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ARTICLES

Research Articles

A study on arsenic and copper extraction capacity of Spirodela polyrhiza from water
A study on arsenic and copper extraction capacity of *Spirodea polyrhiza* from water

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Heavy metals such as arsenic (As), copper (Cu), chromium (Cr), Hg, lead (Pb) and cobalt (Co) cause adverse effects on living organisms by their toxic nature. To remove heavy metals, a variety of conventional treatment technologies have been tested which are not economical and user friendly. So, natural remediation method such as phytoremediation is becoming more popular where plants are used. Phytoremediation is a cost effective and eco-friendly method. This paper accounts the study to exercise the phytoremediation potential of the aquatic plant *Spirodea polyrhiza* for arsenic and copper removal from water. To carry out the study, six plastic bowls each carrying 1 L distilled water were taken where arsenic and copper of known concentration was added for preparing a solution, which contained 1.0, 0.9, 0.7, 0.6, 0.5, and 0.3 mg/L of arsenic and 5.0, 4.6, 4.2, 3.8, 3.4 and 3.0 mg/L of copper. 50 g of *S. polyrhiza* plant was placed in water of each bowl. The concentration of arsenic and copper in water was measured by spectrophotometer using Silver diethylthiocarbamatate (SDDC) and Bicinchoninate methods, respectively and test was performed for 7 days after placing plants in solution. Gross effective floating period for *S. polyrhiza* was found 96 h up to initial concentration of 0.6 mg/L to treat arsenic contaminated water and 3.4 mg/L to treat copper contaminated water. The extraction capacity of *S. polyrhiza* was found more than 80% for all concentration of arsenic and more than 60% for all concentration of copper after 96 h. The removal of arsenic and copper was found to follow the first order kinetics except copper with initial concentration of 5.0 and 4.6 mg/L.

**Key words:** *Spirodea polyrhiza*, phytoremediation, first order kinetics.

**INTRODUCTION**

Environmental protection and conservation are facing new challenges due to the raise of global development (Duruibe et al., 2007). Because of globalization, industrialization and urbanization are increasing rapidly which creates problems like pollution and water pollution is one of them. Consequent to water pollution, there is a scarcity of fresh water in every part of the world. Heavy metal pollution is one of the reasons of water pollution. Heavy metals can occur naturally or can be found in industrial waste. Heavy metal pollution is a widespread problem and has direct effect on human and environmental health (Hogan, 2012). Heavy metals are
toxic at higher concentrations. Common heavy metals are cadmium (Cd), lead (Pb), cobalt (Co), zinc (Zn), chromium (Cr), copper (Cu) and arsenic (As) (Agarwal, 2009; Merrill et al., 2007).

Among the various heavy metals, arsenic and copper are well-known toxic metal. Arsenic contamination is a great threat to millions of people in many countries of the world such as China, Bangladesh, Nepal, Myanmar and Thailand (Bissen and Frimmel, 2003). Arsenic creates many human health problems. Symptoms of acute arsenic poisoning are nausea, vomiting, diarrhoea, cyanosis, cardiac arrhythmia and confusion. Symptoms of chronic arsenic poisoning are less specific (Ng et al., 2003). These include depression, numbness, sleeping disorders and headaches. Arsenic related health effects are usually not acute, but mostly encompass cancer, mainly skin cancer (Wang et al., 2007). The World Health Organizations (WHO) provisional guideline of 0.01 mg/L has been adopted as the drinking water standard. However, many countries have retained the earlier WHO guideline of 0.05 mg/L as their standard including Bangladesh and China.

Copper is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer and wood preservatives (Periasamy and Namasiyavam, 1996). Copper can be found in many kinds of food, water and air. Because of that, people absorb eminent quantities of copper each day by eating, drinking and breathing. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, liver and kidney damage (Kalavathy et al., 2005). The WHO provisional guideline for copper is 1.0 mg/L which is also for the Bangladesh drinking water quality standard has been adopted worldwide.

