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Importance of Maize (*Zea mays*) tassel in the Reduction of Heavy Metal load.

[1]Sabrin Sultana , [2]Dr. Monalisa Bora Deka*

[1]Scientific Officer ,[2] Deputy Director Research

Research Division

University Of science and Technology, Meghalaya,India

Abstract

The increase of pollution in the environment is major concern and the presence of heavy metals in water bodies is harmful for flora and fauna as well as human. Even, water of the Ganga River which is considered to be the pure water is also polluted. Thus, to reduce the heavy metals viz. mercury, iron and chromium loads of the water samples collected from the Ganga River and distilled water. We used maize tassel (male flowers of *Zea mays*) which is usually an agricultural by product. It acts as adsorbate and has adsorption capacities for all mercury, iron and chromium and was found to be comparable to those of other commercial adsorbents currently in use for the removal of heavy metals from aqueous solutions. Adsorption of heavy metals by maize tassel might be attributed to their protein, carbohydrates and phenolic compounds, which have metal binding functional groups, such as carbonyl, hydroxyl, and amino groups.

The Ganga water samples were taken from Haridwar and Varanasi and distilled water preserved in bottles. Mercury, iron and chromium were observed in these pre treatment samples. The reading for mercury, iron and chromium of the water samples were observed at different concentration using UV-Spectrophotometer (2731 EI). Further, maize tassel was cleaned and pulverized to fine pieces and 0.1 gm powder were added to these water samples and kept for 24 h at room temperature. The water that drained out of the tassel and then the obtained post treatment samples were analyzed for the amount of metals remaining in it. Batch experiments was conducted on stimulated solutions using tassel powder as adsorbent and the effect of pH and concentration on the extent of mercury, iron and chromium removal was studied.

Index Terms- Adsorption, Spectrophotometer, Heavy metals and Maize tassel.

1.Introduction

Pollution is the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the ecosystem i.e. physical systems or living organisms. Pollutants, the components of pollution, can be either foreign substances/energies or naturally occurring contaminants. Pollutants may cause primary damage, with direct identifiable impact on the environment, or secondary damage in the form of minor perturbations in the delicate balance of the biological food web that are detectable only over long time periods.

Heavy metals are thus, commonly defined as those having a specific density of more than 5 g/cm^3. The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury, iron, chromium and arsenic (arsenic is a metalloid, but is usually classified as a heavy metal). A heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity (Duffus, 2002).

Heavy metal pollution can arise from many sources but, most commonly arises from the purification of metals, e.g., the smelting of copper and the preparation of nuclear fuels. Electroplating is the primary source of chromium and cadmium. Through precipitation of their compounds or by ion exchange into soils heavy metal pollutants can localize and lay dormant. Unlike organic pollutants, heavy metals are non degradable and do not decay and thus, pose a challenge for remediation. Heavy metals occur naturally in the ecosystem with large variations in concentration.

Precipitation and adsorption are two common methods for the treatment of heavy metals pollution in water (Murathan and Butun, 2006). Coagulation, ion exchange, and ion exchange combined with precipitation are also widely used. Adsorption of heavy metals by these materials might be attributed to their protein, carbohydrates and phenolic compounds, which have metal binding functional groups, such as carbonyl, hydroxyl, sulphate, phosphate, and amino groups.

In this study water samples from river Ganga were used for analysis. The River Ganga rises in the Gangotri glacier in the Himalaya Mountains at an elevation of 7138 m above mean sea level. It enters the plains at Hardwar and meanders over a distance of above 2290 km across UP, Bihar and West Bengal, and receives a wide array of chemical constituents including toxicants from a variety of natural and anthropogenic sources (Kar *et al*., 2008). Among the heavy metal we have analyzed mercury, iron, chromium and copper.

Maize tassel is the male part of the maize plant. Its major purpose is the production of pollen grains which fertilize the female part of the maize flower which then develops into a cob. Pollination and fertilization in a maize field covers a period of not more than 21 days if the plants germinate within 1 week. This means tassel has no production value after fertilization. Farmers involved in seed production normally cut off the tassel after pollination period.

