**Research Article**

# Biosorption of Heavy Metals by Aquatic Weeds

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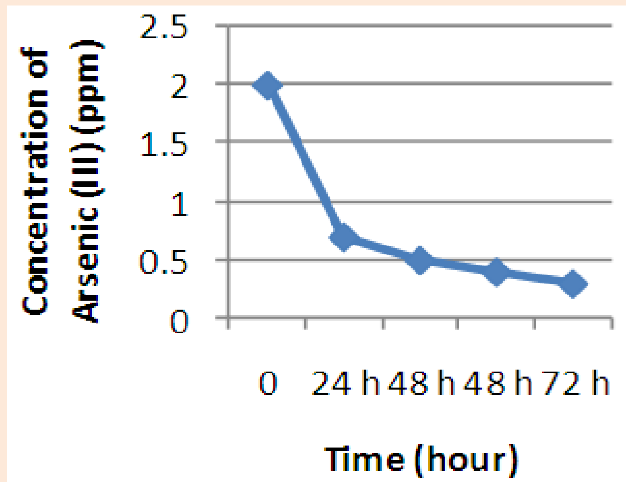
**Abstract**

The aqueous solution of Cr(VI) and As(III) have been tested in the laboratory for biosorption by different aquatic weeds of this area. In addition to this, biosorption kinetics have been studied also for fluoride. The aquatic weeds taken were Eicchornea Crassipes, Lemna Minor and Azolla Microfilla. Eicchornea Crassipes was found to be a good adsorbent of Arsenic (III) aqueous solution where as Azolla Microfilla has been found to be effective in biosorption of heavy metals. Aquatic weeds were not very effective in removal of fluoride from aqueous solution. Different mass of aquatic weeds were taken in 100ml 2ppm solution up to a certain period (3 days) and the experiment is done with a fixed mass of bio absorbent up to different interval of time e.g. 1day, 2day and 3days. Heavy metal removal capacity increases up to a certain time interval and after that the release of heavy metals also takes place. It has been found that the removal of heavy metal by biosorbents follow a first order kinetics. The studies show that aquatic weeds found in abundance in this area can be exploited as an alternative source of removal of heavy metals from aqueous medium but longer duration of time taken in removal and release after certain time are impediments of bioremediation.

**Keywords:** Bioremediation, Arsenic(III), Cr(VI), Aquatic weeds.

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## Introduction

Arsenic, a common contaminant of water, is mobilized through a no of natural processes e.g. weathering processes, biological activity and anthropogenic activities [1]. Heavy metal ions emitted into the environment are hazardous to human health [2]. Heavy metals find their way in ground, industrial and waste water [3]. Arsenic is one of the most toxic elements which exist as arsenite ($AsO_3^{3-}$) and arsenate ($AsO_4^{3-}$) in water [4]. Arsenic contamination in ground water has been reported over the world and in the doab land of Bhagalpur district and in the southern part of the Ganges River where patients having skin pigmentation, liver and lung cancer have been reported [5, 6, 7]. This worsening situation of ground water arsenic contamination necessitated the methods of eco-friendly and cheap methods of removal of arsenic. Several techniques e.g., ion exchange, reverse osmosis and adsorption by bentonite minerals are in practice [8, 9, 10]. It is important to note that this doab land between the Koshi and the Ganga has a variety of aquatic weeds e.g. Eicchornea crassipes, Azolla microfila and Lemna minor. These aquatic weeds have been tried for removal of arsenic from aqueous solution. Efforts have been made to select the aquatic weeds which can lower the arsenic concentration below the permissible limit [11, 12].