Several techniques based on the principal of precipitation, ion exchange, electrolysis, solvent extraction, reverse osmosis, membrane and bio-sorption process (McNeill and Edwards, 1997; Tiravanti et al., 1997; Kumari et al., 2006) have been established to remove metals from water. It is very difficult to select an appropriate one. Some are effective but not economical. Some are not user friendly, technologically not sound, post treatment required, and skill manpower required. Sometimes water standard cannot be maintained.

Among these methods, phytoremediation technology has become increasingly popular. Aquatic plants and their associated microbes are used to absorb metals from surrounding water and are extremely efficient. It is considered a clean, cost effective and non-environmentally disruptive technology (Hannink et al., 2001).

Ebel et al. (2007) studied on Eichhoria crassipes and found that it has high growth rate, high tolerance to pollution and has absorption capacity of heavy metal. It is an efficient plant for wastewater treatment (Fang et al., 2007; Ebel et al., 2007). Myriophyllum aquaticum, Ludwigina palustris and Mentha aquatic could effectively remove Fe, Zn, Cu and Hg from contaminated water (Kamal et al., 2004). Lemna minor could accumulate Cu and Cd from contaminated wastewater (Kara, 2004; Hou et al., 2007). Myriophyllum spicatum was an efficient plant for the metal contaminated industrial wastewater treatment (Lesage et al., 2007).

Greater duckweed (Spirodela polyrhiza) was tested under laboratory condition by Rahman et al. (2007, 2008) to investigate arsenic uptake efficiency and mechanisms interaction with PO$_4^{3-}$ and Fe ions. They observed that As (v) uptake by S. polyrhiza was negatively correlated with phosphate uptake and positively correlated with iron uptake. Total arsenic was extracted by the plant about 56%.

Arsenic removal from water by E. crassipes was performed by Alvarado et al. (2008) and the results found that it had a removal rate of 600 mg arsenic ha$^{-1}$ d$^{-1}$ under field condition and a removal recovery of 18% under laboratory condition.

The potentiality of the rootless duckweed Wolffia globosa for arsenic accumulation and tolerance was investigated by Zhang et al. (2009). It was found that this plant can accumulate >1000 mg of arsenic kg$^{-1}$ dry weight (dw) and can tolerate up to 400 mg arsenic kg$^{-1}$ dw.

Loveson et al. (2013) studied on the efficiency of S. polyrhiza to improve the quality of two polluted wetland. In first wetland, percentage reduction of heavy metals such as Pb, Cu, Zn, Cr, Hg, Co and Mg after 8 days treatment period was 95, 79, 66, 53, 26, 20 and 7%, respectively. Again for the same treatment period of 8 days second wetland’s heavy metals such as Cd, Fe, Pb, Cu, Zn and Hg reduced by 100, 98, 91, 74, 62 and 53%, respectively.

The present study establishes to develop the phytoremediation potential of the aquatic plant S. polyrhiza for arsenic and copper from water.

**MATERIALS AND METHODS**

**Selection of plant material**

Young aquatic plants S. polyrhiza (L) Schleiden were collected from a lake of Shahjalal University of Science and Technology and rinsed with tap water to remove any epiphytes and insect larvae grown on plants. The plants were placed in pots with tap water under natural sunlight for 1 day to allow them to adapt the new environment.

**Sample preparation**

Stock solution of arsenic and copper was prepared in the laboratory. Solution was added to each bowl containing 1 L distilled water for preparing arsenic concentration of 0.3, 0.5, 0.6, 0.7, 0.9 and 1 mg/L and copper concentration of 3, 3.4, 3.8, 4.2, 4.6 and 5 mg/L.
Experimental setup

The whole experiment was carried out in the water supply and sanitation laboratory of Department of Civil and Environmental Engineering of Shahjalal University of Science and Technology. Six identical plastic bowls (radius 9" and depth 4") were used in this experiment (Figure 1). Each bowl was kept in open air for growing plants naturally. Spectrophotometer and other subsidiary equipment were used to perform the work.