Materials and Methods

The water samples were collected in tightly corked sterilized bottles. The maize tassel was rinsed with distilled water and oven dried for 24 hours at 100^0 C. the material was then milled using a mixer grinder (Zvinowanda *et al*., 2009). Standard protocols were followed according to Vogel (1961). Dithizone method was used for the detection of mercury in acidic, alkaline and neutral medium. The solution of mercuric chloride of pH 3, 7 and 12 were prepared. Two flasks of each solution were prepared. One flask is the standard while other contains the maize tassel. The flask with maize tassel was kept at the shaker for 24 hours. 100ml water sample was placed in a 500ml distillation flask. 5-10ml of 5% $KMnO_4$ was added and refluxed for four hours. Cooled and a few ml of 30% H_2O_2 was added to remove $KMnO_4$. Samples were boiled to remove excess H_2O_2. Cooled and a few drops of 1M H_2SO_4 was added. The metal twice was extracted with 10ml dithizone solution. The extracts were combined and the absorbance was measured at 490 nm against the reagent blank. The standard solution was diluted and the series of standard solutions was prepared containing mercury in the range of 2-10 mg/l (ppm). The procedure was repeated for these solutions and the calibration graph was constructed. The amount of mercury in the water sample was determined from the calibration graph. o-phenanthroline method was used to detect iron at 515nm through spectrophotometer. An aliquot portion of the unknown slightly acidic solution containing 0.1-0.5 mg of iron was taken and transferred to a 50ml volumetric flask. Determined by the use of a similar aliquot portion containing a few drops of bromophenol blue, the volume of sodium acetate solution required to bring the pH to 3.5 ± 1. The same volume of acetate solution was added to the original aliquot part and then 4ml each of hydroquinone and o-phenanthroline solution was added. The volume was make up to the mark with distilled water, mixed well, and allowed to stand for one hour to complete the reduction of iron. The intensity of the colour produced was compared with the standard. The wavelength of 510nm was used

Results

PHYSICAL PARAMETERS

The water samples were found to be colourless and odourless. The pH of sample-1 (S-1) was observed to be acidic (5.33) and that of sample-2 (S-2) was alkaline (7.85). Total solids were found to be 1.2 mg/l for S-1 and 1 mg/l for sample-2. The total suspended solids were 0.8 mg/l for sample-1 and 0.6 mg/l for S-2 while, total dissolved solids were found to be 0.4 mg/l for both of the samples. The size of the maize tassel varied from 0.3-0.6 cm.

Table 2: Physical parameter of water samples collected from the Ganga River

Sample	Colour	Odour	pH	T.S.(mg/l)	T.S.S.(mg/l)	T.D.S.(mg/l)
S-1	Colorless	Odourless	5.33	1.2	0.8	0.4
S-2	Colorless	Odourless	7.85	1	0.6	0.4

Table 4: Pre-treatment values

Sample	Alkalinity	Acidity	D.O.	B.O.D	C.O.D
S-1	-ve	+ve	6.4	0.6	0.1776
S-2	+ve	-ve	6.08	0.4	0.176

Table 5: Post-treatment values

Sample	Alkalinity	Acidity	D.O.	B.O.D.	C.O.D.
S-1	-ve	-ve	9.6	0.4	0.1696
S-2	-ve	-ve	8.0	0.3	0.1728

CHEMICAL PARAMETERS

Alkalinity:

The alkalinity of water is the capacity of that water to accept protons. The Ganga water sample of Varanasi was found to be alkaline before treatment while, after treatment the sample did not showed any alkalinity.

Acidity:

The acidity of water is the capacity of that water to donate protons. The Ganga water sample of Haridwar was found to be acidic before treatment while, after treatment the sample did not showed any acidity.

Dissolved oxygen:

Dissolved oxygen of water is a paramount important to all living organisms. Deficiency of dissolved oxygen gives bad odour to the water due to anaerobic decomposition of organic waste. The optimum value for good quality water has been 4-6 mg/l of dissolved oxygen (Sharma, 2001). If the dissolved oxygen values are lower than the optimum value, then the water is expected to be polluted. In the present study, the dissolved oxygen ranged from 6.08-6.4 mg/l of untreated water and 8-9.6 of treated water. This shows that both the samples possessed a value on the upper limit and refers to good amount of dissolved oxygen. Therefore, the water along the river stretch can be regarded as safe with respect to dissolved oxygen and good for wildlife and fisheries.

Biological Oxygen Demand:

Biological oxygen demand is a way of expressing the amount of organic compound in the Ganga water as measured by the volume of oxygen required by bacteria to metabolize it under aerobic conditions. If the amount of organic matter in the Ganga water is more, the more oxygen will be utilized by bacteria to degrade it.

The value of biological oxygen demand ranged from 0.3-0.6 mg/l. The highest value in the present study was found in the untreated water sample. The value of biological oxygen demand in the treated water sample was 0.3-0.4 mg/l which is equal to maximum permissible limit for drinking i.e. 2 mg/l or less hence water is safe.

