Comparative Study on Biosorption of Zn(II), Cu(II) and Cr(VI) from Textile Dye Effluent Using Sawdust and Neem Leaves Powder

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Abstract: The performance of the low cost adsorbents such as sawdust and neem leaves powder in removing the heavy metals like Zn(II), Cu(II) and Cr(VI) from textile dye effluent are reported. Adsorbent dosage, pH and contact time were taken as parameters for biosorption study. Removal of heavy metal ions from the textile dye effluent increases with increase in adsorbent dosage. The influence of pH and contact time was maximum for removal of heavy metal ions. The presence of the decreased heavy metal toxicity in the treated textile dye effluent was evaluated through the percentage of seed germination of *Vigna mungo* L. On comparison, sawdust was found to be good adsorbent compared to neem leaves powder.

Keywords: Atomic absorption spectroscopy (AAS), Adsorbent dosage, pH, Contact time, *Vigna mungo* L, Seed germination.

Introduction

Generally, dyes are widely used in textile industry to colour the textile products. But, these dyes are left out without any treatment into the water bodies as industrial waste. Even, low concentration of dyes in water affects the aquatic life and food web, because of the presence of the high amount of heavy metals¹. Heavy metals such as lead, chromium, mercury, zinc, arsenic, cadmium, copper and nickel, *etc.*, discharged into water resources leads to various severe health complications because of their nondegradability and toxicity. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural process such as biomagnifications, concentration may become elevated to such an extent that they begin exhibiting toxic characteristics².

Nowadays, many environmental researchers have turned their interest on reduction of heavy metal ions in water resources, due to their known toxicity and carcinogenicity³. Removal of heavy metal ions from water is hard task, because of high cost in treatment methods. There are number of methods available for the removal of toxic metal ions from textile dye effluent. They are reverse osmosis, ion exchange, chemical precipitation, electrodialysis and lime coagulation. These techniques are not only expensive but also suffer with incomplete removal, high reagent and energy requirements and generation of toxic sludge⁴.

In recent years, biosorption has been suggested as being cheaper and more effective than chemical or physical technologies⁵. Low cost, high efficiency, minimization of chemical and biological sludge are the most important advantages of biosorption technique. Moreover, biosorbent regeneration and metal recovery is also possible⁶. 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 chelators⁷. Natural materials that are available in large quantities or certain waste products from agricultural operation may have the potential as inexpensive sorbents. This study explores the viability of sawdust and neem leaves powder as natural biosorbents for the removal of heavy metals from textile dye effluent.

Experimental

The dye effluent was taken from textile dyeing industry located in and around Thirupur, Tamilnadu, India. The collected dye effluent was kept in the closed air tight container.

Biosorbent collection and preparation

Sawdust of *Tectona grandis* was collected from local saw mill and it was extensively washed with double distilled water to remove impurities. Then it was dried for 5 h at 100 °C and cooled⁸ in desiccator for 24 h.

The neem leaves were collected from twinges into clean plastic bags washed with double distilled water to remove dust and soluble impurities. Initially leaves were dried at room temperature under shade for 6 hours and kept in hot air oven at 80 °C till it turns pale yellow. Thus it was crushed, sieved and then stored into plastic bag for the use of biosorption studies⁹.

Analysis of metal ions

Heavy metals present in the textile dye effluent were quantitatively assessed using Atomic Absorption Spectroscopy (AAS). This method quantitatively determines the concentration of zinc, copper, chromium, iron, magnesium and 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 carbon¹⁰.

Seed germination seeds

For germination study, 25 seeds of black gram (*Vigna mungo* L) were placed in sterilized glass petri dishes of uniform size lined with two filter paper discs. These filter discs were then moistened with 5 mL of distilled water for control and with the same quantity for untreated dye effluent and treated dye effluent. Three replications of each treatment were carried out. The seeds which are 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 radical through seed coat and it was expressed in percentage¹¹.