Experimental procedures

50 g of plants were transplanted into every pot of arsenic and copper test and allow them to take water containing arsenic and copper. Water was collected from each bowl after 1, 2, 4 and 6 h in first day to measure the remaining amount of arsenic and copper in water. From the next day, water was collected once a day and it continued up to 7 days. Concentration of arsenic and copper in water was measured by spectrophotometer using Silver diethyldithiocarbamate (SDDC) method (SM 3500-As B, 1999) and Bicinchoninate method (Method 8506, Hach Handbook of Water Analysis, 1979), respectively. No external agent was required during the experiment period.

Kinetic modeling

It was found out whether the extraction of arsenic and copper from water by *S. polyrhiza* follows first order kinetics or not.

RESULTS AND DISCUSSION

Experimental results for arsenic

As *S. polyrhiza* was extracting arsenic from water, the concentration of arsenic in water decreased with time and within 6 h concentration of arsenic in water decreased from 1, 0.9, 0.7, 0.6, 0.5 and 0.3 mg/L to 0.401, 0.561, 0.296, 0.151, 0.235 and 0.087 mg/L, respectively.

Figure 2 shows a graph representing the remaining concentration of arsenic in water in first 6 h. From graph it was found that for all the water samples the plot was steep in first hour. It means extraction rate was higher in the first hour. But after that it was going from steep to flat trend which indicate that the extraction rate was decreasing with time in the first 6 h.

Figure 3 shows a graph representing the arsenic concentration in water during 7 days. From graph it was found that the concentration of arsenic gradually decreased up to 96 h (that is, up to 5th day) from planting of plants to solution for all water samples. After 96 h, concentration of arsenic in water decreases from 1, 0.9, 0.7, 0.6, 0.5 and 0.3 mg/L to 0.187, 0.149, 0.083, 0.051, 0.042 and 0.01 mg/L, respectively. But after 5th day and up to 7 days from planting of plants to solution concentration of arsenic of 1, 0.9 and 0.7 mg/L started to increase and concentration of 0.6, 0.5 and 0.3 mg/L maintained static condition. The final concentration of arsenic up to 7 days for 1, 0.9, 0.7, 0.6, 0.5 and 0.3 mg/L was found as 0.203, 0.162, 0.098, 0.048, 0.039 and 0.01 mg/L, respectively.

After 96 h, the colour of leaves of *S. polyrhiza* was changed; they began to die. It can be predicted that for this reason the concentrations of arsenic of sample 0.7, 0.9 and 1.0 mg/L were increasing. After 96 h the ability of *S. polyrhiza* to absorb high concentration of arsenic (>0.6 mg/L) were decreased and they started to discharge arsenic.

After 96 h or at 5th day it was found that some samples
with initial concentration of 0.6, 0.5 and 0.3 mg/L reached to the margin of 0.05 mg/L or below which is the Bangladesh drinking water quality standard. But some samples with initial concentration of 1, 0.9 and 0.7 mg/L did not reach that margin. So in this case further treatment is required to ensure Bangladesh drinking water quality standard.

From the above analysis, it can be concluded that 0.6 mg/L is the boundary line of initial arsenic concentration to reach the level of Bangladesh drinking water quality standard at 96 h after phytoextraction by *S. polyrhiza* and when the initial concentration is more than 0.6 mg/L the remaining concentration of arsenic increases with time after 96 h. So, it can be said that the gross effective floating period for *S. polyrhiza* was 96 h up to initial concentration of 0.6 mg/L to treat arsenic contaminated water.

After completion of the experiment, removal percentage was calculated and it was seen that removal percentage was more than 80% for all concentration at 5th day or after 96 h. At the same time 1st day removal percentage was also calculated and seen that percentage of removal obtained on the 1st day more than 50% except 0.9 mg/L concentration of arsenic and it was 37.66% (Figure 4). So it can be said that the major portion of all concentrations of arsenic was extracted on first day except 0.9 mg/L.