Chemical Oxygen Demand:

Chemical oxygen demand is a measure of oxygen required for chemical oxidation. In the present study, the chemical oxygen demand ranged from 0.1696-0.1776 mg/l. The lowest chemical oxygen demand was recorded for treated sample of Haridwar. However, the value of chemical oxygen demand was less than the maximum permissible limit i.e. 250 mg/l. the present study draws support from Sha *et al.*, (2002)

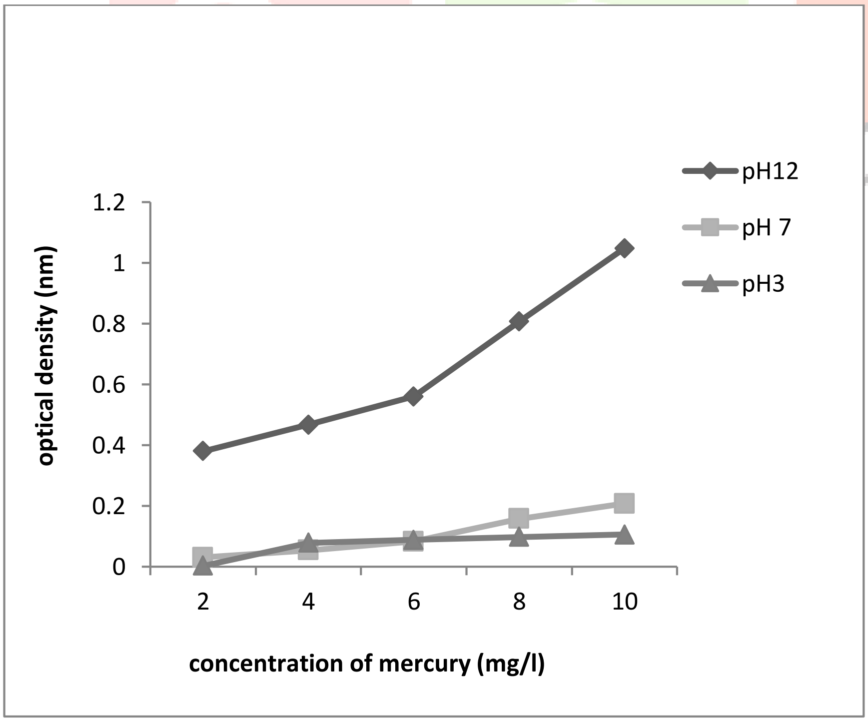

Figure 5: Pre-treatment of mercury at different pH

According to the study (**Fig.5**), at pH 3 there is a slight increase in the optical density as the concentration of the mercury is increasing but it becomes constant after concentration 4 mg/l. At pH 7, there is a slight increase in the optical density but after concentration 6 mg/l there is increase in the optical density but, below 0.2 nm. At pH 12, there is slight increase in the optical density till concentration 6 mg/l but after that there is random increase in the optical density. The absorption at pH 12 is higher than that observed at pH 7 and pH 3.

At pH 12 there is gradual increase in optical density with increase in concentration from 2mg/l to 6mg/l. After, 6mg/l the increase in optical density is uniform and very steep.

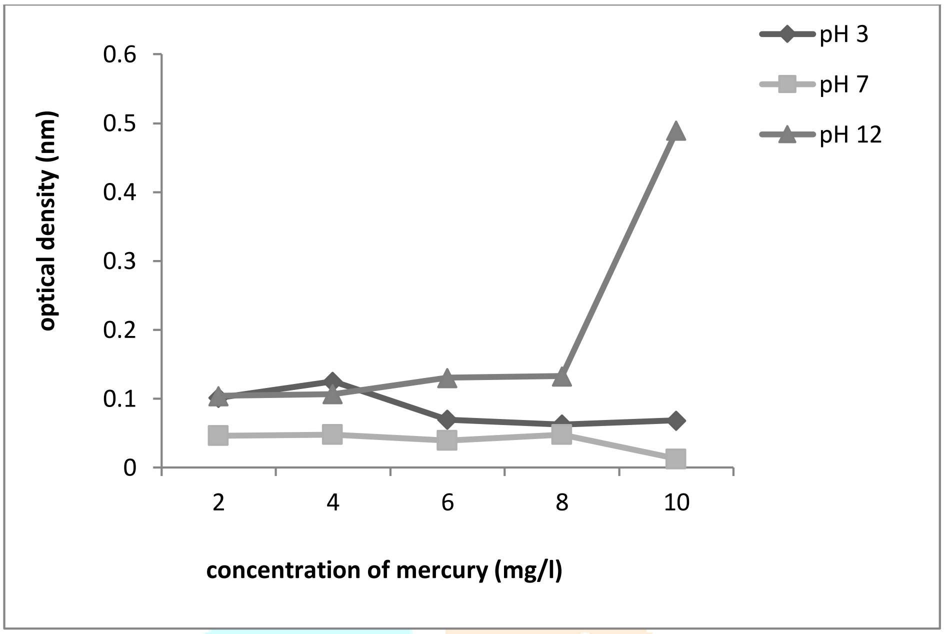

Figure 6: Post-treatment of mercury at different pH

As the distilled water sample was treated with the maize tassel the following were the observations (**Fig.6**):

1) At pH 3, with the increase in concentration there is increase in the optical density and then gradual decrease in the optical density was observed.

