Biosorption of Zn(II), Cu(II) and Cr(VI) from textile dye effluent using activated coconut fiber

K. Gopalakrishnan¹, T. Jeyadoss¹ and V. Manivannan²
¹Department of Chemistry and Biosciences, SRC Campus, SASTRA University, Kumbakonam, Tamil Nadu, India
²Department of Research and Development, PRIST University, Thanjavur, Tamil Nadu, India
kgk_1985@yahoo.co.in; jeyadoss@yahoo.com; manivan_1999@yahoo.com

Abstract: This paper presents the performance of the low cost adsorbent coconut fiber in removing the heavy metals such as Zn(II), Cu(II) and Cr(VI) from textile dye effluent. Biosorption studies were carried out for various parameters such as adsorbent dosage, pH and contact time. The maximum removal of heavy metal ions from the textile dye effluent using activated coconut fiber was evaluated successfully through the percentage of seed germination of Vigna mungo L. with the treated adsorbents.

Keywords: Biosorption, Zn(II), Cu(II), Cr(VI), activated coconut fiber, textile dye effluent, seed germination, Vigna mungo L.

Introduction
Dyes are widely used in industries such as textile, rubber, paper, plastics and cosmetics to color the products. These dyes are invariably left as industrial wastes into the environment without pretreatment. Dyes, even in low concentration, affect the aquatic life through food web due to the large degree of heavy metals presents (Mckay, 1982). The discharge of heavy metals such as lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, copper, nickel, etc., into aquatic ecosystems constitute a severe health hazard to aquatic biotic systems, mainly due to their non-degradability and toxicity. Due to their mobility in natural water ecosystems, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment (Ahalya et al., 2006).

In recent decade, many researchers have focused their interest on heavy metals due to their known toxicity and carcinogenicity (MacCarthy et al., 1995). The removal of the toxic metal ions from water is very difficult due to the high cost of treatment methods. There exist several methods for the removal of toxic metal ions from dye effluent viz. reverse osmosis, ion exchange, chemical precipitation, electrodealkysis and lime coagulation. These techniques are not only expensive but also inefficient in complete removal, high reagent and energy requirements and generation of toxic sludge (Ahalya et al., 2005).

Biosorption has been suggested as being cheaper and more effective than chemical or physical technologies (Volesky & Holan, 1995). The major advantage of biosorption over conventional treatment methods includes low cost, high efficiency, minimization of chemical and biological sludge (Kratochvil et al., 1998). Natural materials that are available in large quantities or certain waste products from agricultural operations may prove to be potential as inexpensive sorbents. After these materials have been expended, they can be disposed of without expensive regeneration since their cost is low. The abundance and availability of agricultural by-products make them good sources of raw materials for activated carbon (Chuah et al., 2005). The mechanism of binding of metal ions by adsorbents may depend on the chemical nature of metal ions (species size and ionic charge), the type of biomass, environmental conditions (pH, temperature, ionic strength) and existence of competing organic or inorganic metal chelators (Wilde & Benemann, 1993). The objective of this study is to investigate the feasibility of using activated coconut fiber as natural biosorbent for the removal of heavy metals like Zn(II), Cu(II) and Cr(VI) from textile dye effluent.

Materials and Methods
Textile dye effluent
The dye effluent was collected from textile dyeing industry located in and around Thirupoor, Tamilnadu, India. The collected samples were maintained under sterile conditions in a closed air tight container for further study.

Biosorbent collection and preparation
Coconut fiber was collected from coir industry located in Thanjavur, Tamilnadu. The raw material was washed thoroughly with tap water to remove earthly matter and dried at 383 K in an electrical oven for 24 h. After cooling the raw material to room temperature, activated coconut fiber was prepared by thermal pyrolysis of coconut fiber at 823 K for 2 h (Ash et al., 2006).

Characterization of biosorbents
The physicochemical characteristics like moisture content, particle density, ash content, acid extractable components, water soluble components, lignin, etc. of activated coconut fiber was studied.

Analysis of metal ions
Heavy metals of textile dye effluent were quantitatively assessed using AAS. This method quantitatively determines the concentration of zinc, copper, chromium, iron, magnesium, mercury, etc. utilizing a nitric acid / hydrogen peroxide microwave digestion. The methodology utilizes a pressure digestion/dissolution of the sample and is incomplete relative to the total oxidation of organic carbon (Habib-ur-Rahman et al., 2006).

Seed germination study
A total of 25 seeds of black gram (Vigna mungo L) were placed in sterile glass petri dishes of uniform size lined with two filter paper discs. These filter paper discs
were then moistened with 5 ml of distilled water for control and with the same quantity of untreated dye effluent and treated dye effluent separately. Replications were maintained for each treatment. The number of seeds that germinated were counted and removed from the petri dishes at the time of first count on each day until there is no further germination. The criterion of germination which we took was the visible protrusion of radial through seed coat and it was expressed in percentage (Meyer & Kelher, 1992).