**Experimental results for copper**

Figure 5 shows a graph representing the remaining concentration of copper in water in first 6 h. In first hour the plot was steep which means extraction rate was higher but after that there was fluctuation of removal concentration. Within 6 h initial concentration of 3.4 and 5.0 mg/L started to increase and then again decreased.
Concentration of copper in water decreased from 5.0, 4.6, 4.2, 3.8, 3.4 and 3.0 mg/L to 3.63, 2.97, 2.65, 2.38, 1.57 and 1.91 mg/L, respectively within 6 h.

Figure 6 shows a graph representing the copper concentration in water during 7 days. From graph it was found that the concentration of copper gradually decreased up to 5 days. But there was also fluctuation of removal concentration. All the initial concentrations of copper showed fluctuation without 3.0 mg/L. Within 5 days concentration of copper in water decreased from 5.0, 4.6, 4.2, 3.8, 3.4 and 3.0 mg/L to 1.75, 1.56, 1.3, 1.0, 0.68 and 0.45 mg/L, respectively. But after 5 days and up to 7 days concentration of copper of 5.0, 4.6, 4.2 and 3.8 mg/L started to increase and concentration of 3.4 and 3.0 mg/L maintained static condition. The final concentration of copper up to 7 days for 5.0, 4.6, 4.2, 3.8, 3.4 and 3.0 mg/L was found as 1.79, 1.62, 1.81, 1.04, 0.59 and 0.69 mg/L, respectively.

After 96 h, leaves of S. polyrhiza changed their colours and began to die. It can be predicted that for this reason the copper concentrations of sample 5.0, 4.6, 4.2 and 3.8 mg/L were increased. After 96 h their absorbent ability of high concentration of copper (>3.4 mg/L) were decreased and they started to discharge copper.

Some samples with initial concentration of 3.0, 3.4 and 3.8 mg/L reached to the margin of 1.0 mg/L or below
which is the Bangladesh drinking water quality standard and some samples with initial concentration of 4.2, 4.6 and 5.0 mg/L did not reach that margin after 96 h or at 5th day. But they can reach that margin. For that further treatment is necessary.

So, it can be said that the gross effective floating period for *S. polyrhiza* was 96 h up to initial concentration of 3.4 mg/L to treat copper contaminated water.

From Figure 7, it can be said that removal percentage was more than 60% for all concentration of copper at 5th day or after 96 h. At the same time 1st day removal percentage was also calculated and seen that percentage of removal obtained on the 1st day more than 35% except 5.0 mg/L concentration of copper and it was 27.44%.

**Theory of first order kinetics**

The velocity of chemical reaction is proportional to the product of the mass of active reactants present and hence for a single reactant, the velocity \( (dA/dt) \) is proportional to the unreacted substance \( (A) \), where \( dA \) is the change in concentration of reactant over time interval \( dt \). So, the decrease in concentration over this time period can be written as:

\[
-d[A]/dt = k[A]
\]  
(1)

Where \( k \) is the reaction rate constant.

Integrating and applying the boundary conditions, the equation of first order kinetics is found.

\[
\ln[A]/[A]_0 = -kt
\]

\[
[A] = [A]_0e^{-kt}
\]  
(2)

The final Equation 2 is the exponential form of first order removal kinetics.

The removal of arsenic was found to follow the first order kinetics. According to Equation 2, ln \( A_0/A \) and time \( t \), yield a linear relationship if \( k \) is constant. The values of rate constant \( (k) \) and corresponding correlation coefficient
Figure 8. Arsenic concentration at different initial concentration.

Figure 9. Copper concentration at different initial concentration.

Table 1. Equation of removal kinetics with correlation coefficient for arsenic.