2) At pH 7, the optical density is almost constant but after concentration 8 mg/l there is gradual decrease in the optical density.

3) At pH 12, there is a slight increase in the optical density but after concentration 8 mg/l there is sudden increase in the optical density.

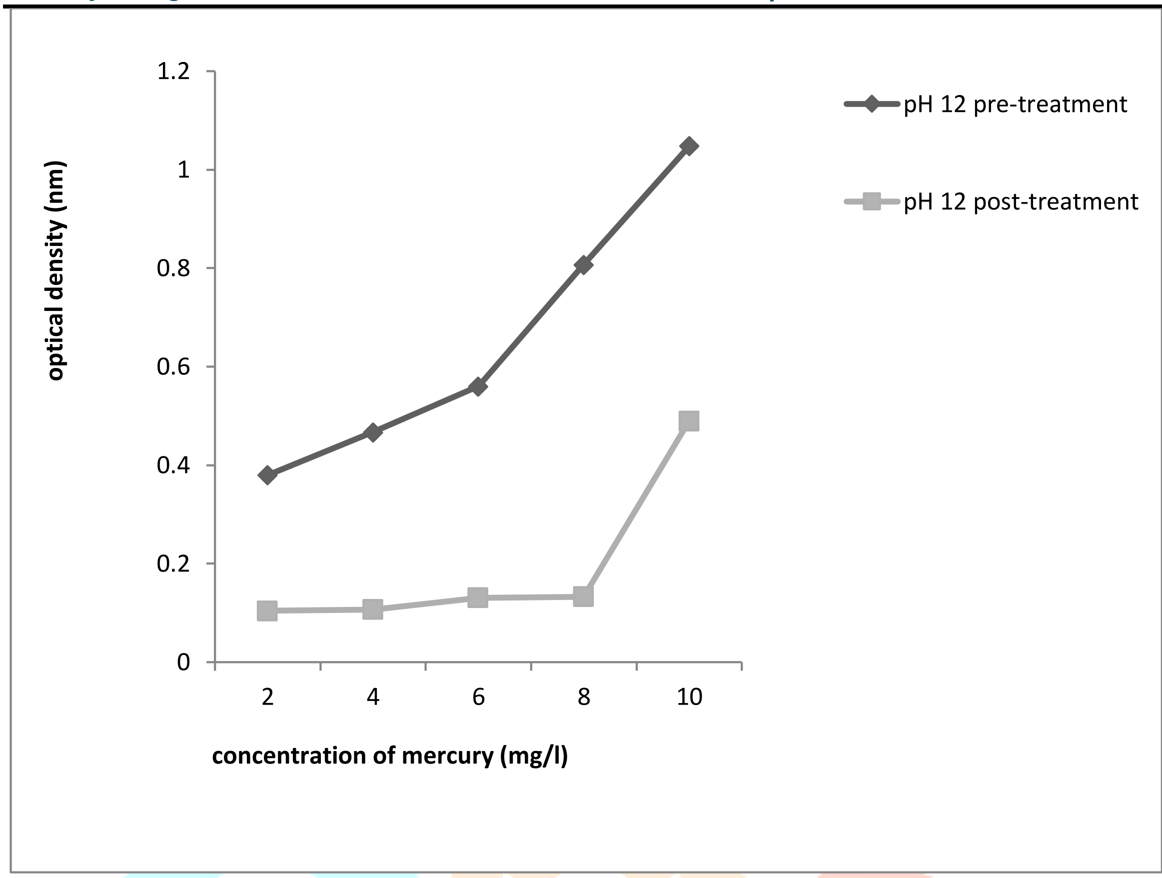

Figure 9: Pre and Post-treatment of mercury at pH 12

At pH 12, the maximum decrease in the mercury level was observed at 8 mg/l concentration (83.55%) while, minimum decrease was observed at 2 mg/l (72.55%). Thus, we conclude that as the concentration of mercury increases there is increase in the adsorption of mercury by maize tassel but it starts decreasing after a limit. The average percentage decrease in the concentration of mercury was found to be 72.42% (**Fig.9**).

