratio. Removal of heavy metals by carbon can be a combination of factors such as adsorption, hydrogen bonding, precipitation and physical removal of insoluble metal complexes (Ricordel *et al*., 2001). The authorities of Industrial Toxicology Research Center, Lucknow, India have been involved in developing suitable low cost, efficient indigenous adsorbents/carbons capable of removing various pollutants from industrial effluents. The COD removal kinetics by rice husk and coconut shell carbons at different temperatures was approximately represented by a first order reaction. The present study suggests that the biological materials are suitable for removal of Chromium (VI) and other related toxic substances from the polluted areas.

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