<table>
<thead>
<tr>
<th>Initial concentration of arsenic (mg/L)</th>
<th>Equation of removal kinetics</th>
<th>$R^2$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>$y = 0.195e^{0.02x}$</td>
<td>$R^2 = 0.893$</td>
</tr>
<tr>
<td>0.5</td>
<td>$y = 0.358e^{0.02x}$</td>
<td>$R^2 = 0.944$</td>
</tr>
<tr>
<td>0.6</td>
<td>$y = 0.330e^{0.02x}$</td>
<td>$R^2 = 0.770$</td>
</tr>
<tr>
<td>0.7</td>
<td>$y = 0.468e^{0.01x}$</td>
<td>$R^2 = 0.824$</td>
</tr>
<tr>
<td>0.9</td>
<td>$y = 0.709e^{0.01x}$</td>
<td>$R^2 = 0.932$</td>
</tr>
<tr>
<td>1.0</td>
<td>$y = 0.645e^{0.01x}$</td>
<td>$R^2 = 0.802$</td>
</tr>
</tbody>
</table>

$(R^2)$ values obtained from all experimental data are summarized in Table 1. Arsenic removal by *S. polyrhiza* can be represented by the first order kinetics as the values of $R^2$ is constantly greater (Figure 8).

The values of rate constant (k) and corresponding correlation coefficient ($R^2$) values obtained from all experimental data are summarized in Table 2. Copper removal by *S. polyrhiza* can be represented by the first order kinetics as the values of $R^2$ is constantly greater except copper with initial concentration of 5.0 and 4.6 mg/L. For the initial concentration of 5.0 and 4.6 mg/L greater values of $R^2$ is 0.909 and 0.651, respectively. So, they did not follow the first order kinetics (Figure 9).

**Conclusion**

The extraction of arsenic and copper from water using
S. polyrhiza was studied in this research. After 96 h the ability of S. polyrhiza to absorb high concentration of arsenic (>0.6 mg/L) and copper (>3.4 mg/L) were decreased and they started to discharge arsenic and copper. Arsenic with initial concentration (≤0.6 mg/L) and copper with initial concentration (≤3.8 mg/L) need further treatment to reach that margin. Gross effective floating period for S. polyrhiza is 96 h up to initial concentration of 0.6 mg/L to treat arsenic contaminated water and 3.4 mg/L to treat copper contaminated water. The removal percentage was more than 80% for all concentration of arsenic and for copper the removal percentage was more than 65% for all concentration. It was also revealed that the major portion of all concentration of arsenic that is more than 50% was extracted on 1st day except 0.9 mg/L. But for copper it was more than 35% for all concentration except 5.0 mg/L. The removal or accumulation of arsenic and copper from water by S. polyrhiza follows first order removal kinetics except copper with initial concentration of 5.0 and 4.6 mg/L.

### Conflict of Interest

The author(s) have not declared any conflict of interest.

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### Table 2: Equation of removal kinetics with correlation coefficient for copper.

<table>
<thead>
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<th>Initial concentration of copper (mg/L)</th>
<th>Equation of removal kinetics</th>
<th>R² Value</th>
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<tbody>
<tr>
<td>3.0</td>
<td>$y = 2.580e^{0.01x}$</td>
<td>0.858</td>
</tr>
<tr>
<td>3.4</td>
<td>$y = 2.460e^{0.01x}$</td>
<td>0.853</td>
</tr>
<tr>
<td>3.8</td>
<td>$y = 3.176e^{0.01x}$</td>
<td>0.884</td>
</tr>
<tr>
<td>4.2</td>
<td>$y = 3.432e^{0.01x}$</td>
<td>0.745</td>
</tr>
<tr>
<td>4.6</td>
<td>$y = 3.790e^{0.01x}$</td>
<td>0.647</td>
</tr>
<tr>
<td>5.0</td>
<td>$y = 4.061e^{0.01x}$</td>
<td>0.809</td>
</tr>
</tbody>
</table>


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