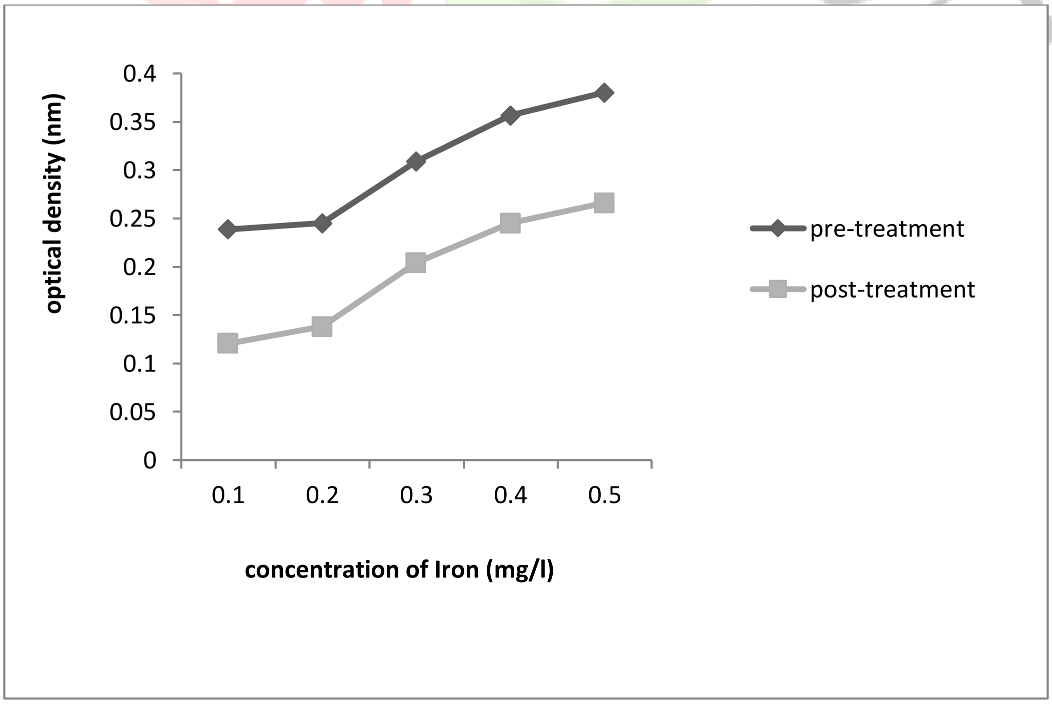

Figure 11: Pre and post-treatment of Iron

According to the above **figure.11**, as the concentration of iron increases in the solution there is increase in the optical density. In the pre-treatment, the optical density first increases slightly then there is a steep increase in the optical density. In post-treatment, the optical density is lower than the pre-treatment, the optical density first increases slightly then there is steep increase in the optical density. Almost the decrease in the optical density is uniform at all the concentration only slightly less at 0.2 mg/l concentration. The average percentage decrease at all concentrations ranges from 30.07%-49.39%.