Another toxic element_found in the ground water sample of this area is Cr(VI) [13]. Chromium (VI) is toxic and carcinogenic in nature. The deaths due to liver cancer by the ingestion of Cr(VI) contaminated ground water have been reported in this area. Several methods for removal of Cr(VI) are chemical precipitation oxidation, ion exchange and adsorption. Adsorption of Cr(VI) by rice husk, plant derived material and bentonite minerals have been studied.[8] Besides this, biomass of agricultural products have been found effective in removal of Cr(VI) from aqueous medium[14]. Aquatic weeds are available in abundance and among them the plants having the capability to accumulate high concentration of heavy metals have been selected. Some of the important plants for study e.g Water hyacinth (Eicchornea crassipes), Lemna minor and Azolla microfila have also been tested for Cr(VI) [15, 16, 17]. Cr(VI) biosorption is supposed to take place by anionic adsorption [18]. Similar experiments have been repeated for the removal of fluoride from aqueous medium as the villages on the southern bank of the Ganges have been found to be severely affected [19, 20, 21]. Thus the study aims to explore low cost locally available aquatic weeds for the removal of Cr(VI), As(III) and $F^-$ from aqueous medium.

## Materials and Methods/Experimental

The aquatic weeds e.g. Eicchornea crassipes, Azolla microfila and Lemna minor have been collected from the local area. The roots of these plants have greater heavy metal uptake capacity than stem and leaves. So the roots of these plants have been washed several times by deionised water. 2ppm solution of sodium arsenite ($NaAsO_3$) has been prepared. 2ppm solution of fluoride and Cr(VI) have also been prepared. 100ml of 2ppm As(III) solution is taken in a beaker and fixed mass of Eicchornea crassipes with root is put in the solution for different-time intervals e.g. 24h., 48h. and 72h. Varying masses of Eicchornea crassipes were taken in 2ppm 100ml sodium arsenite solution up to 72h and and arsenic content-determined by merckoquant kit and AAS Perkin elmer. Similar experiment was carried out for fluoride test. Fluoride concentration was measured by Picco Fluorimeter and Ion selective electrodes available in the laboratory. 2ppm 100ml $K_2Cr_2O_7$ solution was taken in a beaker and the experiment was repeated by taking different masses of Eicchornea crassipes up to a certain interval of time. The Cr(VI) concentration has been measured by UV double beam spectrophotometer pharo300.

Another aquatic weed Azolla Microfilla collected from local sources in Naugachia and Bhagalpur has been washed many times by distilled water and deionised water. 10g of Azolla was taken in 2ppm 100ml sodium arsenite solution and left in solution up to 24h. 48h. and 72h. Residual arsenic concentration is measured by merckoquant kit and AAS Perkin Elmer. Such type of tests has been done for fluoride and on hexavalent chromium.

Lemna minor, a common aquatic weed, collected from local ponds is also washed from distilled water and put in 2ppm 100ml solutions of sodium arsenite, $K_2Cr_2O_7$ and sodium fluoride respectively. The concentration of As (III), Cr(VI) and $F^-$ have been measured after filtration.

## Results and Discussion

The adsorbents e.g. Eicchornea crasippes, Lemna minor and Azolla Microfilla has been tested for removal capacity of Arsenic (III), Cr (VI) and $F^-$ ions. With an adsorbent dose of 10g Lemna minor in 2ppm 100ml solution of $NaAsO_3$, the concentration of As (III) decreased from an initial concentration of 2ppm to 0.01 ppm in 72 h and upto 0.1 ppm in 48 h (**Table 1**, **Figure 1**). With a similar dose of adsorbent in 2 ppm $K_2Cr_2O_7$ solution, the concentration of Cr(VI) decreased from 2ppm to 0.07ppm in 72h and to 0.44 ppm in 48h (**Table 2**, **Figure 2**). With 10g. of Lemnaminor in 100ml NaF solution, (**Table 3**, **Figure 3**) the concentration decreased from 2ppm to 1.43 ppm in 72h. and to 1.516ppm in 48h. With varying masses of Eicchornea crassipes up to 72h, the concentration of Fluoride, Arsenic(III) and Cr(VI) was measured. The maximum removal of fluoride up to 0.06ppm takes place with 19.16g of Eicchornea crassipes in 100ml 2ppm NaF solution (**Table 4**, **Figure 4**). With fixed mass of Azolla microfilla upto 24h in 100 ml 2ppm NaF solution, the concentration of Fluoride decreased from 2ppm to 1.079 ppm (**Table 5**, **Figure 5**). Some release of Fluoride is taking place when 10g Azolla microfilla is kept in 100 ml 2ppm NaF solution upto 72h.