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 sawdust and neem leaves powder were determined and represented in Table 1. The bulk density and particle density influence the adsorption of metal ions. The decline 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. The particle density value will be less than 2.2 for finer materials. In the present study, the bulk density and particle density values obtained are closer to fine in nature. Moisture content, though does not concern with the adsorption power, dilutes the adsorbents and therefore necessitates the use of addition of more adsorbents to offer the required weight. Ash content generally gives a suggestion about inorganic constituents associated with carbon. In any case, the actual amount of individual inorganic constituents will vary from one type to another as they are mainly derived from different sources. Lignin is a chemical component present in the sawdust and neem leaves powder showing good heavy metal adsorption property from textile dye effluent. The ability of lignin to act as a sequestering agent for heavy metal ions is well known.

Table 1. Characteristics of sawdust and neem leaves powder

S.No	Name of the parameter	Sawdust	Neem leaves powder
1.	pH	6.25	6.15
2.	Bulk Density, g/cc	1.20	0.84
3.	Particle Density, g/cc	2.05	1.09
4.	Moisture, %	8.29	2.47
5.	Organic Carbon, %	6.42	1.79
6.	Water Holding Capacity, %	81.29	48.21
7.	Matter Soluble in Water, %	1.79	0.53
8.	Matter Soluble in Acid, %	98.21	99.47
9.	Ash, %	10.46	14.57
10.	Lignin, mg kg ⁻¹	4.59	0.62

Effect of Adsorbent dosage

The influence of adsorbent dosage on the removal of heavy metal ions can be studied by varying the adsorbent concentration ranging from 10 to 50 g/L by keeping the volume of the effluent solution constant. The effect of adsorbent dosage on the removal of Zn(II), Cu(II) and Cr(VI) by sawdust at optimum temperature (T) 23 °C and time (t) 60 minutes is shown in Figure 1. At first, 12% of Zn(II) was removed at 10 g/L, which increased with the increase of adsorbent dosage and reaching the maximum of 54% at 50 g/L. Likewise, 18.5% of Cu(II) was removed at initial dosage of 10 g/L, which increased with the increase of adsorbent dosage reaching the maximum of 68% at 50 g/L. Similarly, 11% of Cr(II) was removed at initial dosage of 10 g/L, which increased with the increase of adsorbent dosage and the maximum was 60.5% at 50 g/L. The effect of adsorbent dosage on the removal of Zn(II),

Cu(II) and Cr(VI) by neem leaf powder at optimum temperature (T) 23 °C and time (t) 60 minutes is shown in Figure 2. At earliest, 12% of Zn(II) was removed at 10 g/L, which increased with the increase of adsorbent dosage and reaching the maximum of 56% at 50 g/L. The same, 21.5% of Cu(II) was removed at initial dosage of 10 g/L, which increased with the increase of adsorbent dosage reaching the maximum of 66.5% at 50 g/L. Similarly, 15% of Cr(II) was removed at initial dosage of 10 g/L, which increased with the increase of adsorbent dosage and the maximum was 64.5% at 50 g/L. Removal of heavy metal ions from the textile dye effluent increases with increase in adsorbent dosage. This can be explained by the accessibility of the transferable sites or surface area on the adsorbents. In the minimum adsorbent dosage level (10 g/L) there will be a diminutive availability of exchangeable sites, ultimately the removal of metal ions at low adsorbent dosage is also minimum. But at the maximum adsorbent dosage level (50 g/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 maximum¹².