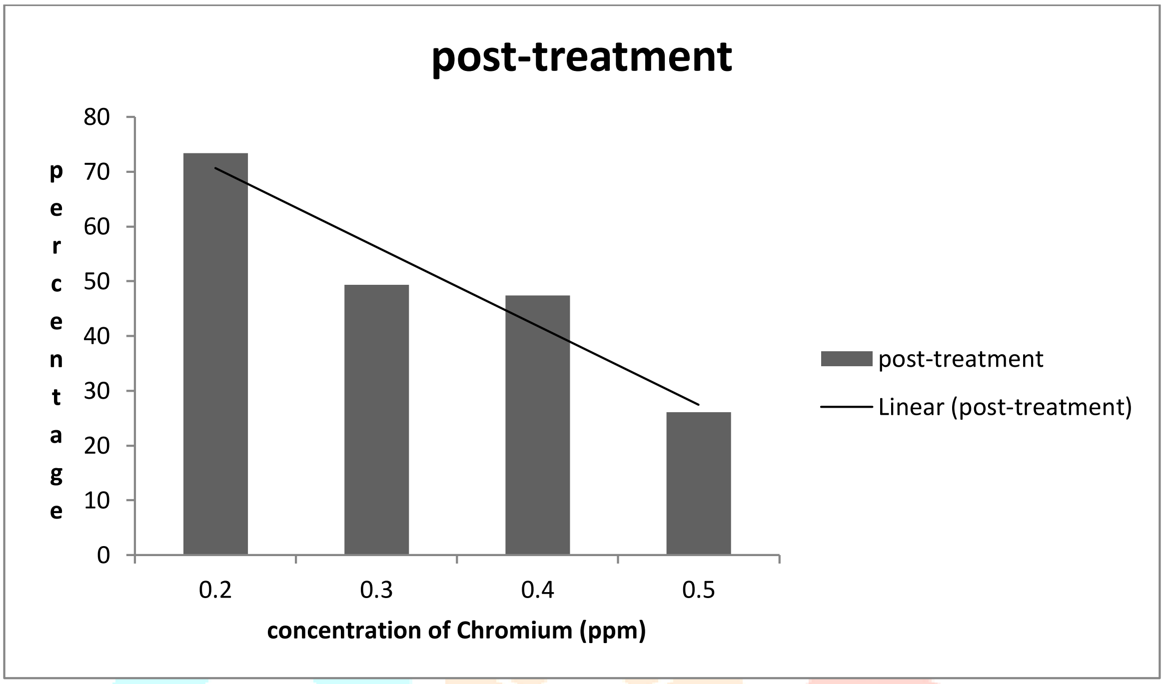

Figure 14: Decrease in Chromium concentration after treatment with Maize tassel

The above **figure 14** shows the percentage decrease in the concentration of chromium after treating the solution with maize tassel. As the concentration of the chromium increases, there is decrease in the adsorption by maize tassel. The trendline is almost linear but two of the solutions (i.e. 0.3 and 0.4 ppm) showed a little deviation. The percentage decrease in optical density ranges from 30 to 70%.

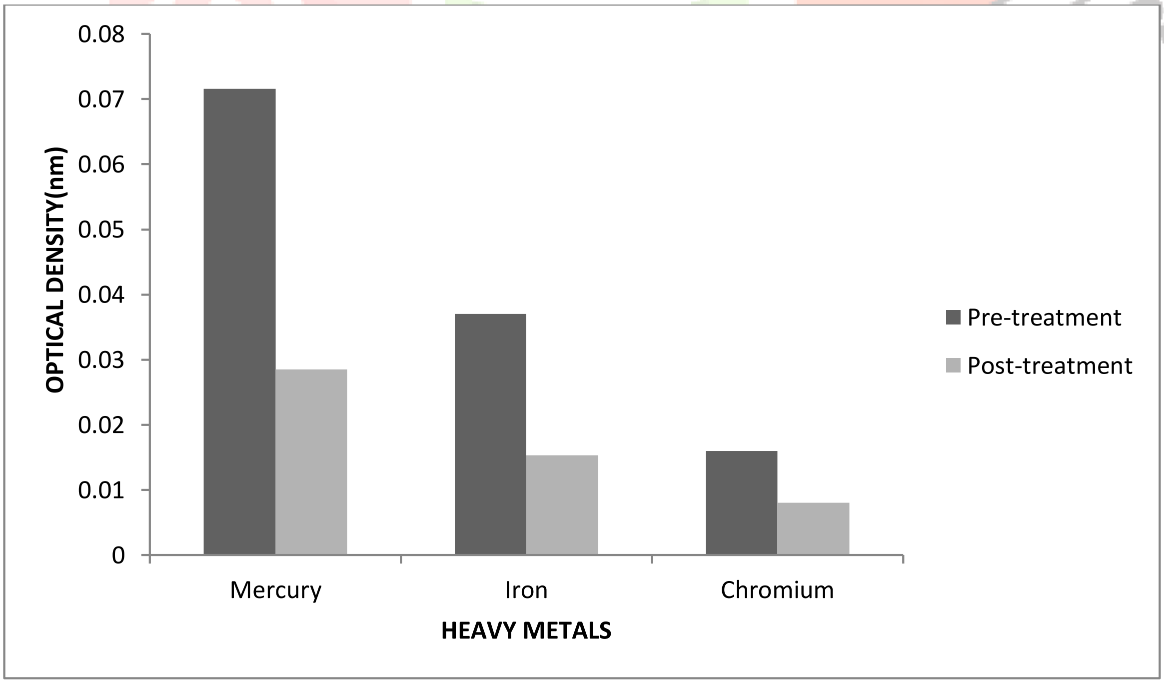

Figure 15: Optical density of different heavy metals in case of S-1

In sample-1, it was observed that in all the heavy metals there were decrease in optical density after using maize tassel. The load of mercury was found to be maximum which were minimized to 60.19% after treatment. The amount of iron in the sample was also measurable which was reduced to 58.65% after treatment and that of chromium was also reduced to 50%

after an interval of 24h. The amount of maize tassel used was 0.1g for each of the heavy metal. However, copper ion was not detected in the sample.