Results and discussion

Characterization of biosorbents

The physicochemical characteristics like moisture content, particle density, ash content, acid extractable components, water soluble components, lignin, etc. of activated coconut fiber were determined (Table 1).

The bulk density and particle density affect the adsorption of metal ions. The decrease in the bulk density enhances the adsorption of metal ions. Finer the size of the adsorbent, greater will be the adsorption. The bulk density value less than 1.2 indicates the adsorbent materials are fine in nature. When this value falls within the range 1.2 -2 the adsorbent materials are medium and the value more than 2 indicates that the adsorbent materials are coarse in nature. The particle density value is less than 2.2 for finer materials, the value 2.2 -4 medium and more than 4 indicating adsorbent materials are coarse in nature. In the present study, the bulk density and particle density values obtained are closer to fine in nature.

Moisture content, though does not affect the adsorption power, dilutes the adsorbents and therefore necessitates the use of addition of more adsorbents to provide the required weight. Ash content generally gives an idea about inorganic constituents associated with carbon. In any case, the actual amount of individual inorganic constituents varies from one type to another as they are mainly derived from different sources.

Lignin component present in the low cost adsorbent activated coconut fiber accounts for heavy metal adsorption from textile dye effluent. The ability of lignin to act as a sequestering agent for heavy metal ions is well known.

Effect of adsorbent dosage

To study the influence of the adsorbent dosage on the removal of heavy metal ions, different trials have been conducted by varying the adsorbent concentration ranging from 10 to 50g/L while keeping the effluent volume constant.

Fig. 1 shows the effect of adsorbent dosage/ removal of Zn(II), Cu(II) and Cr(VI) by activated coconut fiber at optimum temperature (T) 23°C and time (t) 60 minutes. Initially 15% of Zn(II) was removed at 10g/L, which increased with the adsorbent dosage and reaching the maximum of 64% at 50g/L. Likewise, 24% of Cu(II) was removed at initial dosage of 10g/L, which increased with the increase of adsorbent dosage reaching up to the maximum of 67% at 50g/L. Similarly, 20% of Cr(II) was removed at initial dosage of 10g/L, which increased with the adsorbent dosage to a maximum of 72% at 50g/L.

Removal of heavy metal ions from the textile dye effluent increases with higher adsorbent dosage. This can be explained by the availability of the exchangeable sites or surface area on the adsorbents. In the minimum adsorbent dosage level (10g/L) there will be a low availability of exchangeable sites, ultimately the removal of metal ions at low adsorbent dosage is also minimum. But at the maximum adsorbent dosage level (50g/L) there will be a greater availability of exchangeable sites or surface area, ultimately the removal of metal ions at maximum adsorbent dosage is also maximum (Ramana et al., 2002).

Success of removal of heavy metal ions with the effect of adsorbent dosage can be evaluated through the study of the percentage of seed germination of black gram (V. mungo) before and after treatment. Table 2

Table 1. Characteristics of activated coconut fiber

<table>
<thead>
<tr>
<th>Name of the Parameter</th>
<th>Activated Coconut fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.83</td>
</tr>
<tr>
<td>Bulk density (g/cc)</td>
<td>0.87</td>
</tr>
<tr>
<td>Particle density (g/cc)</td>
<td>1.22</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>6.29</td>
</tr>
<tr>
<td>Organic carbon (%)</td>
<td>3.42</td>
</tr>
<tr>
<td>Water holding capacity (%)</td>
<td>87.64</td>
</tr>
<tr>
<td>Matter soluble in water (%)</td>
<td>0.64</td>
</tr>
<tr>
<td>Matter soluble in acid (%)</td>
<td>99.31</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>12.57</td>
</tr>
<tr>
<td>Lignin (mg kg⁻¹)</td>
<td>8.27</td>
</tr>
</tbody>
</table>

Table 2. Effect of adsorbent dosage on Percentage of seed germination of Vigna mungo L

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of seed germination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>97.3 ± 1.86</td>
</tr>
<tr>
<td>Untreated dye</td>
<td>20 ± 3.2</td>
</tr>
<tr>
<td>Activated coconut fiber treated dye</td>
<td>81.3 ± 1.8</td>
</tr>
</tbody>
</table>

The data represents Mean ± S.D.
reports the removal of heavy metals from effluent correlating with the successful seed germination of *V. mungo*. The treated textile dye effluents with absorbent activated coconut fiber at maximum adsorbent dosage level (50g/L) were subjected to the seed germination test. The treatment resulted in better seed germination (81.3 ± 1.8%) while the untreated effluent reduced the seed germination to 20 ± 3.2%. The control value (without addition of effluent) is 97.3 ± 1.86. Clearly, the treatment of effluent with the various adsorbents increased the seed germination capacity.