Different masses of Eicchornea crassipes are taken in 100ml sodium arsenite solution for the sake of As(III) removal study. The concentration of As(III) decreased from 2ppm to 0.02ppm when 14.09g Eicchornea crassipes is kept upto 72h in 100 ml 2ppm sodium arsenite solution. With varying masses of Eicchornea crassipes e.g. 49.88g, 47.06g and 53.70g upto 72h in 100 ml 2ppm sodium arsenite solution gives a constant concentration of 0.1ppm residual As(III) (**Table 6**, **Figure 6**).

Eicchornea crassipes is not a good bioabsorbent of Cr(VI) from aqueous medium. It is crystal clear that release of Cr(VI) is taking place when 19.74g of Eicchornea crassipes is taken in 100 ml 2ppm $K_2Cr_2O_7$ solution upto 72h. The concentration of Cr(VI) increases upto 2.5ppm as a result of release of Cr(VI) (**Table 7**, **Figure 7**).

Similar study has been done with 10g Azolla Microfilla in 100ml 2ppm sodium arsenite solution up to 24h., 48h. and 72h. Arsenic (III) concentration decreased from 2ppm to 0.4ppm in 48h. and upto 0.3 ppm in 72h (**Table 8**, **Figure 8**).

The kinetics of removal of AS(III), Fluoride and Cr(VI)show that removal is a slow process and maximum removal takes place in 72h. Cr(VI) behaves as an oxo anion as $Cr_2 0_7^{2-}$, $HCrO_4^-$, $CrO_4^{2-}$ in aqueous solution with an overall negative charge [22].The total chromate species will be represented as Cr(VI).

The slow rate of chromium adsorption may be due to the electrostatic hindrance or repulsion between the adsorbed Cr(VI) on to the surface and available anionic Cr(VI) in solution [23, 24]. The increased dose of adsorbent resulted in more heavy metal uptake capacity. The variation in removal of arsenite at different adsorbent doses has been shown. The increased arsenic removal has been observed with increasing adsorbent dose. At higher doses, large surface area is available. The suitability of the bioadsorbent material for the removal of Cr(VI), As (III) and $F^-$ ions have been tested.

**Table 1** Arsenic (III) concentration within different time interval of fixed mass of Lemna Minor

| Sample no | Weight | Time | Concentration (ppm) |
|---|---|---|---|
| S1 | 10 g | 24 h | 0.5 |
| S2 | 10 g | 48 h | 0.1 |
| S3 | 10 g | 72 h | 0.01 |
| S4 | 10 g | 72 h | 0.02 |
| S5 | 10 g | 72 h | 0.02 |