Figure 1. Effect of adsorbent dosage on the removal of Zn(II), Cu(II) and Cr(VI) by sawdust. Condition: T = 23 °C and t = 60 minutes

Figure 2. Effect of adsorbent dosage on the removal Zn(II), Cu(II) and Cr(VI) by neem leaves powder. Condition: T = 23 °C and t = 60 minutes

Percentage of seed germination of black gram (*Vigna mungo* L) before and after treatment of textile dye effluent evaluates the success of removal of heavy metal ions with adsorbent dosage. The evaluation of the successful removal of heavy metal ions by the effect of treated effluent on the percentage of seed germination of *Vigna mungo* L with adsorbent dosage is represented in Table 2. After the treatment of textile dye effluent with sawdust and neem leaves powder at maximum adsorbent dosage level (50 g/L) the percentage of seed germination is 73.3±1.8 and 69.3±1.8. However, before the treatment of textile dye effluent with adsorbents the percentage of seed germination is 20±1.8. The control value is 97.3±1.86. These values show that the percentage of seed germination of *Vigna mungo* L increases after the treatment of textile dye effluent with two adsorbents when compared to untreated textile dye effluent.

Table 2. The effect of adsorbent dosage on percentage of seed germination of *Vigna mungo* L.

S.No	Name of the sample	Percentage of seed germination
1.	Water	97.3 ± 1.86
2.	Untreated dye	20 ± 1.8
3.	Sawdust treated dye	73.3 ± 1.8
4.	Neem leaves powder treated dye	69.3 ± 1.8

The data represents Mean ± S.D

Effect of pH

pH plays an important role in biosorption process. Generally, pH can be considered from acidic (1.0) to neutral (7.0). At acidic pH the biosorption occurs fast and removes the metal ions to the maximum extent. Exact pH within the range (1.0-7.0) vary with the nature of different biosorbent. 56% removal of Zn(II) was obtained at pH 1.0 by the treatment with sawdust. 56.5% removal of Zn(II) was obtained at pH 1.0 by the treatment with neem leaves powder. The removal of Cu(II) by the treatment with sawdust was 77% at pH1.0. The removal of Cu(II) by the treatment with neem leaves powder was 74% at pH 1.0. At pH1.0, 63% of Cr(VI) ion removed by the treatment with sawdust. At pH1.0, 60% of Cr(VI) ion removed by the treatment with neem leaves powder. Above facts are shown in Figure 3 & Figure 4. It is quite clear from the results that the pH plays an important role in the adsorption process. Chuah *et al.* reported that in acidic pH, heavy metal ions removal from textile dye effluent is high. Adsorption of Zn(II) increases at highly acidic pH because Zinc ion exists as $\text{Zn}(\text{OH})^+$ and $\text{Zn}(\text{OH})_2$, which are favourable species for adsorption of trace Zinc ions. Adsorption of Cu(II) increases at high acidic pH because of ionic interaction between the metal and the adsorbent increases. 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).

Figure 3. Effect of pH on the removal of Zn(II), Cu(II) and Cr(VI) by sawdust. Powder. Condition: $T = 23^\circ\text{C}$ and $t = 60$ minutes

Figure 4. Effect of pH on the removal of Zn(II), Cu(II) and Cr(VI) by neem leaves powder. Condition: $T = 23^\circ\text{C}$ and $t = 60$ minutes

Percentage of seed germination of black gram (*Vigna mungo* L) before and after treatment of textile dye effluent evaluates the success of removal of heavy metal ions (with pH). The evaluation of the successful removal of heavy metal ions by the effect of treated effluent on the percentage of seed germination of *Vigna mungo* L with pH is represented in Table 3. After the treatment of textile dye effluent with various adsorbents such as sawdust and neem leaves powder at acidic pH (1.0) the percentage of seed germination is 42.6 ± 1.8 and 41.3 ± 1.8 . However, before the treatment of textile dye effluent with various adsorbents the percentage of seed germination is 20 ± 1.8 . The control value is 97.3 ± 1.86 . These values show that the percentage of seed germination of *Vigna mungo* L is increased after the treatment of textile dye effluent with the various adsorbents when compared to untreated textile dye effluent.

Table 3. The effect of pH on percentage of seed germination of *Vigna mungo* L.

