Use of Millet Husk as a Biosorbent for the Removal of chromium and Manganese Ions from the Aqueous Solutions.

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ABSTRACT
Movement of heavy metal ions into the water sources has made it unfit for consumption. Rural areas situated near the industrial area are facing the problem of contaminated water. Present work is an effort to develop a self sufficient, easy to assemble and eco friendly system for the removal of heavy metal ions from the water. Millet husk readily available in the rural areas of eastern Rajasthan has been tried and tested for the removal of chromium and manganese ions from the aqueous system. The results are exciting and indicate that it could be used for the removal of heavy metal ions from the water. A column of 12 inches height and 2 inches diameter of pretreated millet husk was used as a biosorbent. This column is sufficient to treat a 50 ml solution (0.012g/L) of chromium ions and 65ml solution (0.001g/L) of manganese ions. The rate of flow of the solution was kept 2ml/min at room temperature and Ph3-4.

Key words: biosorbent, millet husk, biosorption, Chromium ions, manganese ions.

INTRODUCTION
Growing industries gave good job opportunities and pace to the economic growth of India and at the same time pose serious threat to the environment. Water being most important part of industries and environment has been affected most. Quality of water in the nearby areas of the industrial growth is facing a serious problem of heavy metal contamination. Surface water as well as underground water is equally affected. About 20 metals have been identified as toxic to human health and out of this half are emitted into the environment in quantities that pose risk to human health.

A number of chemical and physical processes are available for the removal of these toxic ions from the water samples. Of all the available processes which can remove these toxic ions from water have some or the other technical or economical problem. A study of such systems and their difficulties has been reported [1]. Therefore some methods which are environment friendly and low cost are desirable. A study on the different types of biosorbents and their probable use has been presented by Volesky et al [2]. Here is a useful method which in recent years has gained a lot of attention.

Biosorption can be defined as a 'non directed physico-chemical interaction that may occur between metal/radionuclide species and microbial cells [3]. A variety of micro organisms as biosorbents have been identified and reported[4-7] for the removal of heavy metal ions. Some plant wastes like obtained from agriculture farms have also been reported to be efficient biosorbents[8-15]. Removal of chromium[16-18], iron[16,19], lead[19,20] and copper [19-21]have also been studied and reported .

In the present paper the biosorption of lead, copper and cadmium on the two biosorbents that are available in plenty in southern Rajasthan are reported.

MATERIALS AND METHOD
Preparation of biosorbent
The biowaste that is the husk of millet and oat have been procured from the nearby village. The husk was washed thoroughly with water to remove sand etc. Then it was treated with dilute HCl to remove natural colour of the husk and then again washed with demineralised water. Thoroughly washed husk have dried in an hot air oven at about 60 °C for 24 hours. The properly dried husk is now ground to a fine powder and kept in air tight jars and taken as and when required.

A steel column of 20 inches height and 2 inches diameter has been taken. The biosorbent was filled into the column till a height of 12 inches only. All the experiments have been carried out using this column only.
Preparation of the solutions: Standard solutions (1000mg/L) of chromium (VI) and manganese (VII) were prepared in the laboratory by dissolving potassium dichromate and potassium permanganate in doubly distilled water. Stock solutions were kept in covered and labeled bottles. These stock solutions were used after further dilution according to the requirement. The pH of the solutions was adjusted using NaOH and HCl.

Method
The test solution containing metal ions was allowed to flow through the prepared column of 12 inches height and 2 inches diameter. The flow of test solution was maintained by using a burette. The flow rate was maintained 3 ml/min for all the experiments except when effect of variation of the rate of flow was studied. A clean tumbler properly washed with deionised water was used to collect the percolated water. All the test solutions were examined before and after the treatment using atomic absorption spectrophotometer. Sorption efficiency (%) of the biosorbent was calculated in terms of amount of metal ion adsorbed per gram of the biomass using following formula.

\[
Q = \frac{(C_0 - C)}{M} \times V
\]

Sorption efficiency (%) = \( \frac{C_0 - C}{C_0} \times 100 \)

Where Q is the amount of metal ion biosorbed per gram of the biomass mg/g, \( C_0 \) and C are the initial and final concentrations of the test solution. V is the volume of the test solution; M is the mass of the biomass (g).

RESULTS AND DISCUSSIONS
Effect of pH on the sorption capacity of the biosorbent
Biosorption of metal ions on to the surface of the biosorbent is greatly influenced by the pH of the solution. It is expected the sorption of the metal ions increase with increase in the pH of the solution. The possible reason may be that at lower pH, H+ and H2O+ ions compete with the metal ions for adsorption onto the surface of biosorbent. At higher pH less no of H+ ions are there to occupy the adsorbent sites are available for the metal cations. The pH of the solution was varied from 2 to 7. The pH of the normal water is around 7 therefore the pH 7 is chosen to conclude the adsorption capacities of the biosorbent. The case is different with the chromium ions. Chromium ions are available as anions CrO_4^{2-} or HCrO_4^- in the solution therefore they showed a different character. It has been found that biosorption of chromium decrease with increase in the pH of the solution. Probable reason may the presence more number of positive sites on the biosorbent at lower pH which can adsorb chromate ions. Similar is the case with the manganese ions.