Solution: 100 ml 2ppm sodium arsenite solution

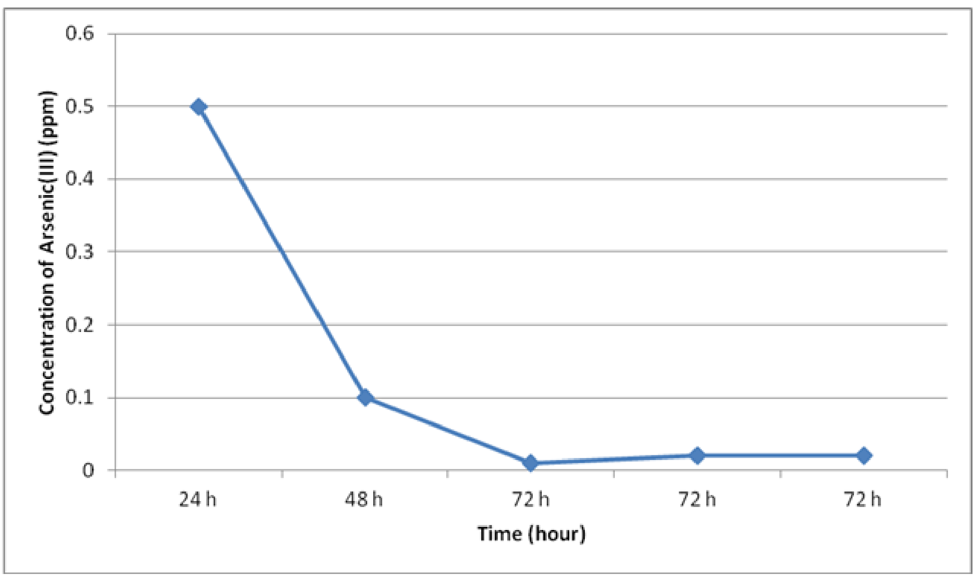


**Figure 1** Effect of contact time of fixed mass of Lemna minor on the concentration of Arsenic(III)

**Table 2** Cr (VI) concentration within different time interval of fixed mass of Lemna Minor

| Sample no | Weight | Time | Concentration (ppm) |
|---|---|---|---|
| S1 | 10g | 0 | 2 |
| S2 | 10g | 24h | 0.50 |
| S3 | 10g | 48h | 0.44 |
| S4 | 10g | 72h | 0.07 |

Solution: 100 ml 2ppm Cr (VI) solution

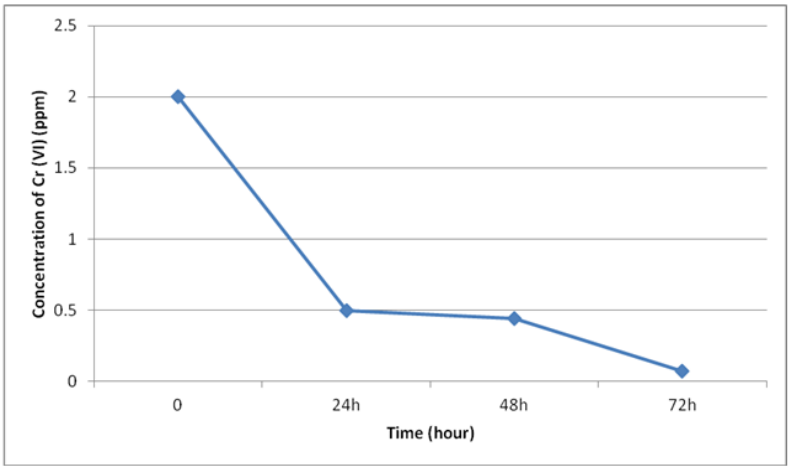


**Figure 2** Effect of contact time of fixed mass of Lemna minor on the concentration of Cr (VI)

**Table 3** Fluoride concentration within different time interval of fixed mass of Lemna Minor

| Sample no | Weight | Time | Concentration (ppm) |
|---|---|---|---|
| - | - | 0 | 2 |
| S1 | 10 g | 24 h | 1.8 |
| S2 | 10 g | 48 h | 1.516 |
| S3 | 10 g | 72 h | 1.43 |
| S4 | 10 g | 72 h | 1.45 |

Solution: 100 ml 2ppm NaF solution.