S.No	Name of the sample	Percentage of seed germination
1.	Water	97.3 ± 1.86
2.	Untreated dye	20 ± 1.8
3.	Sawdust treated dye	42.6 ± 1.8
4.	Neem leaves powder treated dye	41.3 ± 1.8

The data represents Mean $\pm$ S.D

Effect of contact time

Dadhich Anima *et al.*, reported that in all transfer phenomena, including adsorption, contact time is an important parameter. Therefore, it is important to study its ability on 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. The contact time obtained at 300 minutes for Zn(II), Cu(II) and Cr(VI) respectively by sawdust is shown in Figure 5. At this time, the maximum removal of Zn(II) was found to be 52.5%, whereas for Cu(II) it was 66.5% and for Cr(VI) it was 59% under optimum condition. Likewise, the contact time obtained at 300 minutes for Zn(II), Cu(II) and Cr(VI) respectively neem leaves powder is shown in Figure 6. At this time, the maximum removal of Zn(II) was found to be 48.5%, whereas for Cu(II) it was 65% and for Cr(VI) it was 60.5% under optimum condition. After 300 minutes there was no adsorption of metal ions by the two adsorbents namely sawdust and neem leaves powder. After this time, the binding sites in the adsorbents are fully occupied by the metal ions.

Figure 5. Effect of contact time on the removal of Zn(II), Cu(II) and Cr(VI) by sawdust. Condition: T = 23 °C

Figure 6. Effect of contact time on the removal of Zn(II), Cu(II) and Cr(VI) by neem leaves powder. Condition: T = 23 °C

Percentage of seed germination of black gram (*Vigna mungo* L) before and after treatment of textile dye effluent evaluates the success of removal of heavy metal ions with contact time. The evaluation of the successful removal of heavy metals by the effect of treated effluent on the percentage of seed germination of *Vigna mungo* L with contact time is represented in Table 4. After the treatment of textile dye effluent with two adsorbents namely sawdust and neem leaves powder at maximum contact time (300 min) the percentage of seed germination is 77.3 ± 1.8 and 74.6 ± 1.8 . However, before the treatment of textile dye effluent with various adsorbents the percentage of seed germination is 20 ± 1.8 and the control value is 97.3 ± 1.86 . These values show that the percentage of seed germination of *Vigna mungo* L increases after the treatment of textile dye effluent with two adsorbents, when it was compared with untreated textile dye effluent.

Table 4. The effect of contact time on percentage of seed germination of *Vigna mungo* L.

S.No	Name of the sample	Percentage of seed germination
1.	Water	97.3 ± 1.86
2.	Untreated dye	20 ± 1.8
3.	Activated rice husk treated dye	77.3 ± 1.8
4.	Activated coconut fibre treated dye	74.6 ± 1.8

The data represents Mean $\pm$ S.D

Conclusion

This study clearly shows that the sawdust and neem leaves powder which are cheap and abundantly available can be used as an effective adsorbents for removal of Zn(II), Cu(II) and Cr(VI) from textile dye effluent. This adsorption process can be concluded with factors such as adsorbent dosage, pH, contact time and percentage of seed germination. The increase in adsorbent dosage increases the removal of heavy metal ions from textile dye effluent. At pH 1.0, the maximum removal of Zn(II), Cu(II) and Cr(VI) ions occurs. The study of pH effects has confirmed that ion exchange is the major mechanism of removal of metal ions using sawdust and neem leaves powder. 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 sawdust and neem leaves powder.

From our investigation, it is quite interesting to know that the percentage of seed germination of *Vigna mungo* L increases after the textile dye effluent treated with sawdust and neem leaves powder. But, sawdust was found to be better than the neem leaves powder in the removal of heavy metal ion from the textile dye effluent. Moreover, treated effluent contains heavy metal ions in trace amounts, which is acting as a micronutrient for enhancement of seed germination. So, this process may lead to produce liquid fertilizer and hold a promise for commercial exploitation in the agricultural field.

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