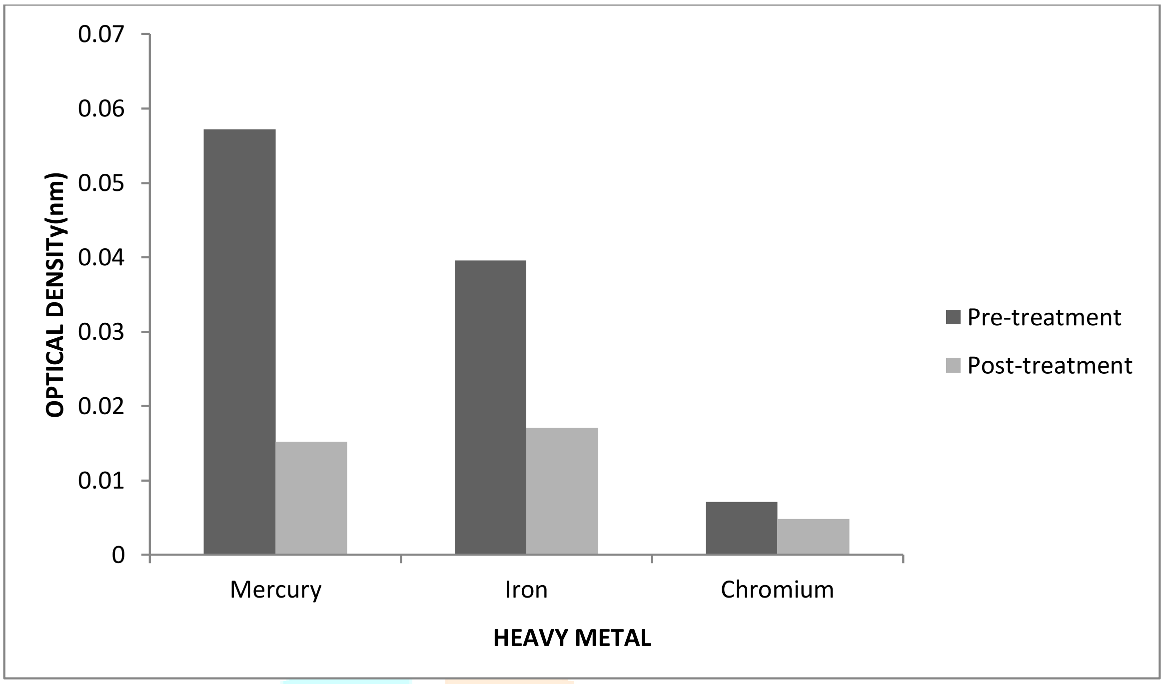

Figure 16: Optical density of different heavy metals in case of S-2

In S-2, the amount of mercury, iron and chromium was found to be measurable whose concentrations were decreased after using maize tassel to 73.42%, 56.82% and 32.39% respectively. The amount of maize tassel used was 0.1g for each of the heavy metal and the duration for treatment was 24h. However, copper ion was also not detected in the S-2.

Table 6: Result for pre-treatment of copper

S.No.	Initial reading	Final reading	Average (ml)
1	0	8.7	8.7
2	8.7	17.4	8.7
3	17.4	25.5	8.1

Amount of sodium thiosulphate used = 8.5 ml

Amount of copper present = 0.54 gm [1 ml of sodium thiosulphate = 0.06354 gm of copper (Vogel, 1961)]

Table 7: Result for post-treatment of copper

S.No.	Initial reading	Final reading	Average
1	0	5.2	5.2
2	5.2	10.5	5.3
3	10.5	15.8	5.3

Amount of sodium thiosulphate used = 5.3 ml

Amount of copper present = 0.34 gm

Copper was only detected in distilled water and not in both the samples from the Ganga River. For detection of copper titration method was used. The percentage decrease in the amount of copper was 37.6%.

Adsorption of mercury was found to be highly pH dependent as compared to the iron and chromium those were detected at the particular pH. Obtained results for distilled water gave an adsorption capacity of 35.81% at pH 3, 69.45% at pH 7 and 83.55% at pH 12 for mercury. Maximum adsorption capacity of iron was 49.39% in the pH range of 3.5-4.5 at room temperature. Maximum capacity of chromium was 73.42% at pH range of 4 keeping the temperature and duration constant.

For the Ganga water samples from Haridwar (S-1) an adsorption capacity of 60.19% and the Ganga water sample from Varanasi (S-2) 73.7% was observed for mercury. Maximum capacity for iron in S-1 and S-2 were 58.65% and 56.82% respectively. Maximum adsorption capacity for chromium in S-1 and S-2 were 50% and 32.39% respectively. Even maize tassel tends to neutralize the pH if it is acidic or basic in the water sample.

These results have demonstrated the immense potential of maize tassel as an alternative adsorbent for toxic metal ions remediation in polluted water and waste water. Maize tassel is of no use for maize plants after fertilization therefore, it can be collected and stored for the reduction of heavy metals. Thus, the water before being supplied for sanitation and drinking purposes can be pre-treated in a large tanks using maize tassel.

Discussions

Maize tassel is the male part of the maize plant. The tassel is a group of stemmy flowers that grow at the apex, or top, of the maize stalk. Each maize plant grows these tassels on top after the major growing of the plant is complete and when it is time for the ears of corn to begin growing. The tassel produces pollen which falls off and is blown by the wind to reach the silk of the ears. The silk is the female flower of the maize plant. The tassel as an agricultural byproduct has no production value after fertilization. Farmers involved in seed production usually cut them off to ensure maximum utilization of the stored plant food (Dadzie *et al.*, 2011).