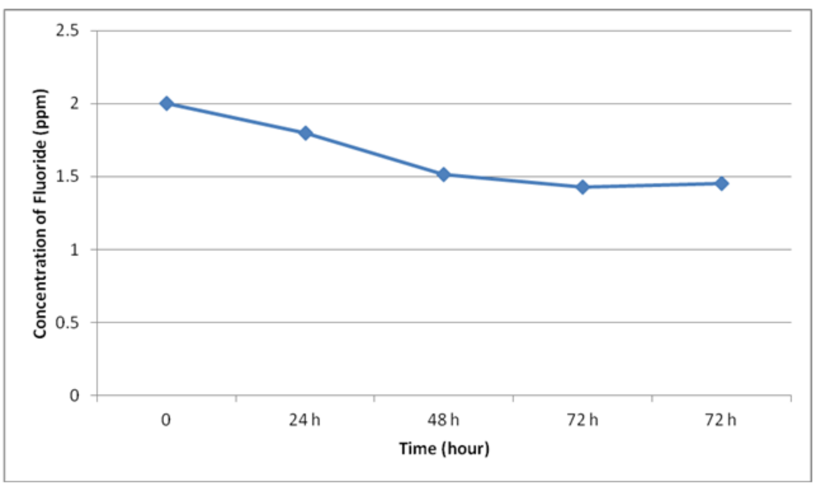


**Figure 3** Effect of contact time of fixed mass of Lemna Minor on the concentration of Fluoride

**Table 4** Fluoride concentration with different mass of Eicchornea Crassipes

| Sample No | Weight of aquatic weed | Concentration of fluoride (ppm) | Time |
|---|---|---|---|
| - | - | 2 | 0 |
| S1 | 14.86g | 0.11 | 72h |
| S2 | 12.46g | 0.06 | 72h |
| S3 | 23.50g | 0.07 | 72h |
| S4 | 30.52g | 0.13 | 72h |
| S5 | 19.16g | 0.06 | 72h |

Solution: 100 ml 2ppm fluoride

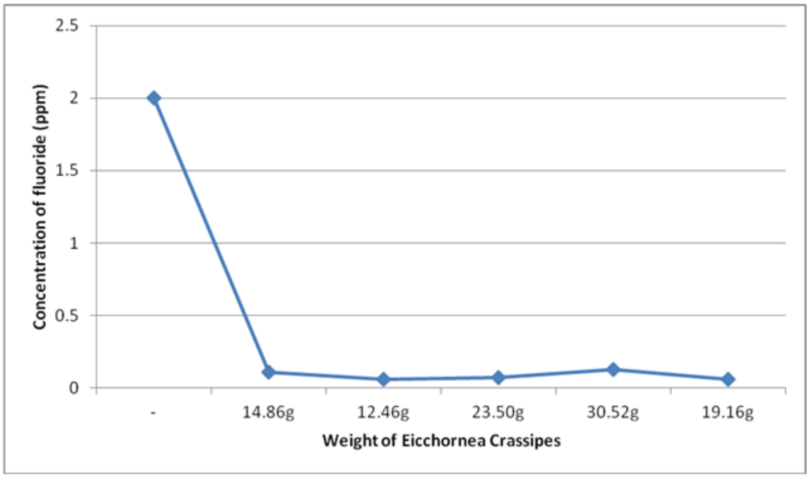


**Figure 4** Effect of different mass of Eicchornea crassipes on the concentration of Fluoride

**Table 5** Fluoride concentration within different time interval of fixed mass of Azolla Microfilla

| Sample no | Weight | Time | Concentration |
|---|---|---|---|
| - | - | 0 | 2 |
| S1 | 10 g | 24 h | 1.079 |
| S2 | 10 g | 48 h | 1.097 |
| S3 | 10 g | 72 h | 1.308 |
| S4 | 10 g | 72 h | 1.120 |

Solution: 100ml 2ppm NaF solution.

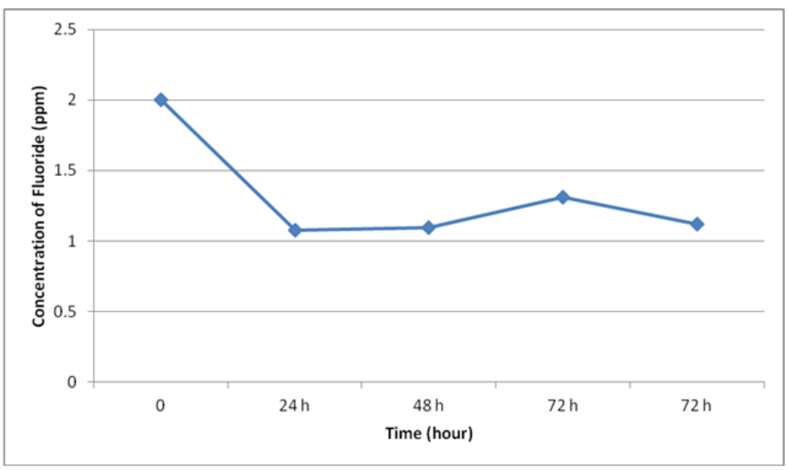


**Figure 5** Effect of contact time of fixed mass of Azolla Microfilla on the concentration of Fluoride

**Table 6** Arsenic (III) concentration with different mass of Eicchornea Crassipes

| Sample No | Weight | Concentration (ppm) | Time |
|---|---|---|---|
| - | - | 2 | 0 |
| S1 | 49.88g | 0.1 | 72h |
| S2 | 47.06g | 0.1 | 72h |
| S3 | 53.70g | 0.1 | 72h |
| S4 | 30.35g | 0.05 | 72h |
| S5 | 14.09g | 0.02 | 72h |