**Effect of pH**

The optimum pH suitable for the removal of Zn(II), Cu(II) and Cr(VI) ion by activated coconut fiber was observed at pH 1.0. At this pH the maximum of removal of Zn(II), Cu(II) and Cr(VI) ion were 61.5%, 77.5% and 67%, respectively.

It is quite obvious from the results (Fig. 2) that the pH plays an important role in the adsorption process. Removal of heavy metal ions such as Zn(II), Cu(II) and Cr(VI) from the textile dye effluent increases at acidic pH. Adsorption of Zn(II) increases at highly acidic pH because, zinc ion exists as Zn(OH)+ and Zn(OH)2+, which are favourable species for adsorption of trace zinc ions. Adsorption of Cu(II) increases at high acidic pH because of increased ionic interaction between the metal and the adsorbent. Similarly, adsorption of Cr(II) increases at high acidic pH because of redox reaction between the sorbent surface groups and sorbate. Higher H+ ion concentration could strengthen the redox reaction and enable the carbon to adsorb more Cr(VI) (Chuah *et al.*, 2005).

Table 3 shows the influence of pH on the removal of heavy metals in the effluent and the seed germination of *V. mungo* was used as end point in the evaluation of effluent treatment. The treatment of textile dye effluent with absorbent activated coconut fiber at acidic pH (1.0) resulted in enhanced seed germination (53.3 ± 1.8 %). However, untreated textile dye effluent reduced the seed germination to 20 ± 3.2. The control value measured was 97.3 ± 1.86. Clearly, the results show that the percentage of seed germination of *V. mungo* increased after the treatment of textile dye effluent with activated coconut fiber when compared to untreated textile dye effluent but which is still lower to the control because of the acidity of the treated effluent.

**Effect of contact time**

Contact time is an important parameter in all transfer phenomena including adsorption. Consequently, it is important to study its effect on the capacity of removal of heavy metal ions by low cost adsorbents. Removal efficiency increased with an increase in contact time and this can be explained by the affinity of the adsorbents towards metal ions (Ramana *et al.*, 2002).

Fig. 3 represents that with activated coconut fiber, the optimum biosorption time was obtained at 300 minutes for Zn(II), Cu(II) and Cr(VI) respectively. At this time, the removal of Zn(II) was maximum of 55.5%, whereas for Cu(II) and Cr(VI) it was 67% and 64.5%, respectively.

Table 4 represents the removal of heavy metals as influenced by the contact time. After the treatment of textile dye effluent with activated coconut fiber at maximum contact time (300 min.) the percentage of seed germination was 84 ± 3.2. However, before the treatment of textile dye effluent with various adsorbents the percentage of seed germination

### Table 3. Effect of pH of treated effluent on percentage of seed germination of *Vigna mungo* L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of seed germination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>97.3 ± 1.86</td>
</tr>
<tr>
<td>Untreated dye</td>
<td>20 ± 3.2</td>
</tr>
<tr>
<td>Activated coconut fiber treated dye (pH 1)</td>
<td>53.3 ± 1.8</td>
</tr>
</tbody>
</table>

The data represents Mean ± S.D.

### Table 4. Effect of contact time of treated effluent on percentage of seed germination of *Vigna mungo* L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% of seed germination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>97.3 ± 1.86</td>
</tr>
<tr>
<td>Untreated dye</td>
<td>20 ± 3.2</td>
</tr>
<tr>
<td>Activated coconut fiber treated dye</td>
<td>84 ± 3.2</td>
</tr>
</tbody>
</table>

The data represents Mean ± S.D.
was 20 ± 3.2. The control value was found to be 97.3 ± 1.86. These values show that the percentage of seed germination of V. mungo increased with increased contact time of treatment of the textile dye effluent with the various adsorbents.

**Conclusion**

The present study clearly shows that coconut fiber, which is cheap and abundantly available can be used as an effective adsorbent in activated form for removal of Zn(II), Cu(II) and Cr(VI) from textile dye effluent. This adsorption process is also dependent on numerous factors such as adsorbent dosage, pH and contact time. The increase in adsorbent dosage also increases the removal of metal ions from textile dye effluent. The maximum percentage removal of Zn(II), Cu(II) and Cr(VI) ions occurs between pH 1.0-2.0. The study of pH effects has confirmed that ion exchange is the major mechanism of removal of metal ions using activated coconut fiber. The time obtained was 300 minutes for Zn(II), Cu(II) and Cr(VI) respectively. At this time the maximum removal of Zn(II), Cu(II) and Cr(VI) were observed under optimum condition using activated coconut fiber. From the present investigation, it is quite interesting to know that the percentage of seed germination of V. mungo treated with textile dye effluent increased after the textile dye effluent was treated with adsorbent such as activated coconut fiber.

Coconut fiber as an agro-industrial waste has negligible cost and has also been proved to be an efficient biosorbent for the removal of heavy metal ions such as Zn(II), Cu(II) and Cr(VI) from textile dye effluent. Heavy metal ions bound to the coconut fiber can be recovered through eco friendly method.

**References**