A heavy metal is one that has relatively high atomic mass. They include arsenic, iron, cadmium, chromium, copper, lead, manganese and mercury. Contamination of drinking water by heavy metals can produce adverse effects for consumers. These metals are usually generated from industrial settings such as tanneries and mining industries and eventually find their way into the river water systems (Dadzie *et al.*, 2011).

There are several chemical and physical methods of removing pollutants from contaminated water but these methods usually come with disadvantages such as generating some health effects as well as costing higher than the biological methods. The use of maize tassel which is environmentally friendly and readily available to ameliorate heavy metals in river water is reported (Dadzie *et al.*, 2011). Reduction of heavy metals has been tried with other biological products like rice husk (Wong *et al.*, 2003), coconut shell (Bhattacharya and Venkobachar, 1984; Gasser, 2007).

Fig. 3 shows an FTIR of tassel which was obtained after diluting the sample in the ratio 1:20 in KBr. The FTIR spectrum of tassel was used to identify functional groups present on the surface maize tassel that could be responsible for uptake of heavy metal species. The spectrum of the adsorbent was measured within the range of 4000–600 cm^{-1} wave number. The absorption peak around 3466cm^{-1} could possibly be due to the presences of OH or NH_2 groups (Guo and Lua, 2000). The

peaks observed at 2921 cm−1 can be assigned to stretching vibration of the C H group. The absorption peaks at 1734, 1643 and 1036cm−1 are associated with the presence of C=O, C=C and C-O respectively. The FTIR of used tassel is shown in **Fig. 4**. This spectrum has less number of peaks compared to the unused tassel. The prominent absorption peaks in the used tassel are observed at 3344.5, 2360.6, 2340.1, 1636.4, 668.1 and 620.1 cm−1. A shift of peaks is evident since there is emergence of new peaks which could be associated to the uptake of Pb(II) and/or
Its speciation products (Choi *et al.*, 2009).

The pH of the samples was found to be acidic and alkaline which were neutralized after post-treatment. There was improvement in D.O., B.O.D. and C.O.D. after post-treatment. Refer to the results section for the values.

At all concentrations and at different pH there is decrease in optical density after post treatment. This implies that maize tassel is responsible to decrease the concentration of mercury, iron, chromium and copper. Many papers have reported of decrease in heavy metals using maize tassel (Zvinowanda *et al*., 2009). Reduction of heavy metals was noted at different pH like 3, 7 and 12. The results indicate that the optical density is better at pH 12 than compared to pH 7 and pH 3. This observed increase in adsorption capacity with increasing pH may be explained with respect to two concomitant phenomena. There is a decrease in the positive charge that tends to accumulate on the adsorbent surface at acidic pH (due to H+), facilitating a closer approach of metal ions to the active sites; this decrease in surface positive charge also results in a lowering of coulombic repulsion of the adsorbing metal ions. The trend of increased adsorption at elevated pH observed in the present study agrees with the reported work done on Pb(II) and Cu(II) removal using rice husk(Wong *et al.*, 2003) and Pb (II) using maize tassel (Zvinowanda *et al*., 2009).

The observed increase in adsorption at different concentration levels can be attributed to the availability of the active sites within the tassel adsorbent which were not fully occupied at short time interval. As the concentration of solution increased the active sites were becoming fully occupied such that the adsorbent was getting to its saturation point with increase in contact time. It can also be observed that the adsorption of heavy metal ions by maize tassel were very rapid in the first 1 h followed by a gradual process. Equilibrium was attained between 4 and 24 h (Zvinowanda *et al*., 2009).

Optical densities shows decreasing trend in relation to increase in concentration in case of iron and chromium. Almost linear trend is observed. This might be true because with the increase in concentration of iron and chromium ions, the amount of maize tassel were constant at 0.1 gm. Hence, it may be that the adsorption surface of maize tassel might be saturated at high concentration of iron and chromium ions.

All the three heavy metals were present in the sample (S-1) and (S-2). The optical density showed decrease in all of them. Highest decrease was in mercury 60.19% and 73.42% for S-1 and S-2 respectively and lowest in chromium 50% and 32.39% for S-1 and S-2 respectively. The copper was not detected in both the sample as per the results of the titration according to Vogel, (1961). Other authors have also mentioned about the reduction of heavy metals using biological products (Zvinowanda *et al*., 2009; Omoloye, 2009; Dadzie *et al*., 2011).

Thus, the significance of this study is that the maize tassel has immense potential as an alternative adsorbate for toxic metal ions in polluted water and comparable to the other commercial products.

The future prospect of this study is that maize tassel is an important agriculture by-product to be used for phytoremediation. After fertilization in maize plants these tassels has no production value and hence, can be collected and stored for purification of water before, being supplied for sanitation and drinking purpose.

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