Solution: 100 ml 2ppm sodium arsenite

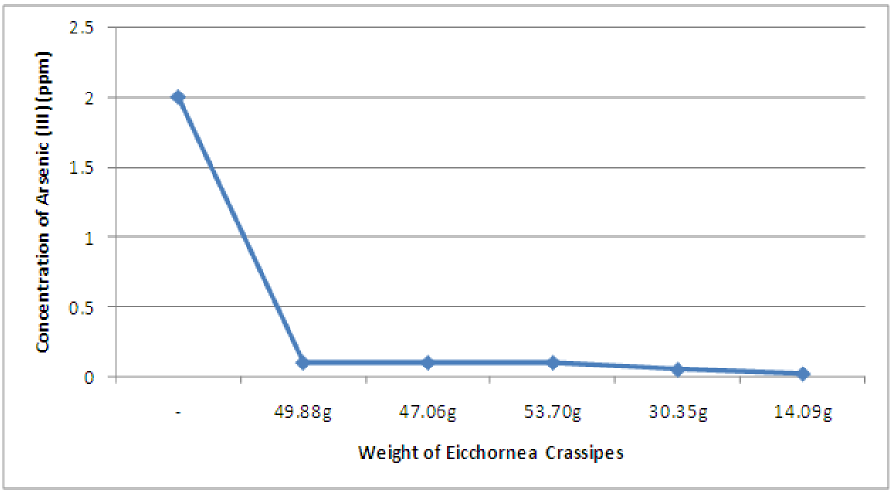


**Figure 6** Effect of different mass of Eicchornea crassipes on the concentration of Arsenic (III)

**Table 7** Cr(VI) concentration with different mass of Eicchornea Crassipes

| Sample No | Weight | Concentration (ppm) | Time |
|---|---|---|---|
| _ | _ | 2 | 0 |
| S1 | 33.57g | 2.5 | 72h |
| S2 | 24.07g | 2.45 | 72h |
| S3 | 19.74g | 2.50 | 72h |
| S4 | 15.23g | 1.97 | 72h |
| S5 | 23.04g | 2.45 | 72h |

Solution: 100 ml 2ppm $K_2Cr_2O_7$ solution

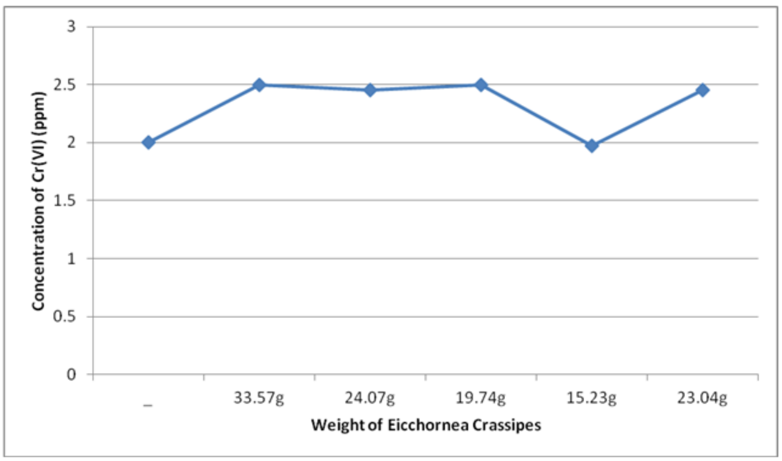


**Figure 7** Effect of different mass of Eicchornea crassipes on the concentration of Cr(VI)

**Table 8** Arsenic (III) concentration within different time interval of fixed mass of Azolla Microfilla

| Sample no | Weight | Time | Concentration (ppm) |
|---|---|---|---|
| - | - | 0 | 2 |
| S1 | 10 g | 24 h | 0.7 |
| S2 | 10 g | 48 h | 0.5 |
| S3 | 10 g | 48 h | 0.4 |
| S4 | 10 g | 72 h | 0.3 |

Solution: 100ml 2ppm sodium arsenite solution.