It is clear from the following table that the extent of adsorption decreases with increase in the pH of the solution for manganese ions and chromate ions. The results are shown in table 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>Percentage removal of Cr(VII)</th>
<th>Percentage removal of Mn(VII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>78%</td>
<td>75%</td>
</tr>
<tr>
<td>2</td>
<td>88%</td>
<td>90%</td>
</tr>
<tr>
<td>3</td>
<td>65%</td>
<td>82%</td>
</tr>
<tr>
<td>4</td>
<td>49%</td>
<td>32%</td>
</tr>
<tr>
<td>5</td>
<td>18%</td>
<td>12%</td>
</tr>
<tr>
<td>6</td>
<td>8%</td>
<td>2%</td>
</tr>
<tr>
<td>7</td>
<td>2%</td>
<td>0</td>
</tr>
</tbody>
</table>

Effect of Rate of flow of solution through column
Rate of flow of solution through the biosorbent column effect the net percentage removal of metal ions from the solution. If the solution travels quickly down the column then the metal ions get less time to adhere to the surface of the biosorbent. Similarly if the rate of flow through the column is slow than the metal ions will get sufficient time to get adhere to the surface of the biosorbent. Therefore the effect of rate of flow on the percentage removal of the ions from the test solutions must be considered and studied. Following figures illustrates that with the increase in the contact time between the adsorbent and the metal ions from test solutions percentage removal of the ions is also increased. The results are shown as below in table 2.
Table 2

<table>
<thead>
<tr>
<th>Rate of flow of solution (mL/min)</th>
<th>Percentage removal of Cr(VII)</th>
<th>Percentage removal of Mn(VII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>88%</td>
<td>90%</td>
</tr>
<tr>
<td>4</td>
<td>72%</td>
<td>53%</td>
</tr>
<tr>
<td>6</td>
<td>66%</td>
<td>48%</td>
</tr>
<tr>
<td>8</td>
<td>62%</td>
<td>34%</td>
</tr>
<tr>
<td>10</td>
<td>53%</td>
<td>20%</td>
</tr>
</tbody>
</table>

Effect of height of column
Keeping the diameter of the column fix and varying the height of the column it is seen that the sorption of ions is greatly influenced. Increase in the height of the column means increase in the number of adsorption sites. Therefore the extent of sorption is to increase with the increase in the height of the column. Height of the column is varied from 8 inches to 14 inches. Results are shown below in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Height of column in inches (diameter 2 inches in all the cases)</th>
<th>Percentage removal of Cr(VI)</th>
<th>Percentage removal of Mn(VII)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>23%</td>
<td>18%</td>
</tr>
<tr>
<td>4</td>
<td>35%</td>
<td>34%</td>
</tr>
<tr>
<td>6</td>
<td>50%</td>
<td>52%</td>
</tr>
<tr>
<td>8</td>
<td>64%</td>
<td>68%</td>
</tr>
<tr>
<td>10</td>
<td>76%</td>
<td>83%</td>
</tr>
<tr>
<td>12</td>
<td>88%</td>
<td>90%</td>
</tr>
</tbody>
</table>

Effect of initial concentration of the metal ion solution
Initial concentration of metal ions in the solutions affects the rate sorption of ions on the sorbent surface. Initially the rate of adsorption increase with increase in initial concentration of the ions in solution. This is due to large number of adsorption sites available for few metal ions in the solution. On further increase in the concentration the rate of adsorption nearly become stable when number of metal ions and number of adsorption sites become equal. Beyond this concentration there is no increase in the rate of adsorption. The initial concentration of metal ions taken for the study is 20 mg/L each. The equilibrium is reached at about 80 mg/L and then after no further increase in the rate of adsorption is noticed. The results are shown below in table 4.

Table 4

<table>
<thead>
<tr>
<th>Initial concentration of the metal ions (mg/L)</th>
<th>Metal uptake of Cr(VII) (mg/g)</th>
<th>Metal uptake of Mn(VII) mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>40</td>
<td>4.8</td>
<td>3.6</td>
</tr>
<tr>
<td>60</td>
<td>5.4</td>
<td>5.2</td>
</tr>
<tr>
<td>80</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>100</td>
<td>7.2</td>
<td>6.8</td>
</tr>
</tbody>
</table>

CONCLUSION
Biosorption capacities of *Pennisetum typhoides* (millet husk) are found enough for the removal of chromium and manganese ions from the waste water. The optimum ph range for the purpose lies in the acidic range. There is a need to study the system in more detail and find the practical utility. Widely available and ecofriendly biowastes like husk of millet and oat can serve the purpose of water purifier in the rural areas.

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REFERENCES


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