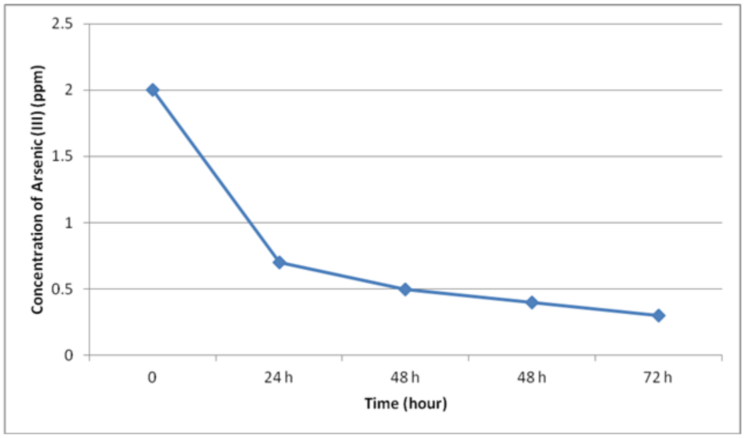


**Figure 8** Effect of contact time of fixed mass of Azolla Microfilla on the concentration of Arsenic (III)

**Table 9** Chromium (VI) concentration within different time interval of fixed mass of Azolla Microfilla

| Sample no | Weight | Time | Concentration (ppm) |
|---|---|---|---|
| - | - | 0 | 2 |
| S1 | 10 g | 24 h | 0.83 |
| S2 | 10 g | 48 h | 1.05 |
| S3 | 10 g | 48 h | 1.17 |
| S4 | 10 g | 72 h | 0.45 |

Solution: 100ml 2ppm sodium arsenite solution.

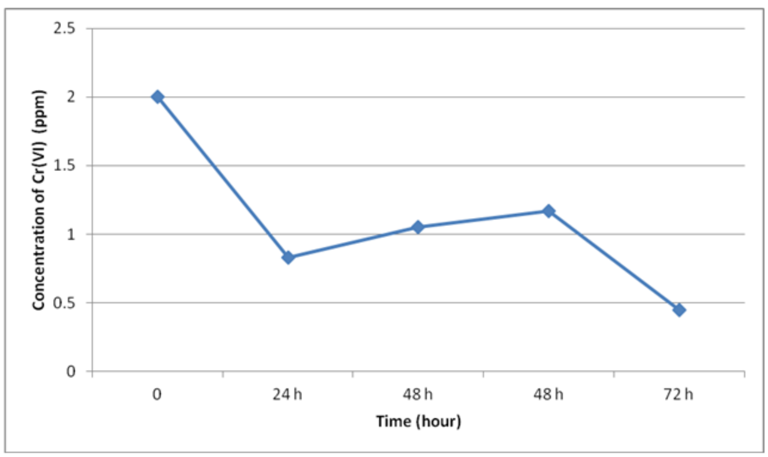


**Figure 9** Effect of contact time of fixed mass of Azolla Microfilla on the concentration of Cr(VI)

## Conclusion

Eicchornea crassipes, Lemna minor and Azolla microfilla are useful as bioadsorbent for the removal of heavy metal from contaminated water. The studies have shown that Lemna minor can accumulate quantity of As(III), Cr(VI) and Fluoride ions. Eicchornea crassipes is not useful in bio remediation of Cr(VI). The potential of Eicchornea crassipes as an adsorbent for the removal of As (III) and Fluoride ion in the laboratory has been established. The way for developing the cost effective and eco-friendly techniques has been explored. Azolla microfilla, commonly known aquatic weed is helpful in bio-remediation of As (III), Cr(VI) and $F^-$ ions. But the remediation process is very slow.

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